

# European Union Risk Assessment Report

CAS No: 1306-06-19  
7440-43-9

EINECS No: 215-146-2  
231-152-8

cadmium oxide and cadmium metal  
Part I - environment

**Cd**

**CdO**

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**CADMIUM OXIDE AND CADMIUM METAL**  
**Part I – Environment**

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**RISK ASSESSMENT**

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# CADMIUM OXIDE AND CADMIUM METAL

## Part I – Environment

CAS No: 1306-19-0 and 7440-43-9

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## RISK ASSESSMENT

*Final Report, 2007*

Belgium

This document has been prepared by Belgium on behalf of the European Union. The work has been prepared by the Federal Public Service Health, Food Chain Safety and Environment.

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Risk assessment: update based on recent site-specific exposure data regards all scenarios (except disposal)

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<b>Final report:</b>	<b>2007</b>

## Foreword

We are pleased to present this Risk Assessment Report which is the result of in-depth work carried out by experts in one Member State, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93<sup>1</sup> on the evaluation and control of the risks of “existing” substances. “Existing” substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 tonnes per year.

There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as “Rapporteur”, undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.

The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94<sup>2</sup>, which is supported by a technical guidance document<sup>3</sup>. Normally, the “Rapporteur” and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Health and Environmental Risks (SCHER) which gives its opinion to the European Commission on the quality of the risk assessment.

If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the “Rapporteur” to develop a proposal for a strategy to limit those risks.

The Risk Assessment Report is also presented to the Organisation for Economic Co-operation and Development as a contribution to the Chapter 19, Agenda 21 goals for evaluating chemicals, agreed at the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992 and confirmed in the Johannesburg Declaration on Sustainable Development at the World Summit on Sustainable Development, held in Johannesburg, South Africa in 2002.

This Risk Assessment improves our knowledge about the risks to human health and the environment from exposure to chemicals. We hope you will agree that the results of this in-depth study and intensive co-operation will make a worthwhile contribution to the Community objective of reducing the overall risks from exposure to chemicals.

**Roland Schenkel**  
Director General  
DG Joint Research Centre



**Mogens Peter Carl**  
Director General  
DG Environment



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<sup>1</sup> O.J. No L 084, 05/04/199 p.0001 – 0075

<sup>2</sup> O.J. No L 161, 29/06/1994 p. 0003 – 0011

<sup>3</sup> Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]

## 0 OVERALL RESULTS OF THE RISK ASSESSMENT<sup>4</sup>

### 0.1 General remark on the scope, the approach and the limitations of the study

The present document contains the semi-integration of three study reports that were started at different years and conducted over different time lines i.e. the so-called overall or global RAR, the targeted risk assessment on batteries ('TRAR') and the update risk assessment. The first and main report was started in 1997 and based essentially on exposure data from around 1996. Few years later the study on batteries was initiated as a separate investigation and exposure data are mainly from 1999/2000. This report was previously presented as a separate document, the TRAR, in Annex to the first report. Finally, an update assessment for the local scenarios was started end 2004 and based on site specific exposure data for the reference year 2002.

The structure of the present document still reflects to some degree the scope and content of each of these three studies and reports (see **Table 0.1**). More in particular, Section 2 (production volumes, uses) and 3 (i.e. Section 3.1 environmental exposure and Section 3.3 risk characterisation) present the following general structure: first the subsections related to all production and use scenarios are given with the exception of those related to batteries and their further life-cycle. Then the subsections follow dedicated to the batteries' related issues (inclusive their waste management). Finally the subsections reporting update site-specific informations on all production, processing and use scenarios are given (thus the scenarios of the overall RAR and of the TRAR). However no disposal scenarios are included in this update.

The regional exposure assessment (see Section 3.1.3.4 and further) and the effect assessment (see Section 3.2) are common to all three studies and thus do not present the aforementioned substructure.

Table 0.1 Overview of the structure of the present document as composed of the three studies and reports related to the risk assessment of cadmium metal and cadmium oxide for the environment

Section : Current document	Content	Source document identification and its section
1.	General substance information	Global/overall RAR (1.)
2.1.1.	Production process	Global/overall RAR (2.1.1)
2.1.2	Production volume	Global/overall RAR (2.1.2)
2.1.2.1	Data for the reference year 1996	Global/overall RAR (2.1.2)
2.1.2.2	Update data (for the reference year 2002)	Update document (2.1.2)
2.2	Uses	
2.2.1	General overview	Global/overall RAR (2.1.3)
2.2.2	Batteries	TRAR (on/in batteries) (2.)
2.2.3	Update data (for the reference year 2002)	Update document (2.2.1)
2.3	Legislative control measures	Global/overall RAR (2.2)

Table 0.1 continued overleaf

<sup>4</sup> Conclusion (i) There is a need for further information and/or testing.  
 Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.  
 Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Table 0.1 continued Overview of the structure of the present document as composed of the three studies and reports related to the risk assessment of cadmium metal and cadmium oxide for the environment.

Section: Current document	Content	Source document identification and its section
2.4	Voluntary control measures	Global/overall RAR (2.3)
2.5	Other supranational instruments	Global/overall RAR (2.4)
3.1	Environmental exposure	Global/overall RAR (3.1)
3.1.1	Methods and definitions	Global/overall RAR (3.1.1)
3.1.2	Emissions	Global/overall RAR (3.1.2)
3.1.2.1	Source of data	Global/overall RAR (3.1.2.1)
3.1.2.2	Emissions during production and use	Global/overall RAR (3.1.2.2)
3.1.2.2	Releases due to batteries' related scenarios	TRAR (on/in batteries) (3.1.2)
	Life cycle stage 1	TRAR on/in batteries (3.1.2.1)
	Life cycle stage 2	TRAR on/in batteries (3.1.2.2)
	Life cycle stage 3	TRAR on/in batteries (3.1.2.3)
	Life cycle stage 4	TRAR on/in batteries (3.1.2.4)
	Life cycle stage 5	TRAR on/in batteries (3.1.2.5)
	Summary	TRAR on/in batteries (3.1.2.6)
3.1.2.3	Releases based on update site-specific exposure data (reference year 2002)	Update document (3.1.1.1)
	Cd metal and CdO production	Update document (3.1.1.1.1)
	Release during processing and use	Update document (3.1.1.1.2&3)
	Releases during the production of other non-ferrous metals	Update document (3.1.1.1.4)
3.1.3		
3.1.3.1	Local exposure assessment: production, processing and use scenarios excl. those related to batteries	Global/overall RAR (3.1.2.3)
	Aquatic compartment	Global/overall RAR (3.1.2.3.1)
	Sediment	Global/overall RAR (3.1.2.3.2)
	Atmospheric compartment	Global/overall RAR (3.1.2.3.3)
	Terrestrial compartment	Global/overall RAR (3.1.2.3.4)
3.1.3.2	Local exposure assessment: batteries related scenarios	TRAR on/in batteries (3.1.3.2)
	Aquatic compartment	TRAR on/in batteries (3.1.3.2.1)
	Sediment	TRAR on/in batteries (3.1.3.2.1)
	Atmospheric compartment	TRAR on/in batteries (3.1.3.2.1)
	Aquatic compartment	TRAR on/in batteries (3.1.3.2.4)

Table 0.1 continued overleaf

Table 0.1 continued Overview of the structure of the present document as composed of the three studies and reports related to the risk assessment of cadmium metal and cadmium oxide for the environment.

Section : Current document	Content	Source document identification and its section
3.1.3.3	Local exposure assessment: update data (reference year 2002)	Update document
	Aquatic compartment: calculated PECs	Update document (3.1.2.1 and 3.1.2.2)
	Terrestrial compartment	Update document (3.1.3)
	Atmospheric compartment	Update document (3.1.4)
	Non compartment specific effects relevant to the food chain	Update document (3.1.5)
3.1.3.4	Regional and continental exposure assessment	Global/overall RAR (3.1.2.4)
	Regional and continental concentrations calculated according to TGD	Global/overall RAR (3.1.2.4.1)
	An alternative model predicting regional and continental concentrations in soils	Global/overall RAR (3.1.2.4.2)
	Measured regional data in the environment	Global/overall RAR (3.1.2.4.3)
3.2	Effects assessment	Global/overall RAR (3.2)
3.3	Risk characterisation	
3.3.1	Introduction	Global/overall RAR (3.3.1)
3.3.2	Risk characterisation for production and use (excluding batteries)	Global/overall RAR (3.3.2 to 3.3.6)
3.3.3	Risk characterisation for battery related life cycle steps	TRAR in batteries (3.3.1 to 3.3.4)
3.3.4	Risk characterisation for all scenarios: update data (year 2002)	Update document (3.3.1 to 3.3.4)
4	Human health	In separate document/report
5	Results	
5.1	Introduction	
5.2	Local level: current situation (updated for 2002)	Update document (4.2), TRAR (5.1) and global/overall RAR (5.2)
5.3	Local level: disposal step: future situation and/or sensitivity analysis	TRAR (5.2)
5.4	Regional level	Global/overall RAR (5.2) [TRAR (5.3)]

Important All references to 'Global or overall RAR', 'TRAR in/on batteries' and 'Update document' are references to the previously stand-alone source documents.

### **0.1.1 The so-called ‘global’ or ‘overall’ risk assessment on cadmium (based on data from around 1996)**

This study is focused on assessing the risks of the two priority substances cadmium metal and cadmium oxide as foreseen under the Regulation 793/93/EEC, and thus especially during the production and the intentional use of these two specific substances.

Several other studies on ‘cadmium’ (generic) are dealing with other fields and/or compounds (e.g. the studies and reports performed in the framework of the Fertiliser Directive (76/116/EEC), the Cadmium Directive (91/338/EEC), the Ambient Air Directive, etc).

The present study does not cover all fields and all compounds and it is advised to consult the aforementioned studies for detailed (risk) assessment of these compounds in these fields.

The current study essentially covers the production of cadmium metal and cadmium oxide, the use of these substances in the production of stabilisers, pigments, alloys and plated products. Further down-stream uses are not or only limitedly included.

However, major attention is attributed to the most important application, i.e. batteries with the whole life-cycle covered, thus including the main waste management options (recycling, incineration and landfill). For more details on the scope and limitations of the latter study i.e. the so-called targeted risk assessment of cadmium (oxide) as used in batteries, reference is made to the NiCd batteries’ related (sub)sections. In addition to the standard current scenarios an attempt was made to include some future scenarios.

For the environment, at regional level, the inventory of anthropogenic cadmium emissions has attempted to include all cadmium sources, thus including emissions from fertilisers, sludge, waste incineration, other industrial activities, etc. Sources and data were retrieved from open literature and unpublished reports available at the time this section was most importantly revised (reporting year 2000, based mainly on data from the 90’s). Stormwater and combined sewer overflows, being identified as a significant Cd-source to the surface water, have not been quantified in this assessment and may not be entirely covered.

The risk of cadmium (oxide) to the marine environment is not assessed (it is judged inappropriate to apply freshwater chemistry and ecotoxicity thresholds to the marine environment).

Cadmium in fertilisers (where cadmium is present as an impurity of the phosphate nutrient) and the potential risk linked with the use of sewage sludge on arable land, is covered to the extent needed for an appropriate assessment of the indirect exposure pathway (i.e. the use of fertilisers and sewage sludge is taken into account at the regional and continental scale). For more detailed in-depth examination of the fertilisers’ topic, reference is made to the studies of national authorities and the EC reports made in that framework (see Legislative control measures in Section 2.3). The emissions from the rest of the sewage sludge (applications other than on arable land) could not be quantified.

As to the general assessment’s approach, it was, for several reasons, preferred to adopt the ‘total risk approach’ in contrast with the ‘added’ approach in (some) other risk assessments on metals under the Existing Substances’ Regulation.

In the total risk approach, the risk characterisation is performed on the ‘total cadmium’ concentrations in the environment, i.e. including the natural background and past anthropogenic (diffuse) input. As mentioned above, the anthropogenic sources are limited here by the context of the Regulation. Cadmium emissions of historic origin are taken into account for the soil and

sediment compartment given the (very) long retention time of the substance (generic) in these compartments. The regional and continental risk characterisation for the environment is mainly based on measured data because of the limited predictive power of the exposure models at that scale.

More specifically, the following observations are made related to the environmental part of the present study. It should be born in mind that these findings are of the utmost importance in the development of an adequate risk reduction strategy.

It is estimated in the actual assessment that the emissions by cadmium(oxide) producing and using companies contribute only 3.8% to the total emissions of cadmium in water and 3.8% to total emissions to air. For water, the total EU emission by the Cd(O) producing and using plants is estimated at 1.5 tonnes/year (see **Table 3.155**). Emissions of other sources at regional level are estimated at > 39.2 tonnes/year (see **Table 3.155**: Cd EU emission data to water). Hence, it is concluded that the cadmium emission from the cadmium(oxide) industry only amounts to 3.8% (1.5 tonnes versus a total of 1.5 + 39.2 tonnes) of the total cadmium emission to surface water.

The total European emissions to air from all other sectors is estimated at > 124 tonnes Cd per year while the total EU cadmium(oxide) industry emission is estimated at 4.7 tonnes/year (approximately 3.8% of the total 124 + 4.7 tonnes emitted).

Total Cd emissions to agricultural soils are mainly related to P fertiliser application and are about 230 tonnes Cd year<sup>-1</sup> (see **Table 3.156**). Additional net Cd sources are imported animal feed, sewage sludge and atmospheric deposition. The Cd deposition onto agricultural land, derived from Cd(O) production, processing and recycling is estimated to be 1.2 tonnes Cd year<sup>-1</sup> (i.e. 4.7 tonnes Cd year<sup>-1</sup> multiplied by 0.27, the fraction surface area that is agricultural soil).

The actual assessment assumes good waste practices by all cadmium(oxide) producers and users.

Some *future* scenarios are included in the assessment.

Related to the *arable soil* compartment (within Section 4 of the human part of the present study, in separate document):

A number of scenarios were developed to represent agricultural practices in the EU. Besides other input and output factors these scenarios relate to distinct uses of fertilisers. The impact of the food-chain being more critical for human than for the ecosystem, the assessment is limited to the derivation via food-chain modelling of the so-called critical soil cadmium concentration and the comparison of the predicted future soil concentrations with this threshold.

### **0.1.2 The so-called Targeted Risk Assessment on cadmium as used in batteries**

This study previously presented as stand-alone document and shortly called TRAR on batteries, is focused on assessing the risks for the environment of cadmium as used in NiCd batteries over different life cycle stages such as manufacturing, recycling and disposal. Guidance on how to estimate the emissions from the waste disposal stage is not provided within the Technical Guidance Document (TGD, 1996). The revised TGD includes some sections on waste disposal but no specific guidance is given on how to quantify these emissions. A full assessment of cadmium from NiCd batteries from the waste life cycle stage is thus not included. This section gives an overview of the concern areas that have been assessed in the present TRAR/batteries' related (sub)sections and which areas that have not been dealt with, either because of lack of methodology or because those areas are regarded as being outside the scope of the study.

Emissions of the disposal phase were quantified for Municipal Solid Waste (MSW) landfills and MSW incinerators only where the contribution of sealed portable NiCd batteries to the waste stream have been considered. Industrial NiCd batteries, representing 20% of the cadmium used in NiCd batteries, are recycled and/or disposed off in industrial landfills. The emissions related to the disposal of industrial NiCd batteries i.e. via industrial landfills and hazardous waste incinerators are not addressed in this report.

Quantifying the specific cadmium emissions caused by landfills or incineration of NiCd batteries is hampered by the fact that available data on landfill and incineration emissions always represent the total emissions of cadmium containing materials present in the waste stream. Therefore the total cadmium emissions were calculated first. By using a specific allocation key specific contribution of NiCd batteries to the overall cadmium emission/risk could be quantified. Since waste management strategies may differ considerably between the Member States, due consideration is given to these differences by means of including several scenarios (with the extremes: 100% land-filling and 100% incineration).

Main emissions of cadmium from incineration of waste are expected to occur through air<sup>5</sup> and the disposal and/or re-use of incineration residues (bottom ash and fly ash). The re-use and/or land-filling of incineration residues may result in a long-term diffuse emission potentially contaminating groundwater, surface water and soil. Neither the delayed cadmium emissions of the re-use of incineration residues nor the impact of future expected increase in cadmium content of bottom ash and fly ash on the re-usability of these incineration residues have been quantified. The major environmental concerns associated with metals in landfills are usually related to the generation and eventual discharge of leachate into the environment. The risks associated with the discharge of these leachates in surface water have been quantified. The contamination of the groundwater compartment due to fugitive emissions of landfills has been quantified in this report but no risk characterisation on this compartment has been performed

If NiCd batteries cannot be collected efficaciously, the future cadmium content in the MSW is predicted to increase. The impact of this potential increase on future emissions has been assessed for MSW incineration only. The impact of a future change in the MSW composition on the composition of the leachate of a landfill could not be judged based on the current lack of knowledge and methodology. The contribution of NiCd batteries on the overall cadmium content is calculated for a worst case scenario where only 10% of the NiCd batteries is being collected and a scenario in which 75% of the NiCd batteries is being collected.

Within the approach used in the TRAR/batteries' related (sub)sections to estimate the cadmium emissions associated with waste management strategies such as land-filling and incinerations different assumptions have been made that lack validation due to the limited availability of data on this subject. Although due to this paucity of data it is sometimes difficult to really judge if all assumptions taken are indeed worst case, as a general premise it was tried to use reasonable worst case conditions (based on expert judgment) to perform the calculations. In other cases average values were used instead of worst case estimates in order to conserve the environmental realism of the estimates. **Table 3.253** in Section 3.3.3.1 provides an overview of the assumptions and default values taken in this report and the associated level of conservatism introduced with them.

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<sup>5</sup> Although a quantitative risk characterisation for exposure of organisms to airborne cadmium has not been done due to lack of useful data on the effects of airborne cadmium in environmental organisms, the (calculated) cadmium air emissions and concentrations of MSW incinerators are used in the risk assessment of man indirectly exposed via the environment (see Section 4 of the RAR in a separate document).

However, by means of a rudimentary sensitivity analysis an attempt was made to determine the key parameters having an effect on the overall results.

An overview of the different scenarios for the disposal phase investigated in the TRAR/batteries' related (sub)sections of this report is given in Section 5, **Figure 5.1**. The risk assessment for the waste life cycle step was made in a comparative way meaning that the risks of the total cadmium was compared with the risks of the total cadmium without NiCd batteries' contribution.

### **0.1.3 Update assessment for site-specific exposure data (reference year 2002)**

The update report provides a re-assessment of the risks of the two priority substances cadmium metal and cadmium oxide on the basis of new emission information collected from cadmium and cadmium oxide production and processing industries (i.e. cadmium metal production, cadmium oxide production, production and recycling of NiCd batteries, production of cadmium containing pigments, production of cadmium containing stabilisers) for the reference year 2002. Concerning the use of Cd/CdO in alloys, plating and other uses, no update information was submitted to the Rapporteur.

Since the finalisation of the final overall Cd/CdO ENV RA report (July 2003) for submission to CSTEE, a number of updates were made regarding the identity of the producing facilities and the produced amounts of each of the priority substances. The number of Cd metal and Cd oxide producing plants reduced from 14 in 1996 to 4 in 2002. The total number of processing plants participating in the update exercise by submitting new exposure data was 13 compared to 23 in 1996. Next to the closures of companies in this time period and the stopping of cadmium-related processes, improvements in air and water emission measures have been made by several companies, resulting in a reduction of the total site emissions.

In the update document, re-assessments have been made of PEClocals for different environmental compartments on the basis of update emission information for specific sites. The PECs regional and the PNEC values were extracted from the overall Cd/CdO RAR (July 2005). All these updated values are included in the same integrated report under Section 3.2.

#### **Environment**

As a general remark it is important to stress the general scope and limitations of the present report (see above). Within this RAR no assessment could be done for the atmosphere or for the marine environment.

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to the assessment of:

- the local surface water at 1 Cd metal production site (site 1), and 4 processing (pigments production sites (A and C), plating and alloy) sites/scenarios. Both latter are generic scenarios ('Cd plating' and 'Cd alloys'). Local concentrations are based on modeling using standard default values and could possibly have been refined if substantial monitoring data would have been provided. Monitoring data are available for the Cd metal production site 1: these data indicate risk at background level but do not allow a judgment regarding potential additional risk caused by the site's operations.

- the local surface water at one NiCd batteries recycling site where modeled freshwater Cd concentrations exceed the  $PNEC_{\text{water}}$ . This risk would be removed if no assessment factor (i.e. 2 and reflecting most of the uncertainty) is applied in deriving the PNEC. Monitoring data are available for this site: these data indicate risk at background level but do not allow a judgment regarding potential additional risk caused by the site's operations.
- the modeled regional PEC of surface water has a risk factor of 0.6 using a mean  $K_p$  value for EU while the risk factor is 1.7 using a  $K_p$  value that is distinctly smaller than average. This suggests potential regional risk. However, it is proposed to use measured values for the risk characterization because of the uncertainties in the choice of the natural background (which is combined with the added concentration to derive the regional PEC) and in the coverage of the surface water with small  $K_p$  values. Monitoring data were collected for 13 EU countries (of the EU-16 surveyed) but limitation in data quality (detection limit, geographical coverage etc.) reduced this information to 7 countries (as proxy for regions) for which conclusions can be derived. The regional averages of 90<sup>th</sup> percentiles of measured Cd concentrations of European rivers and lakes in these regions range from 0.0395 to 0.31  $\mu\text{g L}^{-1}$ ). The majority of regional averaged 90<sup>th</sup> percentiles have a risk factor  $< 1$  whereas these values are  $> 1$  in the UK (based on a limited dataset of 1996) and the Walloon region of Belgium. Outliers have a large impact on the risk factors as, for example, 20 sites of the 728 investigated in the largest database of UK (data of 2003) determine risk in UK. The PNEC for water was derived with an assessment factor of 2 reflecting most of the uncertainties in the effects assessment. The Conclusions about risk in the regions mentioned are not affected by either in- or excluding this assessment factor. During the development of the RRS, decision about (possible) reduction measures has to take into account the information on potential cadmium emission sources in these regions. In order to better characterize the regional risks to surface water in part of the EU which have not been covered in this assessment (i.e. eastern and southern Europe are underrepresented in the entire dataset, because detection limits are often too high and because fractionation is often not reported) it might be useful to obtain more information for these regions. It may be that the foreseen monitoring actions under for example the Water Framework Directive will provide this information in the future.
- the local terrestrial compartment: there are potential risks at cadmium plating and alloy production sites.
- the regional terrestrial ecosystem: the 90<sup>th</sup> percentiles of measured Cd concentrations of European soils have risk factors 0.43-1.56 (mean: 0.86; data from 6 EU countries). Regional risk for the terrestrial ecosystem cannot be excluded in one region (UK). However, it should be noted that the 90<sup>th</sup> percentile for the UK (1.4 mg Cd/kg<sub>dw</sub>) falls within the range of the proposed  $PNEC_{\text{soil}}$  (1.15 – 3.2 mg Cd/kg<sub>dw</sub>) based on ecotoxicity to soil microbial processes. Hence risk cannot be excluded but will depend on the magnitude of the assessment factor chosen (either 1 or 2, see Section 3.2.3.6.2) in the derivation of the  $PNEC_{\text{soil}}$ .
- the secondary poisoning (regional level) as measured soil Cd concentrations of European soils have risk factors 0.43-1.56 for poisoning to mammals (mean: 0.86; data from 6 EU countries). Regional risk for the terrestrial ecosystem cannot be excluded in one region (UK). The uncertainty surrounding the effects assessment, however, suggests that this is a borderline situation: the available information shows that literature data on Cd uptake in mammals dwelling in acid soils sensitively influences the effects assessment. If data on acid soils (pH  $< 4.2$ ) are excluded from the effects assessment, a larger PNEC is obtained and risk in the UK would be excluded. That conclusion would only remove concern provided that the P90 value in UK does not refer to acid soils, which is unknown. This analysis is,

moreover, qualitatively because there is no validated model to estimate risk to mammals along the entire range of soil pH.

- the wastewater treatment plants: as risk is predicted for the micro-organisms of the STP for the NiCd battery recycling plant (site 2) discharging its effluent to an off-site STP. Risk to on-site and off-site STP cannot be excluded for Cd plating and alloy industry.

**Conclusion (i)** There is a need for further information and/or testing.

For the aquatic compartment, there is a need for better information regarding the toxic effects of cadmium to aquatic organisms under low water hardness conditions.

In particular, information is required on:

- Cd toxicity testing in very soft waters (H below about 10mg CaCO<sub>3</sub>/L). There are no data for the very soft waters and these areas may be unprotected by the proposed PNEC<sub>water</sub> for soft water (0.08 µg Cd/L).

For sediment<sup>6</sup>, there is a need for further information regarding the bioavailability of cadmium in order to possibly refine the assessment at regional and local level.

In particular:

- the AVS and Organic Carbon normalisation should be further validated (see outcome of **conclusion (i)** program, see separate document: ‘RAR Stage II’)

**Conclusion (ii)** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

This conclusion applies to the assessment of:

- the local surface water and sediment compartment for the CdO production site, for some NiCd batteries production sites (6 and 7) and one NiCd recycling site (site 2) because there are no emissions to water at these sites.
- the local surface water compartment for the Cd metal production site 6, NiCd battery producing sites (3 and 4), Cd pigments producing site B and all (two) Cd stabilizer production sites (X, Y) emitting to the aquatic compartment.
- the local surface water compartment for a hypothetical landfill currently releasing a leachate with 5 µg L<sup>-1</sup> of cadmium directly or indirectly in the aquatic environment, and for current hypothetical incinerator (equipped with an on-site WWTP) discharging total Cd emissions in a river with a dilution factor of 100 to 1,000. Removal of NiCd batteries in the MSW has a negligible influence on the calculated risk ratios.
- no risk is predicted for the micro-organisms in the off-site STP for Cd stabilizer production site (X) discharging its effluents to a municipal STP, for the hypothetical landfill site discharging a leachate with a cadmium concentration of 5µg L<sup>-1</sup> to a STP and for the hypothetical incinerator plant (equipped with an on-site WWTP) discharging to a STP.
- modeled local soil Cd concentrations for Cd metal production, CdO production and processing/user i.e. stabilizers and pigments production plants, NiCd batteries producing and recycling plants and hypothetical MSW incineration plant (equipped with an on-site

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<sup>6</sup> After the TMIV’02 last visit discussion on cadmium in sediment a number of MSs (UK, FR, DE) and Industry commented on the sediment assessment and the current conclusions drawn in line with the outcome of that last TM (for more details, see effects assessment and risk characterisation).

WWTP) (10 years aerial deposition) indicate no risks neither for the terrestrial compartment nor for secondary poisoning.

- modeled regional soil Cd concentrations that include natural soil, industrial soil and 8 different agricultural scenario's are all below the  $PNEC_{soil}$ . All these modeled values are total concentrations that are expected after 60 years (agricultural soils) or far beyond that (natural and industrial soils) with current regional emissions to soil. The starting concentrations are EU average values for the ambient concentrations. If 90<sup>th</sup> percentiles of measured concentrations would have been used in such calculations, then risk cannot be excluded.
- secondary poisoning as field data (body burden: kidney and liver Cd data) of birds (excluding pelagic birds<sup>7</sup>) do not indicate Cd poisoning, even in top predators. No risk to mammals is predicted from modeled regional soil Cd concentrations.

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<sup>7</sup> no risk characterisation of marine environments was made in this report



# CONTENTS

<b>1 GENERAL SUBSTANCE INFORMATION</b> .....	17
<b>1.1 IDENTIFICATION OF THE SUBSTANCE</b> .....	17
<b>1.2 PURITY/IMPURITIES, ADDITIVES</b> .....	17
<b>1.3 PHYSICO-CHEMICAL PROPERTIES</b> .....	18
<b>1.4 CLASSIFICATION</b> .....	20
1.4.1.1 Note on environmental classification and labelling.....	20
<b>2 GENERAL INFORMATION ON EXPOSURE</b> .....	22
<b>2.1 PRODUCTION</b> .....	22
2.1.1 Production processes.....	22
2.1.2 Production volumes.....	25
2.1.2.1 Data for the reference year 1996.....	25
2.1.2.2 Update date (reference year 2002).....	30
<b>2.2 USES</b> .....	31
2.2.1 General overview.....	31
2.2.2 Batteries.....	37
2.2.2.1 Used terminology on Nickel-Cadmium batteries.....	37
2.2.2.2 Ni-Cd chemistry and composition.....	39
2.2.2.3 Production, recycling and use.....	41
2.2.2.3.1 Ni-Cd batteries manufacturing processes.....	41
2.2.2.3.2 Mass balance.....	48
2.2.2.3.3 Ni-Cd batteries producing/recycling companies.....	52
2.2.2.4 Market and sales data.....	52
2.2.2.4.1 General.....	52
2.2.2.4.2 Portable Nickel-Cadmium batteries.....	53
2.2.2.4.3 Industrial Ni-Cd batteries (CollectNiCad 2000c).....	56
2.2.2.4.4 Country by country data.....	57
2.2.2.5 Collection/recycling data.....	62
2.2.2.5.1 Country by country data.....	62
2.2.2.5.2 Collection rate/Collection efficiency.....	65
2.2.3 Updated data (reference year 2002).....	67
2.2.3.1 Introduction.....	67
2.2.3.2 Ni-Cd Batteries.....	69
2.2.3.3 Cd containing Pigments.....	69
2.2.3.4 Cd containing stabilisers.....	70
2.2.3.5 Alloys, plating and other uses.....	70
<b>2.3 LEGISLATIVE CONTROL MEASURES</b> .....	70
2.3.1 EU legislation.....	70
2.3.2 National legislation.....	79
<b>2.4 VOLUNTARY CONTROL MEASURES</b> .....	82
<b>2.5 OTHER SUPRANATIONAL INSTRUMENTS</b> .....	82
<b>3 ENVIRONMENT</b> .....	84
<b>3.1 ENVIRONMENTAL EXPOSURE</b> .....	84
3.1.1 Methods and definitions: added Cd, natural background and ambient concentrations.....	84
3.1.2 Environmental releases.....	85
3.1.2.1 Releases during production and use (excluding batteries' related scenarios).....	85

3.1.2.1.1	Source of data .....	85
3.1.2.1.2	Emission reduction during production and use .....	92
3.1.2.2	Releases due to batteries' related scenarios .....	93
3.1.2.2.1	Life cycle stage 1: Manufacturing of NiCd batteries and/or battery packs .....	94
3.1.2.2.2	Life cycle stage 2: Incorporation into battery-powered devices and applications .....	100
3.1.2.2.3	Life cycle stage 3: Use, recharging and maintenance by end user .....	100
3.1.2.2.4	Life cycle stage 4: Recycling .....	100
3.1.2.2.5	Life cycle stage 5: Disposal .....	104
3.1.2.2.6	Summary: releases to the environment due to battery related life cycle steps .....	159
3.1.2.3	Releases based on update site-specific exposure data (reference year 2002) .....	163
3.1.2.3.1	Cadmium metal and cadmium oxide production .....	163
3.1.2.3.2	Release during processing and use .....	168
3.1.2.3.3	Releases during the production of other non-ferrous metals .....	177
3.1.3	Predicted environmental concentrations (PEC) .....	177
3.1.3.1	Local exposure assessment: in production, processing and use scenarios excluding those related to batteries .....	177
3.1.3.1.1	Aquatic compartment .....	177
3.1.3.1.2	The sediment .....	182
3.1.3.1.3	Atmospheric compartment .....	184
3.1.3.1.4	Terrestrial compartment .....	188
3.1.3.2	Local exposure assessment: batteries' related scenarios .....	192
3.1.3.2.1	Aquatic compartment .....	192
3.1.3.2.2	Sediment compartment .....	204
3.1.3.2.3	Atmospheric compartment .....	209
3.1.3.2.4	Terrestrial compartment .....	213
3.1.3.3	Local exposure: all scenarios: update data (reference year 2002) .....	217
3.1.3.3.1	Aquatic compartment: calculated PECs .....	217
3.1.3.3.2	Terrestrial compartment .....	237
3.1.3.3.3	Atmospheric compartment .....	242
3.1.3.3.4	Secondary poisoning .....	250
3.1.3.4	Regional and continental exposure assessment .....	251
3.1.3.4.1	Regional and continental concentrations calculated according to the TGD .....	251
3.1.3.4.2	An alternative model predicting regional and continental concentrations in agricultural soils .....	276
3.1.3.4.3	Measured regional data in the environment .....	292
3.1.3.4.4	Comparison of measured and calculated data .....	331
<b>3.2</b>	<b>EFFECTS ASSESSMENT .....</b>	<b>332</b>
3.2.1	Methods and definitions .....	332
3.2.1.1	Data quality .....	332
3.2.1.2	Definitions of critical concentrations .....	332
3.2.2	Aquatic compartment .....	333
3.2.2.1	General .....	333
3.2.2.1.1	Data quality: definitions of Reliability Indices (RI's) .....	333
3.2.2.1.2	Source of data and its limitations for risk assessment .....	334
3.2.2.2	Acute and chronic toxicity to fish/amphibians .....	337
3.2.2.3	Acute and chronic toxicity to aquatic invertebrates .....	353
3.2.2.4	Toxicity to primary producers .....	365
3.2.2.5	Discussion .....	370
3.2.2.6	The PNEC <sub>water</sub> .....	371
3.2.2.6.1	The NOEC data .....	371
3.2.2.6.2	Species sensitivity distributions at different levels of data quality .....	371
3.2.2.6.3	Calculation of the generic PNEC <sub>water</sub> .....	383
3.2.2.6.4	PNEC <sub>water</sub> as a function of water characteristics .....	387
3.2.2.7	Conclusion .....	391
3.2.3	Terrestrial compartment .....	392
3.2.3.1	General .....	392

3.2.3.1.1	Data quality: definitions of Reliability Indices (RI's).....	392
3.2.3.1.2	Source of data and its limitations for risk assessment.....	393
3.2.3.2	Toxicity to soil microflora.....	396
3.2.3.3	Toxicity to soil fauna.....	402
3.2.3.4	Toxicity to higher plants.....	408
3.2.3.5	Discussion.....	413
3.2.3.6	The PNEC <sub>soil</sub> .....	413
3.2.3.6.1	Species sensitivity distributions at different levels of data quality.....	413
3.2.3.6.2	Calculation of the generic PNEC <sub>soil</sub> .....	424
3.2.3.6.3	PNEC <sub>soil</sub> in relation to soil properties.....	428
3.2.3.7	Conclusion.....	429
3.2.4	Toxicity to benthic organisms.....	431
3.2.4.1	Influence of sediment properties on toxicity of Cd.....	431
3.2.4.2	Acute and prolonged toxicity to benthic organisms.....	432
3.2.4.3	The PNEC <sub>sediment</sub> .....	436
3.2.5	Atmospheric compartment.....	439
3.2.6	Toxicity for micro-organisms in a sewage treatment plant (STP).....	439
3.2.7	Assessment of secondary poisoning.....	441
3.2.7.1	Source of data and limitations for risk assessment.....	441
3.2.7.2	The aquatic compartment.....	441
3.2.7.2.1	The bioconcentration factor in water.....	441
3.2.7.2.2	The bioaccumulation factor in water.....	448
3.2.7.2.3	Secondary poisoning within the aquatic compartment.....	449
3.2.7.3	The terrestrial compartment.....	453
3.2.7.3.1	Bioconcentration and bioaccumulation factors in soil.....	453
3.2.7.3.2	Secondary poisoning within the lower terrestrial foodchain.....	462
3.2.7.4	The sediment compartment.....	464
3.2.7.4.1	Bioaccumulation in sediment.....	464
3.2.7.5	Toxicity to mammalian and avian organisms.....	467
3.2.7.5.1	Derivation of the PNEC <sub>oral</sub> .....	467
3.2.7.5.2	An alternative approach for wildlife in the terrestrial environment based on renal thresholds.....	472
<b>3.3</b>	<b>RISK CHARACTERISATION.....</b>	<b>484</b>
3.3.1	Introduction.....	484
3.3.2	Risk characterisation for production and use (excluding batteries).....	484
3.3.2.1	The aquatic compartment (including sediment and STP).....	484
3.3.2.2	The terrestrial compartment.....	494
3.3.2.3	Secondary poisoning.....	497
3.3.2.4	The atmospheric compartment.....	499
3.3.2.5	Conclusions.....	499
3.3.3	Risk characterisation for battery related life cycle steps.....	500
3.3.3.1	Overview assumptions and built-in conservatism.....	500
3.3.3.2	The aquatic compartment (including sediment and STP).....	505
3.3.3.2.1	Risk characterisation NiCd producing/recycling plants.....	505
3.3.3.2.2	Risk characterisation MSW incinerators.....	509
3.3.3.2.3	Sediments (assessment without bioavailability correction).....	510
3.3.3.2.4	Future scenarios and sensitivity analysis MSW incinerators.....	511
3.3.3.2.5	Sediment (assessment without bioavailability correction).....	512
3.3.3.2.6	Sensitivity analysis.....	513
3.3.3.2.7	Risk characterisation for MSW landfills.....	513
3.3.3.3	The atmospheric compartment.....	516
3.3.3.4	The terrestrial compartment.....	517
3.3.3.4.1	NiCd producing/recycling plants.....	517
3.3.3.4.2	MSW incinerators.....	517
3.3.4	Risk characterisation for all scenarios: update data (year 2002).....	517
3.3.4.1	The aquatic compartment (including sediment).....	518
3.3.4.2	The terrestrial compartment.....	525
3.3.4.3	The atmospheric compartment.....	526
3.3.4.4	Secondary poisoning.....	527

<b>4 HUMAN HEALTH</b> .....	528
<b>5 RESULTS</b> .....	529
<b>5.1 INTRODUCTION</b> .....	529
<b>5.2 LOCAL LEVEL: CURRENT SITUATION (=UPDATED WITH 2002 DATA AND ASSESSMENT)</b> .....	531
5.2.1 Conclusions on cadmium metal.....	531
5.2.2 Conclusions on cadmium oxide.....	533
<b>5.3 LOCAL LEVEL: DISPOSAL STEP - FUTURE SITUATION AND/OR SENSITIVITY ANALYSIS</b> .....	536
5.3.1 Conclusions on cadmium metal and cadmium oxide.....	536
<b>5.4 REGIONAL LEVEL</b> .....	537
5.4.1 Conclusions on cadmium metal and cadmium oxide.....	537
<b>6 REFERENCES</b> .....	540
<b>Annex A</b> The Nordberg-Kjellström kinetic model .....	608
<b>Annex B</b> Metallothionein .....	613
<b>Annex C</b> Cadmium exposure and End-Stage Renal Disease (ESRD).....	618
<b>Annex D</b> Kidney effects .....	622
<b>Annex E</b> <i>In vitro</i> studies.....	624
<b>Annex F</b> The occurrence of cadmium (metal) in products according to the Swedish product register .....	627
<b>Annex G</b> The occurrence of cadmium oxide in products according to the Swedish product register .....	628
<b>Annex H</b> Check-list for evaluating epidemiological studies .....	629
<b>Annex I</b> EUSES output related to the calculations of regional and continental PECs.....	635
<b>Annex J</b> Temporal trends in measured Cd concentrations in the environment .....	636

EUSES Calculations can be viewed as part of the report at the website of the European Chemicals Bureau:  
<http://ecb.jrc.it>

## **TABLES**

<b>Table 1.1</b> Summary of physico-chemical properties .....	18
<b>Table 2.1</b> Cadmium production plant size distribution for 1996 .....	25
<b>Table 2.2</b> Production sites of metallic Cadmium in the EU ( in the range 10 to >1,000 tonnes/year, EUREX), IUCLID 1997.....	25
<b>Table 2.3</b> Raw EU production, import, export and consumption data of cadmium metal in metric tonnes (Industry site specific questionnaire, 1997).....	26
<b>Table 2.4</b> Production sites of cadmium oxide in the EU (EUREX), IUCLID 1997.....	27
<b>Table 2.5</b> Raw EU production, import, export and consumption data of cadmium oxide in metric tonnes (IUCLID, 1997; Industry site specific questionnaire, 1998) .....	27
<b>Table 2.6</b> Production sites of metallic cadmium/CdO in the EU in the range 10 to > 1,000 t/y that stopped production.....	30
<b>Table 2.7</b> Current producers of cadmium metal liable to the Regulation 793/93/EEC .....	30

<b>Table 2.8</b>	EU production, import, export and consumption data on primary cadmium metal in metric tonnes (Industry site specific questionnaire, 2004/2005) .....	30
<b>Table 2.9</b>	Production sites of metallic cadmium in the EU in the range 10 to > 1,000 t/y that stopped production .....	31
<b>Table 2.10</b>	Production sites of cadmium oxide in the EU with volume > 1,000 tonnes/year (reference year: 2002).....	31
<b>Table 2.11</b>	Industrial and use categories of cadmium in the EU (HEDSET, 1994) .....	34
<b>Table 2.12</b>	Industrial and use categories of cadmium oxide in the EU (HEDSET, 1995; Product Registers, 1997 and 1998).....	35
<b>Table 2.13</b>	Overview of the different battery formats and chemistry .....	37
<b>Table 2.14</b>	Format, size and characteristics of Ni-Cd batteries .....	39
<b>Table 2.15</b>	Average chemical composition for a Ni-Cd battery .....	40
<b>Table 2.16</b>	Worldwide Cd processing facilities.....	48
<b>Table 2.17</b>	Cadmium consumption in the Western World (1990 and 1994) or EU (1996) by application ...	48
<b>Table 2.18</b>	Companies producing/recycling Ni-Cd batteries in EU .....	52
<b>Table 2.19</b>	Summary of the market data (million units) available on portable Ni-Cd batteries in the EU....	53
<b>Table 2.20</b>	Portable Ni-Cd batteries EU market, sales by application (million cells/year) reference year 1999.....	55
<b>Table 2.21</b>	Overview EU market corrected for import and export in 1999.....	55
<b>Table 2.22</b>	Overview of the historical reference data for portable Ni-Cd batteries.....	56
<b>Table 2.23</b>	Industrial Ni-Cd batteries EU market sales (tonnes/year) .....	57
<b>Table 2.24</b>	Portable Ni-Cd battery market data (tonnes/year) for EU countries.....	58
<b>Table 2.25</b>	Industrial Ni-Cd battery market data (tonnes/year) for the EU Member States .....	60
<b>Table 2.26</b>	Weight distribution in percent of the market share of Ni-Cd batteries by applications-reference year 1999.....	61
<b>Table 2.27</b>	Weight distribution in percent of the market share of Ni-Cd batteries by applications (reference year 2000).....	62
<b>Table 2.28</b>	Total weight (tonnes/year) of collected/recycled portable Ni-Cd batteries for the individual EU countries .....	63
<b>Table 2.29</b>	Overview of Ni-Cd Collection programs running in various European countries.....	64
<b>Table 2.30</b>	Total weight (tonnes/year) of collected/recycled industrial Ni-Cd batteries for the individual EU countries .....	65
<b>Table 2.31</b>	Consumption data on cadmium metal and cadmium oxide for the major use applications (amounts in metric tonnes and expressed as elemental cadmium).....	67
<b>Table 2.32</b>	Companies formerly producing Ni-Cd batteries and date/year of ceasing production .....	69
<b>Table 2.33</b>	Current producers of Ni-Cd batteries in EU*-16.....	69
<b>Table 2.34</b>	Current recyclers of Ni-Cd batteries in EU*-16 .....	69
<b>Table 2.35</b>	Mass-flow of cadmium within pigments for the year 2003 (in metric tonnes).....	70
<b>Table 2.36</b>	Limitations and prohibitions on the marketing and use of Cadmium and its compounds (Directive 76/769/EEC, amendment Dir. 91/338 and Dir. 99/51/CE) .....	71
<b>Table 2.37</b>	Commission Regulation (EC) 466/2001: Maximum levels of Cd in food from aquatic sources (Official Journal L 077 , 16/03/2001) .....	73
<b>Table 2.38</b>	Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States.....	74
<b>Table 2.39</b>	Directive 80/778/EEC and Directive 98/83/EC on water for human consumption .....	74
<b>Table 2.40</b>	Directive 76/464/EEC: on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Directive 83/513/EEC, the so-called Cadmium Discharges Directive).....	75
<b>Table 2.41</b>	Directive 86/278/EEC: on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (Annex IA) .....	77
<b>Table 2.42</b>	Directive 86/278/EEC: on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (Annex IB).....	77
<b>Table 2.43</b>	Directive 86/278/EEC: on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (Annex IC).....	78
<b>Table 2.44</b>	Danish environmental legislation on cadmium (Danish EPA, Pers. com., 2001). .....	79
<b>Table 3.1</b>	Aquatic emissions from Cd-producing and -processing plants in the EU-16.....	88
<b>Table 3.2</b>	Atmospheric emission from Cd-producing and -processing plants in the EU-16 .....	90
<b>Table 3.3</b>	Total, direct emissions in the EU (tonnes y <sup>-1</sup> ). A comparison of different studies .....	91
<b>Table 3.4</b>	Overview of the main life cycle stages of NiCd batteries .....	93

<b>Table 3.5</b>	Aquatic emissions from NiCd batteries producing plants in the EU (UC 12: Conductive agents).....	96
<b>Table 3.6</b>	Atmospheric emissions from NiCd batteries producing plants in the EU (UC 12: Conductive agents).....	98
<b>Table 3.7</b>	On-site Waste Water Treatment Plant (WWTP) and sludge information (UC 12: Conductive agents).....	98
<b>Table 3.8</b>	Waste information (UC 12: Conductive agents).....	99
<b>Table 3.9</b>	Summary emissions from production of NiCd batteries (life cycle stage 1).....	100
<b>Table 3.10</b>	Aquatic emissions from Cd recycling plants in the EU (Cd recycled from batteries, production scrap and other sources).....	102
<b>Table 3.11</b>	Atmospheric emissions from Cd recycling plants in the EU (Cd recycled from batteries, production scrap and other sources).....	103
<b>Table 3.12</b>	Waste information for Cd recyclers in the EU.....	103
<b>Table 3.13</b>	Summary emission from recycling of NiCd batteries (life cycle stage 4).....	104
<b>Table 3.14</b>	Total cadmium concentrations ( $\text{g tonne}^{-1}$ dry wt.) in MSW.....	106
<b>Table 3.15</b>	Average concentration ( $\text{mg kg}^{-1}$ dry wt.) of metals in MSW components (Maystre et al., 1994 adapted).....	107
<b>Table 3.16</b>	Fraction of Batteries found in MSW: Primary and sealed portable NiCd batteries in various European countries.....	109
<b>Table 3.17</b>	Overview of the clearance rates (% initial market volume/year) used in the models for predicting waste arising due to (sealed) portable NiCd batteries.....	112
<b>Table 3.18</b>	Cadmium content ( $\text{g Cd/tonne waste dry wt.}$ ) in MSW due to sealed portable NiCd batteries. Scenario 1: ban imposed.....	113
<b>Table 3.19</b>	Cadmium content ( $\text{g tonne}^{-1}$ dry wt. waste) in MSW due to portable sealed NiCd batteries. Scenario 2: no ban.....	114
<b>Table 3.20</b>	Future cadmium content of MSW.....	115
<b>Table 3.21</b>	Land-filling and incineration of MSW (in ktonnes WW) in Europe for the period 1995-2001 ..	115
<b>Table 3.22</b>	Land-filling and incineration practices (in %) in Europe for the period 1995-2001.....	116
<b>Table 3.23</b>	Amounts of household waste (ktonnes wet wt.) treated per Flue Gas Cleaning System (reference year 1999) (ISWA, 2002).....	117
<b>Table 3.24</b>	Distribution (%) of Flue Gas Cleaning Systems for different Member States.....	118
<b>Table 3.25</b>	Overall cadmium emissions to air (in $\text{kg year}^{-1}$ ) in Europe due to incineration of MSW. Scenario current incineration 24.4%.....	119
<b>Table 3.26</b>	Cadmium emissions to air (in $\text{kg year}^{-1}$ ) in Europe due to incineration of MSW. Scenario 100% incineration.....	120
<b>Table 3.27</b>	Average cadmium concentrations in incinerator wastewater ( $\text{mg L}^{-1}$ ) (influent) before treatment	121
<b>Table 3.28</b>	Overall cadmium emissions to water and sludge (in $\text{kg year}^{-1}$ ) in Europe due to incineration of MSW. Scenario current incineration 24.4%.....	122
<b>Table 3.29</b>	Overall cadmium emissions to water and sludge (in $\text{kg year}^{-1}$ ) in Europe due to incineration of MSW. Scenario 100% incineration.....	123
<b>Table 3.30</b>	Partitioning of cadmium (%) in the various output fractions of a MSW incinerator.....	124
<b>Table 3.31</b>	Distribution of bottom ash and fly ash for different Member States (reference year 1999) based on ISWA (2002).....	124
<b>Table 3.32</b>	Distribution of bottom ash and fly ash for different Member States Scenario under current incineration scenario of 24.4%.....	125
<b>Table 3.33</b>	Allocation of air emissions to regional/local scale. Scenario current incineration 24.4%.....	130
<b>Table 3.34</b>	Total annual amount of Cd emissions to air and water within the EU from incineration plants ..	131
<b>Table 3.35</b>	Contribution of NiCd batteries to the overall cadmium emissions due to incineration- Scenario $10 \text{ mg kg}^{-1}$ dry wt. total cadmium in MSW.....	132
<b>Table 3.36</b>	Contribution of NiCd batteries to the continental and regional cadmium emissions due to incineration. Scenario $10 \text{ mg kg}^{-1}$ dry wt. total cadmium in MSW.....	132
<b>Table 3.37</b>	Future cadmium content of wastewater produced by the incineration process (influent of on-site treatment plant).....	133
<b>Table 3.38</b>	Future cadmium content ( $\text{mg kg}^{-1}$ dry wt.) of bottom ash and fly ash: current and future scenarios	134
<b>Table 3.39</b>	Total annual amount of overall Cd emissions to air and surface water within the EU from incineration plants- Future scenarios.....	137
<b>Table 3.40</b>	Future contribution of NiCd batteries to the overall cadmium emissions due to incineration....	137
<b>Table 3.41</b>	Contribution of NiCd batteries to the continental and regional cadmium emissions due to incineration.....	138
<b>Table 3.42</b>	Typical contaminant concentrations ( $\mu\text{g L}^{-1}$ ) of municipal solid waste leachates.....	139

<b>Table 3.43</b>	Overview of total cadmium concentrations ( $\mu\text{g L}^{-1}$ ) in leachates of MSW landfills .....	139
<b>Table 3.44</b>	Default values used for the generic landfill .....	146
<b>Table 3.45</b>	Annual leachate generation for a landfill with no top cover and a bottom liner consisting of a single compacted clay liner or a single composite liner .....	147
<b>Table 3.46</b>	Annual leachate generation for a landfill with a daily cover and a bottom liner consisting of a single compacted clay liner or a single composite liner .....	148
<b>Table 3.47</b>	Annual leachate generation for a landfill with an intermediate cover and a bottom liner consisting of a single compacted clay liner or a single composite liner .....	148
<b>Table 3.48</b>	Annual leachate generation for a landfill with a final cover (with or without a composite liner) and a bottom liner consisting of a single compacted clay liner or a single composite liner .....	148
<b>Table 3.49</b>	Amount of leachate generated per ha of landfill over time .....	150
<b>Table 3.50</b>	Local cadmium emissions to water (in kg) for the generic local landfill (surface area of 20 ha) .....	150
<b>Table 3.51</b>	Cadmium fluxes ( $\text{kg year}^{-1}$ ) of operational MSW landfills for some countries.....	151
<b>Table 3.52</b>	Detailed analysis of leachate sample taken at Chapel Farm landfill, Swindon, Wiltshire, 1990-1991 (Robinson, 1995) .....	152
<b>Table 3.53</b>	Overall cadmium emissions to groundwater/surface water and sludge (in $\text{kg year}^{-1}$ ) in Europe due to land-filling of MSW (operational landfills only). Current scenario: 75.6% land-filling.....	154
<b>Table 3.54</b>	Overall cadmium emissions to groundwater/surface water and sludge (in $\text{kg year}^{-1}$ ) in Europe due to land-filling of MSW (operational landfills only). Scenario: 100% land-filling...	155
<b>Table 3.55</b>	Total annual amount of Cd emissions to groundwater/surface water and sludge within the EU from land-filling MSW .....	155
<b>Table 3.56</b>	Contribution of NiCd batteries to the overall cadmium emissions due to land-filling of MSW .....	156
<b>Table 3.57</b>	Contribution of NiCd batteries to the continental and regional cadmium emissions due to land-filling of MSW .....	156
<b>Table 3.58</b>	Variation of model parameters used in the sensitivity analysis .....	157
<b>Table 3.59</b>	Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of NiCd batteries (realistic scenario: 24.4% incineration and 75.6% land-filling). Scenario 10 $\text{mg kg}^{-1}$ dry wt. cadmium .....	160
<b>Table 3.60</b>	Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of NiCd batteries (worst case scenario: 100% incineration). Scenario 10 $\text{mg kg}^{-1}$ dry wt. cadmium .....	160
<b>Table 3.61</b>	Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of NiCd batteries (worst case scenario: 100% land-filling). Scenario 10 $\text{mg kg}^{-1}$ dry wt. cadmium .....	161
<b>Table 3.62</b>	Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 13.2 $\text{mg kg}^{-1}$ dry wt.) .....	162
<b>Table 3.63</b>	Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 24 $\text{mg kg}^{-1}$ dry wt.) .....	162
<b>Table 3.64</b>	Aquatic emissions from Cd metal producing plants in the EU-16 .....	165
<b>Table 3.65</b>	Aquatic emissions from Cd oxide producing plants in the EU-16 .....	166
<b>Table 3.66</b>	Atmospheric emissions from Cd metal producing plants in the EU-16 .....	166
<b>Table 3.67</b>	Atmospheric emissions from Cd oxide producing plants in the EU-16 .....	166
<b>Table 3.68</b>	Waste information for Cd metal producing plants in the EU-16 .....	167
<b>Table 3.69</b>	Waste information for Cd oxide producing plants in the EU-16 .....	167
<b>Table 3.70</b>	Aquatic emissions from NiCd batteries producing plants in the EU-16.....	170
<b>Table 3.71</b>	Aquatic emissions from NiCd batteries recycling plants in the EU-16 .....	170
<b>Table 3.72</b>	Atmospheric emissions from NiCd batteries producing plants in the EU-16.....	171
<b>Table 3.73</b>	Atmospheric emissions from NiCd batteries recycling plants in the EU-16 .....	171
<b>Table 3.74</b>	Waste information for NiCd batteries producing plants in the EU-16 .....	171
<b>Table 3.75</b>	Waste information for NiCd batteries recycling plants in the EU-16.....	172
<b>Table 3.76</b>	Aquatic emissions from Cd pigments producing Plants in the EU-16 .....	174
<b>Table 3.77</b>	Atmospheric emissions from Cd pigments producing plants in the EU-16.....	174
<b>Table 3.78</b>	Waste information for Cd pigments producing plants in the EU-16 .....	174
<b>Table 3.79</b>	Aquatic emissions from Cd stabiliser producing plants in the EU-16.....	176

<b>Table 3.80</b>	Atmospheric emissions from Cd stabiliser producing plants in the EU-16 .....	176
<b>Table 3.81</b>	Waste information for Cd stabiliser producing plants in the EU-16.....	176
<b>Table 3.82</b>	The solid- water partition coefficient of suspended matter ( $K_p$ ) in different freshwaters.....	178
<b>Table 3.83</b>	The local $PEC_{water}$ (dissolved fraction) for Cd-producing and -processing plants in the EU-16. PEC's include background Cd.....	179
<b>Table 3.84</b>	The measured local Cd concentrations in the effluent receiving water and the local $PEC_{water}$ concentrations for Cd-producing and -processing plants in the EU-16.....	181
<b>Table 3.85</b>	The local $PEC_{sediment}$ for Cd-producing and -processing plants in the EU-16. The PEC's include background Cd. All values are expressed as total Cd concentrations and thus not corrected for bioavailability .....	182
<b>Table 3.86</b>	Calculated local $PEC_{air}$ concentrations for Cd-producing and processing plants in EU-16 .....	185
<b>Table 3.87</b>	Calculated and measured local $PEC_{air}$ concentrations for Cd-producing and processing plants in EU-16 .....	187
<b>Table 3.88</b>	The solid-liquid Cd distribution coefficient ( $K_D$ ) in different topsoils <sup>†</sup> .....	190
<b>Table 3.89</b>	Calculated total local $PEC_{soil}$ for Cd-producing and processing plants in EU-16. PEC's include background Cd .....	191
<b>Table 3.90</b>	Local $PEC_{water}$ for NiCd batteries producing plants and Cd recycling plants in the EU emitting to the surface water after on-site WWTP.....	193
<b>Table 3.91</b>	Local $PEC_{water}$ for NiCd batteries producing plants in the EU emitting to the surface water after on site WWTP and followed by STP .....	194
<b>Table 3.92</b>	Measured local Cd concentrations in the effluent receiving water and the local $PEC_{water}$ concentrations for Cd-producing and processing plants in EU .....	195
<b>Table 3.93</b>	Calculated site specific dilution factors for some MSW incinerators in the EU .....	196
<b>Table 3.94</b>	Local PEC water (total cadmium) for MSW incineration plants in the EU. Scenario 1: Dilution factor 100. Scenario 2: Dilution factor 1000.....	198
<b>Table 3.95</b>	Local PEC water (total cadmium without the NiCd contribution) for MSW incineration plants in the EU. Scenario 1: Dilution factor 100. Scenario 2: Dilution factor 1,000 .....	199
<b>Table 3.96</b>	Local PEC water (total cadmium) for MSW incineration plants in the EU.....	199
<b>Table 3.97</b>	Local $PEC_{water}$ for MSW incineration plants in the EU. Future scenarios: collection rate: 10% and 75% (total cadmium concentrations). Dilution Scenario 1: Dilution factor 100. Dilution Scenario 2: Dilution factor 1000.....	200
<b>Table 3.98</b>	Local PEC water for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is $5 \mu g L^{-1}$ . Comparison of both scenarios.....	201
<b>Table 3.99</b>	Local PEC water for MSW landfills emitting directly to the surface water (scenario 1) or indirectly through a STP (scenario 2: STP). Cadmium leachate concentration is $5 \mu g L^{-1}$ . Total cadmium concentrations .....	202
<b>Table 3.100</b>	Local PEC water for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2: STP). Cadmium leachate concentration is $5 \mu g L^{-1}$ . Total cadmium without the NiCd contribution .....	202
<b>Table 3.101</b>	Local PEC water for landfills emitting directly to the surface water (scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is $50 \mu g L^{-1}$ .....	203
<b>Table 3.102</b>	Local $PEC_{water}$ for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is $50 \mu g L^{-1}$ . Total cadmium concentrations.....	203
<b>Table 3.103</b>	Local $PEC_{water}$ for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is $50 \mu g L^{-1}$ . Total cadmium without the NiCd contribution.....	204
<b>Table 3.104</b>	Local $PEC_{sediment}$ for NiCd batteries producing plants and Cd recycling plants in the EU (without correction for bioavailability).....	205
<b>Table 3.105</b>	Local $PEC_{sediment}$ for MSW incineration plants in the EU (without correction for bioavailability).....	205
<b>Table 3.106</b>	Local PEC sediment (total cadmium without the NiCd contribution) for MSW incineration plants in the EU (without correction for bioavailability). Scenario 1: dilution factor 100. Scenario 2: dilution factor 1000 .....	206
<b>Table 3.107</b>	Local $PEC_{sediment}$ (without correction for bioavailability) for MSW incineration plants in the EU .....	206
<b>Table 3.108</b>	Local $PEC_{sediment}$ (without correction for bioavailability) for a generic MSW incineration plant in the EU. Future scenarios: collection rate: 10 and 75%. Total cadmium concentrations. Dilution Scenario 1: Dilution factor 100. Dilution Scenario 2: Dilution factor 1,000 .....	207

<b>Table 3.109</b>	Local PEC sediment (without correction for bioavailability) for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2: STP). Cadmium leachate concentration is $5 \mu\text{g L}^{-1}$ .....	207
<b>Table 3.110</b>	Local PEC sediment (without correction for bioavailability) for MSW landfills emitting directly to the surface water (scenario 1) or indirectly through a STP (scenario 2: STP). Cadmium leachate concentration is $5 \mu\text{g L}^{-1}$ . Total cadmium without the NiCd contribution...	208
<b>Table 3.111</b>	Local PEC <sub>sediment</sub> (without correction for bioavailability) for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is $50 \mu\text{g L}^{-1}$ . Total cadmium .....	208
<b>Table 3.112</b>	Local PEC sediment (without correction for bioavailability) for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2: STP). Cadmium leachate concentration is $50 \mu\text{g L}^{-1}$ . All cadmium without the NiCd contribution ....	209
<b>Table 3.113</b>	Calculated local PEC <sub>air</sub> concentrations for NiCd batteries producing plants and Cd recycling plants in the EU .....	210
<b>Table 3.114</b>	Calculated and measured local PEC <sub>air</sub> concentrations for NiCd producing and Cd recycling plants in EU.....	210
<b>Table 3.115</b>	Calculated local PEC <sub>air</sub> concentration for MSW incineration plant in the EU. Current situation. Total cadmium concentrations.....	211
<b>Table 3.116</b>	Calculated local PEC <sub>air</sub> concentration for MSW incineration plant in the EU). Current situation. Total cadmium without the NiCd contribution.....	212
<b>Table 3.117</b>	Calculated local PEC <sub>soil</sub> for NiCd producing plants and Cd recycling plants.....	215
<b>Table 3.118</b>	Calculated total local PEC <sub>soil</sub> for MSW incineration plants.....	216
<b>Table 3.120</b>	The local PEC <sub>water</sub> (dissolved fraction) for Cd oxide producing plants in the EU-16. PEC's include background Cd .....	218
<b>Table 3.121</b>	The local PEC <sub>water</sub> (dissolved fraction) for NiCd batteries producing plants in the EU-16. PEC's include background Cd .....	219
<b>Table 3.122</b>	The local PEC <sub>water</sub> (dissolved fraction) for NiCd batteries recycling plants in the EU-16. PEC's include background Cd .....	220
<b>Table 3.123</b>	The local PEC <sub>water</sub> (dissolved fraction) for Cd pigments production plants in the EU-16. PEC's include background Cd .....	221
<b>Table 3.124</b>	The local PEC <sub>water</sub> (dissolved fraction) for Cd stabilisers production plants in the EU-16. PEC's include background Cd .....	222
<b>Table 3.125</b>	The local PEC <sub>WWTP/STP</sub> (total fraction) for Cd metal producing plants in the EU-16.....	224
<b>Table 3.126</b>	The local PEC <sub>WWTP/STP</sub> (total fraction) for Cd oxide producing plants in the EU-16.....	224
<b>Table 3.127</b>	The local PEC <sub>WWTP/STP</sub> (total fraction) for NiCd batteries producing plants in the EU-16.....	224
<b>Table 3.128</b>	The local PEC <sub>WWTP/STP</sub> (total fraction) for NiCd batteries recycling plants in the EU-16.....	225
<b>Table 3.129</b>	The local PEC <sub>WWTP/STP</sub> (total fraction) for Cd pigments producing plants in the EU-16.....	226
<b>Table 3.130</b>	The local PEC <sub>WWTP/STP</sub> (total fraction) for Cd stabiliser producing plants in the EU-16.....	226
<b>Table 3.131</b>	The local PEC <sub>sediment</sub> (without correction for bioavailability) for Cd metal producing plants in the EU-16. PEC's include background Cd.....	227
<b>Table 3.132</b>	Local PEC <sub>sediment</sub> (without correction for bioavailability) for Cd oxide producing plants in the EU-16. PEC's include background Cd.....	227
<b>Table 3.133</b>	The local PEC <sub>sediment</sub> (without bioavailability correction) for NiCd batteries producing plants in the EU-16. PEC's include background Cd .....	228
<b>Table 3.134</b>	The local PEC <sub>sediment</sub> (without correction for bioavailability) for NiCd batteries recycling plants in the EU-16. PEC's include background Cd .....	228
<b>Table 3.135</b>	The local PEC <sub>sediment</sub> (without correction for bioavailability) for Cd pigments production plants in the EU-16. PEC's include background Cd .....	229
<b>Table 3.136</b>	The local PEC <sub>sediment</sub> (without correction for bioavailability) for Cd stabilisers production plants in the EU-16. PEC's include background Cd .....	229
<b>Table 3.137</b>	Summary of calculated PECs in surface water for Cd/CdO producing/processing sectors. Clocalsediment and PEC <sub>localsediment</sub> are not corrected for bioavailability.....	230
<b>Table 3.138</b>	Summary of calculated versus measured levels in surface water for Cd/CdO producing/processing sectors .....	231
<b>Table 3.139</b>	Summary of calculated versus measured levels in sediment for Cd/CdO producing/processing sectors (without correction for bioavailability).....	233
<b>Table 3.140</b>	Calculated total local PEC <sub>soil</sub> for Cd-metal producing plants in EU-16. PEC's include background Cd .....	238
<b>Table 3.141</b>	Calculated total local PEC <sub>soil</sub> for Cd-oxide producing plants in EU-16. PEC's include background Cd ( $0.36 \text{ mg kg}^{-1} \text{ ww}$ ) .....	239

<b>Table 3.142</b>	Calculated total local PECsoil for NiCd batteries producing plants in EU-16. PEC's include background Cd.....	239
<b>Table 3.143</b>	Calculated total local PECsoil for NiCd batteries recycling plants in EU-16. PEC's include background Cd.....	240
<b>Table 3.144</b>	Calculated total local PECsoil for Cd pigments producing plants in EU-16. PEC's include background Cd.....	241
<b>Table 3.145</b>	Calculated total local PECsoil for Cd stabiliser producing plants in EU-16. PEC's include background Cd.....	241
<b>Table 3.146</b>	Calculated total local PECair for Cd-metal producing plants in EU-16. PEC's include background Cd.....	242
<b>Table 3.147</b>	Calculated total local PECair for Cd-oxide producing plants in EU-16. PEC's include background Cd.....	243
<b>Table 3.148</b>	Calculated total local PECair for NiCd battery producing plants in EU-16. PEC's include background Cd.....	243
<b>Table 3.149</b>	Calculated total local PECair for NiCd battery recycling plants in EU-16. PEC's include background Cd.....	244
<b>Table 3.150</b>	Calculated total local PECair for Cd pigment producing plants in EU-16. PEC's include background Cd.....	244
<b>Table 3.151</b>	Calculated total local PECair for Cd stabiliser producing plants in EU-16. PEC's include background Cd.....	245
<b>Table 3.152</b>	Summary of calculated versus measured levels in air for Cd/CdO producing/processing sectors.....	245
<b>Table 3.153</b>	Summary of calculated versus measured aerial deposition levels for Cd/CdO producing/processing sectors.....	247
<b>Table 3.154</b>	Direct atmospheric Cd emission in the EU-16 (tonnes Cd/y). Data combined from different source documents as indicated in footnotes. Note that EU totals of the non-ferrous metals producers do not match the sum of the emissions of each country. The EU totals are the most recent data and are based on confidential questionnaires.....	253
<b>Table 3.155</b>	Cd emissions in the EU-16 to water (tonnes Cd/y). Data combined from different source documents as indicated in footnotes. Note that EU totals of the non-ferrous metals producers and of country totals do not match the sum of the emissions of each country. The EU totals are the most recent data and are based on confidential questionnaires.....	255
<b>Table 3.156</b>	Annual Cd input into agricultural soils from phosphate fertilisers and sludge in European countries. Underlined values are used when different values were available for the same country.....	256
<b>Table 3.157</b>	Emission values, total concentration and total PEC values for the regional and continental environment.....	258
<b>Table 3.158</b>	Summary of regional releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (realistic scenario: 24.4% incineration and 75.6% land-filling. Scenario 10 mg kg <sup>-1</sup> dry wt.).....	261
<b>Table 3.159</b>	Summary of regional releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case scenario: 100% incineration. Scenario 10 mg kg <sup>-1</sup> dry wt.).....	261
<b>Table 3.160</b>	Summary of regional releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case scenario: 100% land-filling. Scenario 10 mg kg <sup>-1</sup> dry wt.).....	262
<b>Table 3.161</b>	Summary of regional releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 13.2 mg kg <sup>-1</sup> dry wt.).....	263
<b>Table 3.162</b>	Summary of regional releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 24 mg kg <sup>-1</sup> dry wt.).....	263
<b>Table 3.163</b>	Summary of continental releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (realistic scenario: 24.4 % incineration and 75.6 % land-filling. Scenario 10 mg kg <sup>-1</sup> dry wt.).....	264
<b>Table 3.164</b>	Summary of continental releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case: 100% incineration- Scenario 10 mg kg <sup>-1</sup> dry wt.).....	264

<b>Table 3.165</b>	Summary of continental releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case scenario: 100% land-filling-Scenario 10 mg kg <sup>-1</sup> dry wt.) .....	265
<b>Table 3.166</b>	Summary of continental releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 13.2 mg kg <sup>-1</sup> dry wt.) .....	265
<b>Table 3.167</b>	Summary of continental releases in kg year <sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 24 mg kg <sup>-1</sup> dry wt.) .....	266
<b>Table 3.168</b>	Contribution of NiCd batteries (fraction 0.1) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 24.4%; land-filling 75.6%). Scenario 10 mg kg <sup>-1</sup> dry wt.....	267
<b>Table 3.169</b>	Contribution of NiCd batteries (fraction 0.5) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 24.4%, land-filling 75.6%). Scenario 10 mg kg <sup>-1</sup> dry wt.....	268
<b>Table 3.170</b>	Contribution of NiCd batteries (fraction 0.1) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 100%, land-filling 0%). Scenario 10 mg kg <sup>-1</sup> dry wt.....	269
<b>Table 3.171</b>	Contribution of NiCd batteries (fraction 0.5) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 100%, land-filling 0%). Scenario 10 mg kg <sup>-1</sup> dry wt.....	270
<b>Table 3.172</b>	Contribution of NiCd batteries (fraction 0.1) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (land-filling 100%, incineration 0%). Scenario 10 mg kg <sup>-1</sup> dry wt.....	271
<b>Table 3.173</b>	Contribution of NiCd batteries (fraction 0.5) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (land-filling 100%, incineration 0%). Scenario 10 mg kg <sup>-1</sup> dry wt.....	272
<b>Table 3.174</b>	Contribution of all MSW waste to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (Future scenario 100% incineration). Scenario 24 mg kg <sup>-1</sup> dry wt.....	273
<b>Table 3.175</b>	Contribution of NiCd batteries (fraction 0.32) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (Future scenario 100% incineration). Scenario 13.2 mg kg <sup>-1</sup> dry wt .....	274
<b>Table 3.176</b>	Contribution of NiCd batteries (fraction 0.63) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (Future scenario 100% incineration). Scenario 24 mg kg <sup>-1</sup> dry wt .....	275
<b>Table 3.177</b>	Maximum permissible and currently applied Cd concentrations P fertilisers in European countries (sources: International Fertiliser Industry Association, pers. comm.; Hutton et al., 2001 and references therein); value of Germany is based on a personal communication for the Umweltbundesamt (2002).....	278
<b>Table 3.178</b>	Annual Cd input into agricultural soils from phosphate fertilisers in European countries .....	279
<b>Table 3.179</b>	Annual Cd input into agricultural soils from manure, sludge, lime and compost in European countries. All flux data are country averages, i.e. total load divided by area of arable land and, hence, do not reflect the flux where it is applied.....	281
<b>Table 3.180</b>	Atmospheric Cd deposition in rural areas of European countries (measured, Eu-16 average is calculated) .....	282
<b>Table 3.181</b>	The annual Cd leaching from the plough layer (L, in g ha <sup>-1</sup> y <sup>-1</sup> ). The Cd leaching is calculated for a soil with 0.3 mg kg <sup>-1</sup> total Cd (background concentration) and an annual net water flux out of the plough layer of 0.2 m. The different models used for estimating the K <sub>D</sub> of Cd in soil are referred to in Table 3.88 .....	284
<b>Table 3.182</b>	The Cd content in selected agricultural crops and the estimated annual crop offtake .....	285
<b>Table 3.183</b>	The predicted environmental concentration of Cd in agricultural soil (PEC <sub>soil</sub> , -plough layer only) after 60 years of exposure to current Cd influx in agricultural soils. Seven scenarios are selected that may be representative for European agriculture. Predictions are made using the Cd mass balance approach described in the text. The full description of the scenarios is given in the text.....	290
<b>Table 3.184</b>	Measured or estimated dissolved Cd concentrations in surface water. Underlined data are used for risk characterisation .....	300
<b>Table 3.185</b>	Measured Cd concentrations in surface water classified per reliability index (RI) taken forward to the risk characterisation. The statistics (90 <sup>th</sup> percentile and average) are the	

averages of corresponding values of the regional data from Table 3.184 which meet the criteria of reliability\*. Datasets with RI=4 were discussed on a case-by-case basis above. Datasets with RI>1 include also data of classes with lower RI index (i.e. cumulative number of data)..... 307

**Table 3.186** Measured cadmium concentrations in suspended matter..... 309

**Table 3.187** Measured Cd concentrations in sediments. Underlined data are used for risk characterisation. All values are expressed as total Cd concentrations and thus not corrected for bioavailability. 313

**Table 3.188** Literature data on the Cd concentrations in European sediments. All values are expressed as total Cd concentrations and thus not corrected for bioavailability..... 316

**Table 3.189** Measured Cd concentrations in sediments taken forward to the risk characterisation. The statistics (90<sup>th</sup> percentile and average) are the averages of corresponding values of the regional data from Table 3.187. All values are expressed as total Cd concentrations and thus not corrected for bioavailability ..... 317

**Table 3.190** Measured total cadmium concentrations in soils..... 321

**Table 3.191** Measured Cd concentrations in soils taken forward to the risk characterisation. The statistics (90<sup>th</sup> percentile) are the averages of corresponding values of the regional data from Table 3.190..... 327

**Table 3.192** Measured cadmium concentrations in air..... 328

**Table 3.193** Typical measured regional Cd concentrations in the environment (away from point sources and remote areas = ambient Cd concentrations) and the regional and continental predicted environmental concentrations (PEC's). The measured concentrations and natural background are derived from compilations given in Tables 3.184-3.192 as discussed in the previous section. PEC's are derived from Table 3.157 ..... 331

**Table 3.194** Selected data with RI 1-3 for acute and chronic Cd toxicity to fish/amphibians. Sixty-three tests were reviewed from 27 source documents and 51 tests were selected..... 337

**Table 3.195** Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment ..... 340

**Table 3.196** Selected data with RI 1-3 for acute and chronic Cd toxicity to aquatic invertebrates. One hundred and two tests were reviewed from 42 source documents and 97 tests were selected... 353

**Table 3.197** Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment..... 356

**Table 3.198** Selected data with RI 1-3 for Cd toxicity to primary producers. Twenty-nine tests were reviewed from 21 source documents and 20 tests were selected. All tests were considered to represent chronic exposure to Cd..... 365

**Table 3.199** Toxicity to aquatic primary producers. All underlined data are selected to discuss the critical concentrations (Table 3.198). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment ..... 368

**Table 3.200** Summary of selected Cd toxicity data (µg Cd/L). All data have RI≤3 and are underlined in Tables 3.195, 3.197 and 3.199 ..... 370

**Table 3.201** Summary of the NOEC values (µg Cd/L) of chronic tests in the aquatic compartment for various levels of reliability (RI, defined in the introduction of Section 3.2.2) ..... 371

**Table 3.202** Selected NOEC data of effects of Cd in freshwater. Data derived from Tables 3.195, 3.197 and 3.199 within quality class RI 1-3 ..... 373

**Table 3.203** 'One species, one NOEC': selected NOEC data of effects of Cd in freshwater and calculation of 'geometric mean NOEC's. Data derived from Table 3.202 ..... 376

**Table 3.204** 'Case-by-case selection': selected NOEC data of effects of Cd in freshwater and case-by-case calculation of 'geometric mean NOEC's. Bold, underlined data are selected for the HC<sub>5</sub> calculation. Data derived from Table 3.202..... 377

**Table 3.205** 'One species, one NOEC': lowest NOEC selection. Data derived from Table 3.202 ..... 380

**Table 3.206** Calculation of critical concentrations (µg L<sup>-1</sup>) using the assessment factor method (AFM) or the statistical extrapolation method (SEM, Aldenberg and Slob, 1993) for various levels of data quality ..... 381

**Table 3.207** Overview of multi-species studies about effects of Cd (added as Cd<sup>2+</sup> salt) in the aquatic environment..... 385

<b>Table 3.208</b>	Summarising table for multi-species studies (numbers refer to those in Table 3.207). The water hardness correction is described in Section 3.2.2.6.4. The HC <sub>5</sub> at the water hardness of the MS study is calculated based on hardness corrected NOEC data and retransformation with a lower hardness limit of H = 40 mg l <sup>-1</sup> as CaCO <sub>3</sub> ). The model for the hardness correction is discussed in Section 3.2.2.6.4 .....	387
<b>Table 3.209</b>	Water hardness (in mg CaCO <sub>3</sub> L <sup>-1</sup> ) distribution of surface waters in some EU countries .....	388
<b>Table 3.210</b>	Chronic values as a function of water hardness as reported by US-EPA (2001).....	389
<b>Table 3.211</b>	The PNEC <sub>water,regional</sub> (µg L <sup>-1</sup> ) for different values of water hardness (H, mg CaCO <sub>3</sub> /L). The NOEC data were all first normalised to H=50 from which the HC <sub>5</sub> at a reference hardness was found. The PNEC <sub>water</sub> at that hardness contains a assessment factor of 2. The normalisation was then used to calculate the PNEC <sub>water,regional</sub> values at other values of H.....	390
<b>Table 3.212</b>	The Cd concentrations in membrane filtered soil solution of soils amended with CdO. The solution Cd concentrations are expressed as a percentage of the Cd concentration in the soil solution of the Cd(NO <sub>3</sub> ) <sub>2</sub> treated soil for corresponding soil types and equilibration times. Data in brackets at 99 days incubation are standard deviations (Smolders et al., unpublished) .	394
<b>Table 3.213</b>	Equilibrium speciation in soil contaminated with 50 µg g <sup>-1</sup> Cd added as CdO. The speciation is predicted with MINTEQA2 (Allison et al., 1991). The logK value of the reaction Cd <sup>2+</sup> + H <sub>2</sub> O → CdO (Monteponite) + 2H <sup>+</sup> is -15.12 (database of MINTEQA2). Input parameters: soil moisture content = 0.2 g g <sup>-1</sup> ; soil solution composition Ca(NO <sub>3</sub> ) <sub>2</sub> 5 mM. Sorption of Cd <sup>2+</sup> was assumed to occur on an infinite number of sites. At each soil pH, a solid:liquid concentration ratio K <sub>D</sub> (solution Cd <sup>2+</sup> activity based) was selected that represents a typical value (see Table 3.1.88) .....	395
<b>Table 3.214</b>	Selected data for Cd toxicity to soil microflora. Fifty tests were reviewed from 18 source documents and 36 tests were selected.....	396
<b>Table 3.215</b>	Toxicity to soil microflora. All underlined data are selected to discuss the critical concentrations (Table 3.214). Bold data are used to estimate the HC <sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment.....	399
<b>Table 3.216</b>	Selected data for Cd toxicity to soil fauna. Forty tests were reviewed from 22 source documents and 37 tests were selected.....	402
<b>Table 3.217</b>	Toxicity to soil fauna. All underlined data are selected to discuss the critical concentrations (Table 3.216). Bold data are used to estimate the HC <sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment ....	404
<b>Table 3.218</b>	Selected data for Cd toxicity to higher plants. Seventy-six tests were reviewed from 15 source documents and 54 tests were selected .....	408
<b>Table 3.219</b>	Toxicity to higher plants. All underlined data are selected to discuss the critical concentrations (Table 3.218). Bold data are used to estimate the HC <sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment ....	410
<b>Table 3.220</b>	Summary of selected Cd toxicity data for the terrestrial environment (µg g <sup>-1</sup> ). All data have RI ≤ 3 and a data selection was made to avoid overrepresentation of data from the same test or the same organism (see introduction of effects assessment section) .....	413
<b>Table 3.221</b>	The NOEC values (µg g <sup>-1</sup> ) of the terrestrial compartment for various levels of reliability (RI, defined in the introduction of effects assessment section). The selected data are underlined in preceding Tables 3.215, 3.217 and 3.219 .....	414
<b>Table 3.222</b>	Selected data of effects of Cd in soil. Data derived from Tables 3.215, 3.217 and 3.219 within quality class RI 1-3 .....	415
<b>Table 3.223</b>	'One species, one NOEC': selected NOEC data of effects of Cd in soil on fauna and higher plants, and calculation of "geometric mean" NOEC's. Data derived from Table 3.222.....	418
<b>Table 3.224</b>	'Case-by-case selection': selected NOEC data of effects of Cd in soil on fauna and higher plants, and case-by-case calculation of "geometric mean" NOEC's. Bold, underlined data are selected for the HC <sub>5</sub> calculation. Data derived from Table 3.222.....	418
<b>Table 3.225</b>	Calculation of critical concentrations (µg g <sup>-1</sup> ) using the assessment factor method (AFM) or the statistical extrapolation method (SEM; Aldenberg and Slob, 1993) for Various levels of data quality .....	421
<b>Table 3.226</b>	Phytotoxicity of Cd salts in field trials .....	427
<b>Table 3.227</b>	The PNEC <sub>soil</sub> (µg Cd/g) calculated as the HC <sub>5</sub> value using the statistical extrapolation method (Aldenberg and Slob, 1993) on the NOEC data sorted by soil characteristics. The NOEC data were sorted either by soil texture or by soil pH .....	429
<b>Table 3.228</b>	Selected data with RI 1-3 for Cd toxicity to benthic organisms. Seventeen tests were reviewed from 5 source documents and 14 tests were selected.....	432

<b>Table 3.229</b>	Toxicity to benthic organisms. All underlined data are selected for the effect assessment .....	434
<b>Table 3.230</b>	Toxicity for micro-organisms in a sewage treatment plant or in artificial media .....	440
<b>Table 3.231</b>	The bioconcentration factor (BCF) of Cd in freshwater organisms. The Cd concentrations in the organisms are the product of BCF and Cd concentration in water .....	442
<b>Table 3.232</b>	Comparison of freshwater BCF (L kg <sup>-1</sup> ) found in this study with data found by Taylor (1983) .....	447
<b>Table 3.233</b>	The BAF values for whole body vertebrates (L kg <sup>-1</sup> ) .....	449
<b>Table 3.234</b>	The bioaccumulation factor (BAF) of Cd in freshwater: the Cd concentrations in the organisms are the product of BAF and Cd concentration in water .....	451
<b>Table 3.235</b>	Secondary poisoning of Cd in freshwater .....	452
<b>Table 3.236</b>	The bioaccumulation factors (BAF's) of soil dwelling organisms .....	453
<b>Table 3.237</b>	Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration .....	455
<b>Table 3.238</b>	Secondary poisoning within the lower terrestrial foodchain .....	463
<b>Table 3.239</b>	The BAF values of some benthic organisms .....	464
<b>Table 3.240</b>	Bioaccumulation of Cd in benthic organisms .....	465
<b>Table 3.241</b>	Calculation of PNEC <sub>oral</sub> (mg kg <sup>-1</sup> food) using the assessment factor method (AFM) or the statistical extrapolation method (SEM; Aldenberg and Slob, 1993) .....	467
<b>Table 3.242</b>	Mammalian and avian toxicity data from laboratory feeding studies. Concentrations are expressed per unit fresh weight of the food. Bold and underlined NOEC data are used to estimate the HC <sub>5</sub> .....	469
<b>Table 3.243</b>	Kidney Cd concentrations in mammals and predicted critical soil Cd concentrations at which renal threshold (K-Cd) may be exceeded. Predictions are based on proportional extrapolation (Figure 3.26). Bold and underlined data are used for risk assessment .....	475
<b>Table 3.244</b>	Prediction of critical soil Cd for terrestrial mammals based on values at which the critical kidney Cd concentration (400 µg/g dw) may be exceeded in the average population of different species. The critical soil concentrations is either the lowest value in the database or the HC <sub>5</sub> predicted by statistical extrapolation (Aldenberg and Slob, 1993) .....	481
<b>Table 3.245</b>	The PNEC values derived in Section 3.2 .....	484
<b>Table 3.246</b>	Local risk characterisation for water and sediment. The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L and the PNEC <sub>sediment</sub> is 2.3 mg Cd/kg <sub>dw</sub> (Table 3.245). The factor risk for sediments is calculated for the concentration of added Cd (C <sub>local</sub> sediment, Table 3.85) and for the added and regional Cd (total Cd, i.e. PEC <sub>local</sub> sediment, Table 3.85) without correction for bioavailability .....	485
<b>Table 3.247</b>	Regional risk characterisation for water in datasets varying in data quality (RI*). The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L (Table 3.245). Risk characterisation of dataset with RI=1 included bioavailability corrections (hardness correction) and risk factor given is 90 <sup>th</sup> percentile of risk factors. Datasets with RI>1 include also data of classes with lower RI index (i.e. cumulative number of data). Data refer to period 1995-2002 and details about data treatment are given in Table 3.184 .....	489
<b>Table 3.248</b>	Regional risk characterisation for sediment. The factor risk = PEC/PNEC. The PNEC <sub>sediment</sub> is 2.3 mg Cd/kg <sub>dw</sub> (Table 3.245). All values are without correction for bioavailability .....	493
<b>Table 3.249</b>	Local risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value = 0.9 mg kg <sup>-1</sup> <sub>dw</sub> is equivalent to 0.79 mg kg <sup>-1</sup> <sub>ww</sub> (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3.245) .....	494
<b>Table 3.250</b>	Regional risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value is based on secondary poisoning to mammals (Table 3.245). PEC values derived from Table 3.183 .....	495
<b>Table 3.251</b>	Regional risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC <sub>soil</sub> is 0.9 mg Cd/kg <sub>dw</sub> (Table 3.245) .....	497
<b>Table 3.252</b>	The predicted environmental concentrations in food (PEC <sub>oral</sub> ). The choice for the parameters and the risk for secondary poisoning are discussed in the text. PEC <sub>oral</sub> =(0.5PEC <sub>local</sub> +0.5PEC <sub>regional</sub> )*BC(A)F .....	498
<b>Table 3.253</b>	Overview of the input values used in the emission calculations of MSW landfills and MSW incinerators .....	501
<b>Table 3.254</b>	Local risk characterisation NiCd producing/recycling plants for water, sediment and STP. The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> <sub>dry wt</sub> . The factor risk is calculated for the concentration of added Cd (C <sub>local</sub> sediment) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245) .....	506

<b>Table 3.255</b>	Local risk characterisation incinerators for water and STP (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). Total cadmium concentrations. (Dilution Scenario 1 = DF 100 and Dilution Scenario 2 = DF 1000)	509
<b>Table 3.256</b>	Local risk characterisation incinerators for water (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). Total cadmium without NiCd contribution. (Dilution Scenario 1 = DF 100 and Dilution Scenario 2 = DF 1000)	509
<b>Table 3.257</b>	Local risk characterisation incinerators for sediments (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local, sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. Total cadmium concentrations. (Dilution Scenario 1 = DF 100 and Dilution Scenario 2 = DF 1000)	510
<b>Table 3.258</b>	Local risk characterisation incinerators for sediments (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local, sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. Total cadmium without NiCd contribution	511
<b>Table 3.259</b>	Local risk characterisation incinerator for water and STP (at dilution factor 100 and 1,000). Future scenarios: collection rate: 10 and 75%. The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). Total cadmium concentrations	511
<b>Table 3.260</b>	Local risk characterisation incinerators for sediments for a generic MSW incineration plant in the EU. Future scenarios: collection rate: 10 and 75% (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local, sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. Total cadmium concentrations	512
<b>Table 3.261</b>	Local risk characterisation incinerator for water and STP (at dilution factor 100 and 1,000). Sensitivity analysis: effluent = 0.009 mg L <sup>-1</sup> . The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). Total cadmium concentrations	513
<b>Table 3.262</b>	Local risk characterisation incinerators for sediments for a generic MSW incineration plant in the EU. Sensitivity analysis: effluent = 0.009 mg L <sup>-1</sup> (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local, sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. Total cadmium concentrations	513
<b>Table 3.263</b>	Local risk characterisation landfills (leachate concentration 5 µg L <sup>-1</sup> ) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local, sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). Total cadmium concentrations	514
<b>Table 3.264</b>	Local risk characterisation landfills (leachate concentration 5 µg L <sup>-1</sup> ) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local, sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). All cadmium without NiCd batteries	514
<b>Table 3.265</b>	Local risk characterisation landfills (leachate concentration 50 µg L <sup>-1</sup> ) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local, sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). Total cadmium concentrations	515

<b>Table 3.266</b>	Local risk characterisation landfills (leachate concentration 50 µg L <sup>-1</sup> ) for water and sediment. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC <sub>water</sub> is 0.19 µg Cd/L. The PNEC <sub>sediment</sub> is 2.3 mg kg <sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C <sub>local_sediment</sub> ) and for the added and regional Cd (total Cd, i.e. PEC <sub>sediment</sub> ) without correction for bioavailability. The PNEC for micro-organisms is 20 µg L <sup>-1</sup> (Table 3.245). Total cadmium without NiCd batteries.....	516
<b>Table 3.267</b>	Local risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value = 0.9 mg kg <sup>-1</sup> dry wt. is equivalent to 0.79 mg kg <sup>-1</sup> wet wt. (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3.245).....	517
<b>Table 3.268</b>	Local risk characterisation of Cd/CdO production/processing sites for WWTP/STP, water and sediment (modelled data). The factor risk = PEC/PNEC. The PNEC <sub>micro-organisms</sub> is 20 µg L <sup>-1</sup> , The PNEC <sub>water</sub> is 0.19 µg Cd/L and the PNEC <sub>sediment</sub> is 2.3 mg Cd/kg <sub>dw</sub> . (Table 3.245). The factor risk for sediments is calculated for the concentration of added Cd (C <sub>local_sediment</sub> , Table 3.137) and for the added+regional Cd (total Cd, i.e. PEC <sub>local_sediment</sub> , Table 3.137). The results for the sediment compartment are based on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A conclusion (i) program is ongoing.....	519
<b>Table 3.269</b>	Local risk characterisation for soil (modelled data). The factor risk = PEC/PNEC. The PNEC value = 0.9 mg kg <sup>-1</sup> dw is equivalent to 0.79 mg kg <sup>-1</sup> ww (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3.245).....	525

# 1 GENERAL SUBSTANCE INFORMATION

As much of the (eco)toxicological information on Cadmium metal is derived from Cadmium oxide (and other cadmium compounds), and as a close relationship exists between both priority substances (see mass-balance) it was proposed that both RARs should be merged for the sections 1 to 4 with exception of the risk characterisation in the Human Health part where for each substance a separate section on risk characterisation and conclusions should be developed.

Primary source of information for this section and more particularly Sections 1.1, 1.2 and 1.3, was the 'IUCLID' document provided by Industry (Lead-company) in 1997 as a background document and complement to the HEDSETs.

## 1.1 IDENTIFICATION OF THE SUBSTANCE

CAS-n°:	7440-43-9	1306-19-0
EINECS-n°:	231-152-8	215-146-2
IUPAC name:	Cadmium metal	Cadmium oxide
Synonyms:	Not applicable	Not applicable
Molecular formula:	Cd	CdO
Atomic/Molecular weight:	112.41 (several naturally-occurring isotopes ranging from 106-116 (Lexicon, 1972; WHO, 1992)	128.41
Colour	blue-white (Sax and Lewis, in: ATSDR, 1998)	varies from greenish-yellow through brown to nearly black, depending on the thermal history (due to lattice defects) and on the particle size

## 1.2 PURITY/IMPURITIES, ADDITIVES

	Cadmium metal	Cadmium oxide
Purity (powder):	Min. 99.9%	min. 99.999% (IUCLID, 1997)
Purity (massive):	Min. 99.99%	
Impurities (max.):	for 99.99% Cd metal: Fe: 10 ppm; Cu: 20 ppm; Ni: 10 ppm; Pb: 100 ppm; Zn: 30 ppm, Th: 35 ppm. Other levels are specified for other purity grades. (ASTM B440-00)	n.a. powder reagent grade: max. chloride 0,002%; nitrate 0,01%; sulphate 0,20%; copper 0,005%; iron 0,002%; lead 0,01% (JT Baker chemical Co, 1984)
Additives:	none	none

Remark: It is stated that the purity levels and chemical analyses indicated here are purely arbitrary as many grades of both cadmium metal and cadmium oxide exist. It is recommended that the ranges or specifications should be listed using the appropriate ISO or EN standards (ICdA, com. 2003). However, only the ASTM standard was provided for Cd metal grades 99.95, 99.99 and 99.995%.

### 1.3 PHYSICO-CHEMICAL PROPERTIES

Table 1.1 Summary of physico-chemical properties

Property	Cadmium metal	Cadmium oxide
Physical state:	solid (massive or powder)	solid (powder)
Crystal structure:	distorted hexagonal close-packed	cubic structure with each ion surrounded by six ions of opposite electric charge, octahedrally arranged. Also an amorphous form exists: stable at lower temperatures, forming crystals of the cubic type at red heat
Melting point:	320,9°C (Lexicon, 1972, Sax and Lewis: in ATSDR, 1998; CRC: in IUCLID, 1997)	Decomposes at 900-1000 °C (CRC, 1985; IUCLID, 1997)
Boiling point:	765°C (idem); 767°C (Sax and Lewis: in ATSDR, 1998)	CdO is non-fusible but volatilises at high temperature. Sublimation at 1559°C
Relative density:	8.64 g/cm <sup>3</sup> (Lexicon, 1972, Sax and Lewis: in ATSDR, 1998: analysis by WIAUX S.A., in LISEC, 1998e).	8.15 g/cm <sup>3</sup> (cubic form); 6.95 g/cm <sup>3</sup> (amorphous) (EPA 1985).
Vapour pressure:	1 mmHg at 394°C (Sax and Lewis: in ATSDR, 1998 133 hPa at 394°C (CRC, in: IUCLID, 1997)	1 mmHg at 1000°C (Sax, N.I., 1984)
Water solubility:	quoted as 'insoluble' (The Merck index; in: ATSDR, 1998; CRC, in: IUCLID, 1997). However it was mentioned: 0,05 mg/l at pH 10,5 a curve in function of pH and hardness: at pH 7: solubility is 10 to 100 times higher than at pH 8.5 dependent on the total carbonate concentration (M. Farnsworth, 1980). Measured dissolved cadmium concentrations after 7 days transformation/dissolution test with cadmium metal powder at loading 1 – 100 mg/l, were in the range 0.192 – 0.135 mg/l (at pH +/- 8) (LISEC, 1998e).	quoted as 'insoluble' However measured dissolved cadmium concentrations after 7 days transformation/dissolution test with cadmium oxide powder at loading 1 – 100 mg/l were in the range 0.095 – 0.227 mg/l (at pH +/- 8) (LISEC, 1998f). Soluble in acids and solutions of ammonium salts (Farnsworth, 1980).
Partition coefficient:	No data	No data

Table 1.1 continued overleaf

Table 1.1 continued Summary of physico-chemical properties

Property	Cadmium metal	Cadmium oxide
n-octanol/water(log-value):	Not applicable	Not applicable
Flammability:	<p>Slight fire hazard. The finely divided metal may be pyrophoric in air (MSDS, 1992; IUCLID, 1997)*</p> <p>GLP testing conform EC Testing methods A.10, A.12 and A.13 (BAM, 2002): Cadmium metal 'powder' [particle size distribution (in volume-%): d(0.1): 3.462µm; d(0.5): 7.154 µm; d(0.9): 14.117 µm; mean water content: 0.03] and cadmium 'fine billes' [particle size distribution (in volume-%): d(0.1): 2.485µm; d(0.5): 7.040µm; d(0.9): 15.753µm; mean water content: 0.05] are not flammable and do not have pyrophoric properties in sense of the EC-methods, Dir. 92/69/EEC.</p>	Not flammable
Explosive properties:	Dust/air mixture may be explosive. Even as fine powder, cadmium is hardly explosive (MSDS, 1992; INRS, 1987)	
Self-ignition:	Not applicable	Not applicable
Oxidising properties:	Not applicable	Not applicable
Granulometry:	<p>The average spherical diameter of cadmium powder prepared by distillation is about 18 µm +/- 13.3 µm (S.D.) (inhalable fraction) and the specific surface area : 580.4 cm<sup>2</sup>/g (analysis by WIAUX S.A., in: LISEC, 1998e).</p> <p>Particle size and surface area depend very much upon the specific process and specific application. For example, INMETCO produces a cadmium metal shot which is many times larger than the aforementioned cadmium metal powder (ICdA, com. 2003). See also remark related to flammability testing.</p>	<p>The average spherical diameter of CdO powder prepared by oxidation of Cd metal is about 0.55 µm (respirable fraction) (La Floridienne, 1997).</p> <p>Particle size and surface area depend very much upon the specific process and specific application (ICdA, com. 2003).</p>

Table 1.1 continued overleaf

Table 1.1 continued Summary of physico-chemical properties

Property	Cadmium metal	Cadmium oxide
Odour threshold:	No data	No data
Ionisation potential:	$E^\circ\text{Cd}/\text{Cd}^{2+} = 0.4025 \text{ eV}$ (= fairly reactive)	
Caloric value	0.16 Cal/g	

GLP testing on flammability and pyrophoric properties of the products, Cadmium metal powder and Cadmium 'fine billes' according to the EC Methods A.10, A.12 and A.13 was performed by Industry (ICdA) on a voluntary basis (final report of BAM, October 2002). The substances are not flammable and do not have pyrophoric properties in sense of the EC-methods, Dir. 92/69/EEC and are thus not to be classified (and labelled) related to these properties.

The grade Cadmium 'fines billes' is stated as being the finest grade of Cadmium 'powder' from current EU manufacturing that is put on the market (since 2001). However, other qualities may be manufactured elsewhere e.g. in Japan and China (ICdA, pers. com. 2003).

The physical, thermal, electrical, magnetic, optical, and nuclear properties of cadmium metal are summarised by Morrow (2001), however without indication of testing specifications or the primary source. Where available, this source confirms the aforementioned entries for physico-chemical properties.

## 1.4 CLASSIFICATION

According to Annex I of Directive 67/548/EEC (29<sup>th</sup> ATP) of 16/06/2004.

### Cadmium metal and oxide

#### Classification

Carc. Cat. 2; R45	Category 2 Carcinogen; May cause cancer
Muta. Cat. 3; R68	Category 3 Mutagen; Possible risks of irreversible effects.
Repr. Cat. 3; R62-63	Category 3 Toxic to Reproduction; Possible risk of impaired fertility, and of harm to the unborn child
T; R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
T+; R26	Very toxic by inhalation
N; R50-53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

#### Labelling

T+; N

R: 45-26-48/23/25-62-63-68-50/53

S: 53-45-60-61

### 1.4.1.1 Note on environmental classification and labelling

A general introduction and description of the methodology on classification and labelling of insoluble and sparingly soluble metals, including the dissolution test and the criteria for

classification is given in the RAR on zinc metal<sup>89</sup>. The results of Dissolution and Short-term toxicity tests will be discussed in detail in Section 3 (Environment) of the present Risk Assessment Report.

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<sup>8</sup> [http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK\\_ASSESSMENT/REPORT/zincmetalHHreport072.pdf](http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/zincmetalHHreport072.pdf)

<sup>9</sup> It should be noted that the 'critical surface approach' as suggested in OECD context is not considered in the reports for neither cadmium metal nor cadmium oxide.

## 2 GENERAL INFORMATION ON EXPOSURE

### 2.1 PRODUCTION

#### Cadmium metal

Cadmium is a naturally occurring element with ubiquitous distribution. Although cadmium ores also exist (greenockite) these are not commercially important. Zinc (sulphide) ores are the primary source for cadmium production. Smaller amounts of cadmium are produced during the production of other non-ferrous metals such as lead. In the refining of these ores cadmium is obtained as a by-product (Technical notes on cadmium, 1991).

Whereas the extraction and refining of the primary non-ferrous metal from the ores can be obtained either by pyrometallurgical or electrolytic processes, the final step of cadmium production is done by fractional distillation or electrolysis.

#### Cadmium oxide

Although cadmium oxide is an important commercial compound it is not manufactured from the zinc or mixed non-ferrous metal ores, phosphate rock, coal or other rock forms, as cadmium oxide but indirectly from the cadmium produced as a by-product in the manufacture of zinc and lead. The substance is important commercially for itself and also because of its extensive use in the preparation of other cadmium compounds.

#### 2.1.1 Production processes

##### Cadmium metal

The primary non-ferrous metal can be produced via two distinct types of production.

The formerly used pyrometallurgical processes. Here the residual sintered concentrate (calcine) containing oxidised zinc and cadmium materials is heated to about 1,100 to 1,350°C, reduced by carbonaceous material and the zinc and cadmium volatilised. The metal vapours are condensed and collected as metal dust. Most of the cadmium collects with the zinc metal and may be removed in the refining of zinc by fractional distillation (refluxing). In this process the boiling points of the metals present (cadmium 767°C, zinc 906°C and lead 1,750°C) are well separated and the cadmium can be concentrated in a cadmium-zinc alloy. Further repeating the distillation process under reducing conditions will result in cadmium metal with increasing purity.

The present-day electrolytic process has the following main features. During the production of zinc, at the purification of the solutions of zinc sulphate, before the electrolysis, cadmium is present in dissolved impurities (CdSO<sub>4</sub>). Cadmium is precipitated herein by adding zinc (as zinc powder or dust). The resulting impure cadmium residue (cadmium sponge) is purified and leached with aqueous sulphuric acid solution. A reasonably pure cadmium sponge is produced after two additional acid solution/zinc dust precipitation stages. The sponge is again dissolved in sulphuric acid and the solution, if sufficiently pure, is passed into electrolytic cells where the cadmium is deposited on cathodes (see **Figure 2.1**).

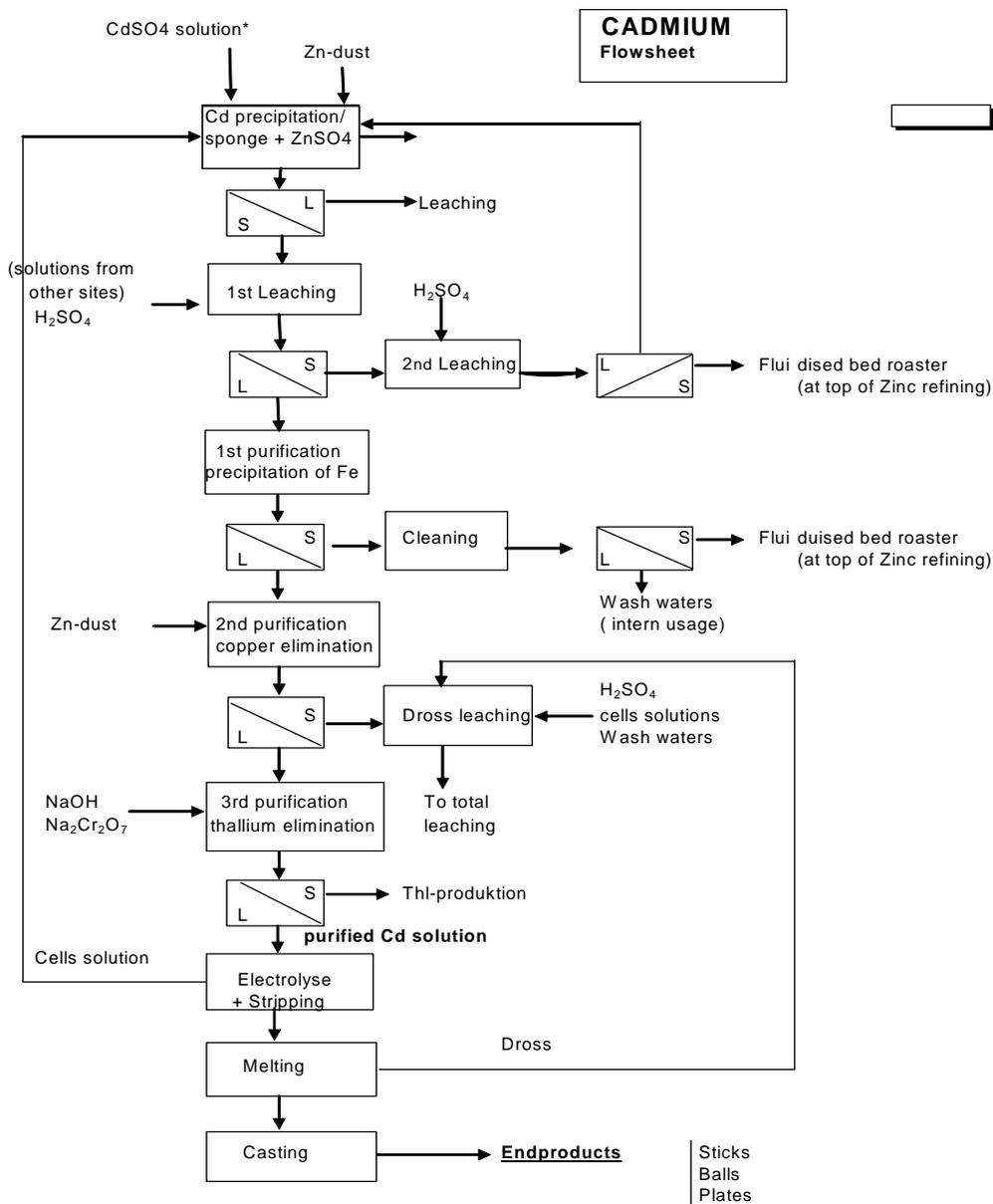
After deposition, the cathodes are stripped and the cadmium melted and cast into the required shapes (sticks and balls). The metal is typically either 99.95 or 99.99% pure. Higher purity

grades for special purposes can be obtained by further vacuum distillation (Lexicon, 1971; Technical notes on cadmium, 1991).

Variations in the production flow-sheet exist from one production site to the other. These may be due to differences in the type of the ores (zinc, lead), origin, form and content, the purity of the end-product that is aimed at, legal environmental criteria and the extent of (auto) recycling activities (scraps, flue dust etc.).

In the EU cadmium metal is produced mainly as a by-product of zinc production via electrolytic processes (approximately 77.5% of the total volume). The rest is obtained in association with pyrometallurgical refining processes (Industry Questionnaire, 1997).

Figure 2.1 Cadmium production flow-sheet: an example of electrolytic process in a closed production system (Union Minière, 1998)



L/S : liquid solid separation (via filter)

\* :  $CdSO_4$  solution is coming from repulping step of the residues after the purification step in the Zinc leaching section

## Cadmium oxide

In the commercial production process, cadmium oxide is prepared by the reaction of cadmium metal vapour with air. For the production of cadmium as part of the refining of zinc ores, we refer to the aforementioned paragraph. Other production possibilities are thermal decomposition of the carbonate, nitrate, sulphate or hydroxide but these are stated not to be in use for current industrial production (IcdA, com., 2003).

Cadmium oxide is available on the market in powder form. Its average particle size (spherical diameter) is 0,5 to 0,55 $\mu\text{m}$  (IUCLID, 1997).

It is packaged in metal drums, big bags, flo bins or containers (IUCLID, 1997).

Figure 2.2 Cadmium oxide production: flow-sheet

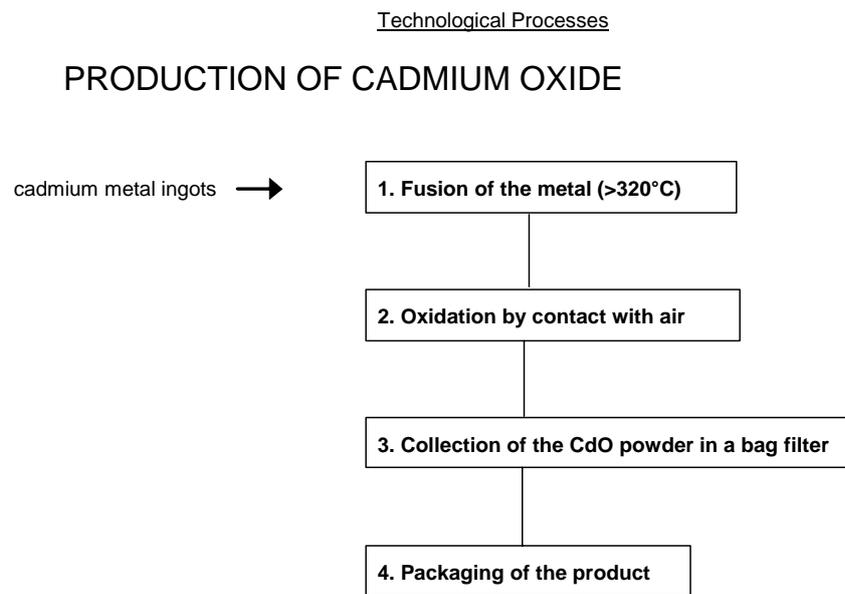
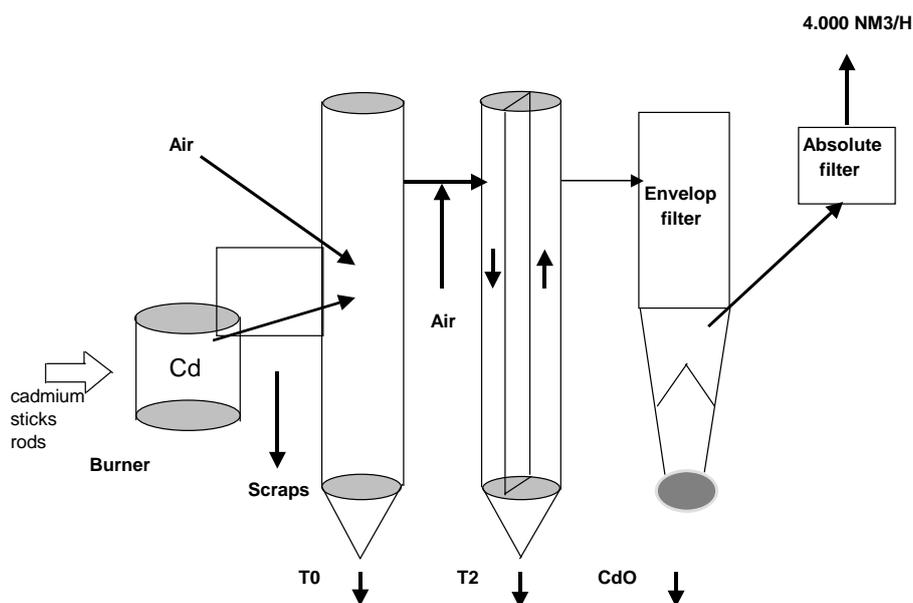


Figure 2.3 Production of cadmium oxide (PC WIAUX company information, 1998)



The manufacturing process for cadmium oxide is partly enclosed. Cadmium metal in ingots is manually placed in furnaces heated at 320°C. Emitted fumes are oxidised by contact with air in a closed system. The produced CdO powder is filtered and collected in bags, flo bins and metal drums or directly into silo. The packaging station has local exhaust ventilation at the discharge point. Workers have to place and adjust the bag or drum under the discharge and to set the process in motion (semi-automated process). Filled bags and drums are subsequently closed and carried to the storage area.

## 2.1.2 Production volumes

### 2.1.2.1 Data for the reference year 1996

#### Cadmium metal

The world primary cadmium production is estimated at 14,000 to 16,000 tonnes/year, the corresponding figure for Europe was approximately 5,000 tonnes/year (1994) – 5,800 tonnes/year (1996) (Industry, 1997), produced at 12 sites all over the EU territorial surface with, in these years, a major site localised in Belgium.

The amount imported in Europe in the same period is estimated at 1,500 tonnes/year – 960 tonnes/year (figure representative for January-July '96) (Eurostat, 1997; in: IUCLID, 1997). Export out of Europe is estimated at 2,200 tonnes/year (1996). This latter figure is obtained by subtracting the total EU consumption from the total EU production (IZA, personal comm., 1997).

Table 2.1 Cadmium production plant size distribution for 1996

Tonnes	Number of cooperating companies
< 300 tonnes	5
300-600 tonnes	4
> 600 tonnes	3

Table 2.2 Production sites of metallic Cadmium in the EU ( in the range 10 to >1,000 tonnes/year, EUREX), IUCLID 1997

Company (and plant)	Country
Produits Chimiques Wiaux SA*	Belgium
Asturiana de Zinc	Spain
Britannia Zinc Limited	UK
Budel Zink BV	The Netherlands
Enirisorse	Italy
Espanola Del Zinc S.A.**	Spain
Metaleurop Nord S.A.S.	France
Metaleurop Weser Zink GmbH	Germany
Norzink	Norway

Table 2.2 continued overleaf

Table 2.2 continued Production sites of metallic Cadmium in the EU  
(in the range 10 to >1,000 tonnes/year, EUREX),  
IUCSID 1997

Company (and plant)	Country
Outokumpu Zinc OY	Finland
Ruhr-Zink GmbH	Germany
Union Miniere Balen***	Belgium

\* Production/conversion stopped in 2001 (plant is closed down; Ind., pers. Comm., 2002)

\*\* Last cadmium production in 1991; since: zinc refinery without cadmium production

\*\*\* Company's name became UMICORE (2001) and production stopped in 2002

Remark: one company identified by the EUREX CD ROM is not included in the risk assessment process (phase 3 company with a production/import volume between 10 and 1,000 tonnes/year). Apparently it concerns a German pigment manufacturer presumably importing/using cadmium metal for further processing only.

An update provided by Industry (IcdA, com., 2003) reveals that Asturiana de Zinc in Spain no longer produces cadmium. Britannia Zinc and Metaleurope (France) have both recently closed down. Española del Zinc and Ruhr-Zink have not produced for many years. Outokumpu and Umicore exited the cadmium production business more recently. The **Table 2.2** needs thus some serious revision. It gives the impression that there are 12 active cadmium production plants in Europe when in fact there are now only three, possibly four: Budel (now known as Pasmenco Budel), Norzink (now known as Norzinc Outokumpu), Enirisorse (now known as Porto Vesme, owned by Glencore) and possibly Metaleurop Weser Zink (recently taken over by Glencore). No more details were submitted.

Table 2.3 Raw EU production, import, export and consumption data of cadmium metal in metric tonnes (Industry site specific questionnaire, 1997)

Year	EU production	EU import	EU export	EU consumption
1994	5,000	1,582	n.d.	n.d.
1995	5,648	2,822	4,953	3,517
1996	5,808	960 (until July)	2,200 (derived)	n.d.

n.d. No data

The available figure for 1996 has been derived from the production figure and the consumption figure of 1995 (assuming that this remained roughly the same in 1996); IZA, personal comm., 1997). The consumption figure for 1995 has been roughly derived from the information on production volumes used downstream in plating, pigments, stabilisers and batteries production facilities (IcdA, 1997).

### Cadmium oxide

The world production of cadmium (metallic) is estimated at 14,000 to 16,000 tonnes/year. The production of cadmium oxide for Europe was approximately 3,070 tonnes/year (1994) – 2,536 tonnes/year (1996) (Industry Questionnaire, 1997), produced at 2 major sites in the EU (Belgium).

Table 2.4 Production sites of cadmium oxide in the EU (EUREX), IUCLID 1997.

Company (and plant)	Country
Floridienne Chimie S.A., Ath	Belgium
Produits Chimiques Wiaux SA*	Belgium

\* Production was taken over by Floridienne in 2000, and was definitively stopped in 2001 (Ind., pers. Comm., 2002)

Remark: one company identified by the EUREX CD ROM is not included in the risk assessment process (the concerned company has a production volume in the range: 10 – 1,000 tonnes/year). It concerns a pigment manufacturer presumably importing/using cadmium metal for further processing – via an in-house production of cadmium oxide - to pigments only.

The amount of cadmium oxide imported in Europe is unknown with the exception of the first half of 1996 (January to July) for which 23 tonnes was reported (IUCLID, 1997). The latter document does not cite information on export. The site-specific information however mentions an important export activity taking place every year (approximately 1,000 tonnes/year leave the EU).

Table 2.5 Raw EU production, import, export and consumption data of cadmium oxide in metric tonnes (IUCLID, 1997; Industry site specific questionnaire, 1998)

Year	Production	Import	Export	Consumption
1994	3,069	n.d.	≥ 1,050	n.d.
1995	2,757	n.d.	≥ 1,350	n.d.
1996	2,536	23 (until July)	1,000	n.d.

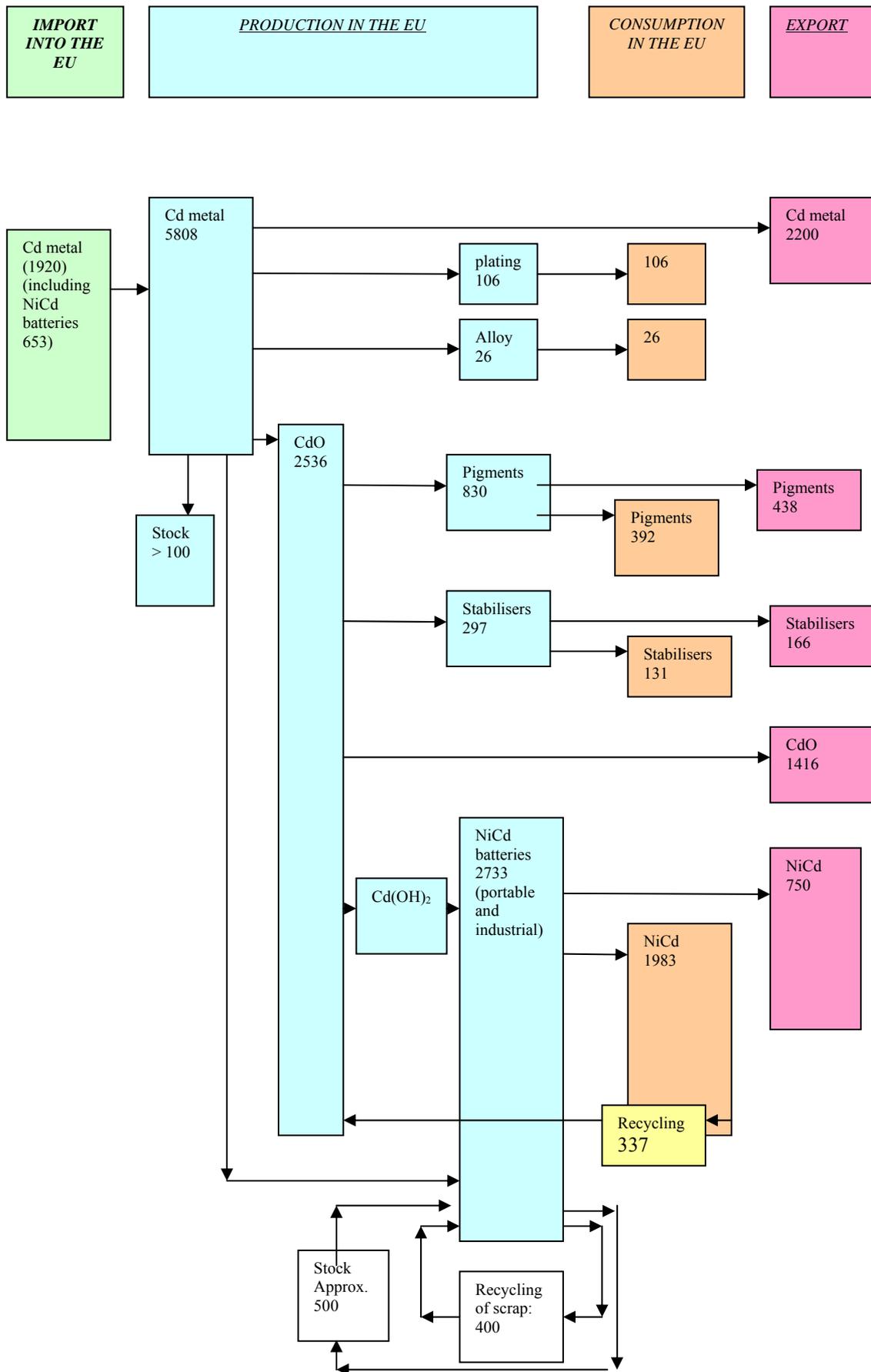
Production, import, export and consumption figures for both priority substances, cadmium metal and cadmium oxide, submitted by Industry are fragmentary.

In 2000, Industry provided a mass-balance for the reference year 1996, accompanied by an explanatory note (see **Figure 2.4** and further), reflecting the best possible estimate at the moment.

An update for the year 2000 was provided in the context of the batteries' targeted risk assessment (see **Figures 2.9** and **2.10** in Section 2.2.2.3.2) and estimates for the year 2002 in the context of the update site-specific assessment (see **Figure 2.11** in Section 2.2.3.1).

Two important confounding factors make it difficult to establish accurate cadmium consumption figures: 1) the conversion of cadmium metal into cadmium oxide and other cadmium compounds and 2) shipments of cadmium-containing residues to zinc smelters from recycling operations (Morrow, 2001).

Figure 2.4 Cadmium mass flow sheet (metric tonnes)- reference year 1996 (Source: IZA-Europe, IcdA, UM and CollectNiCd, 2000 and 2001)



### Explanatory note to the mass-flow of cadmium (as provided by Industry)

The mass balance reveals that 5,808 tonnes of cadmium were produced in Europe in the reference year (1996). The imports were estimated to 1,920 tonnes including the contribution of the metal present in imported consumer/sealed portable nickel-cadmium batteries. Cd metal stocks exists in Rotterdam which may influence the trading balance but the data reported hereafter have been mainly obtained from use at the industrial level for the various applications.

It can be observed that a large industrial activity consists in the transformation of cadmium metal in the oxide: the equivalent of 2,536 tonnes of cadmium are used in the production of cadmium oxide.

The EU regional use of metal reaches the value of 2,638 tonnes, which are distributed for 75.2% to Ni-Cd batteries, 14.9% to pigments, 5% to stabilisers and 5% into alloys and plating.

Portable Nickel-Cadmium batteries are introduced on the market as a power source incorporated in Electrical and Electronic equipment in more than 90% of the cases. This is the origin of a significant export ratio for batteries. This ratio has been estimated between 33% to 50% (according to applications and countries) for the consumer/sealed portable batteries produced in Europe on the basis of the Import- Export balance.

Industrial Ni-Cd batteries are not imported in significant quantities (less than 5%). They are manufactured in European countries and are exported in a significant proportion, estimated to 35% for the global European market. The net export of cadmium from batteries reaches the estimated volume of 750 tonnes.

The largest export quantity is found in the cadmium metal produced by European companies in order to satisfy the demand in USA, Asia and South America. A significant fraction of the cadmium oxide produced in Europe is exported to non-European battery manufacturers which demonstrates the competitiveness of this European industry involved in the transformation of Cadmium into the oxide. When the battery is marketed, the cadmium content is present as cadmium hydroxide (discharged battery) or as cadmium metal (charged battery).

It has been estimated that cadmium from recycling operations reached approximately 337 tonnes from used batteries collected from the market and industrial sources. In addition, there are two types of stocks to be considered. First, the manufacturing rejects and secondly, a cadmium stock for the work in progress. Those have been presented in a closed loop independently of the total inlet and outlet of the primary cadmium. Indeed recycling operations leads to a 99% recovery of the cadmium content of the battery. The metal has a purity higher than 99.9% and is re-used in new battery manufacture. The battery manufacturing capacity will produce a new volume of waste equivalent to the treated one, which is re-introduced in the circuit. At the same time, the management of a stock required for the “work in progress” is considered.

Mass-balances are available for several EU countries, and years (e.g. Denmark for 1996 (Danish EPA, 1994 and 2000), Germany for 1990, 1991, 1992, 1993 and 1994 (UBA, 1996), the Netherlands for 1980 (VROM, 1991), France for 1995/1996 (l'Académie des Sciences Rapport N° 42, 1998) and Greece for 1993 and 1997 (EUPHEMET, 2000). From these documents, the overall consumption patterns and trends are roughly confirmed, with a largely predominant flow of cadmium in batteries that dramatically increased since the eighties and continued during the nineties while most other uses have been declining.

### 2.1.2.2 Update date (reference year 2002)

In 1997, from the companies liable to the Regulation 793/93/EEC, there were 12 companies producing cadmium metal and 2 producers of cadmium oxide. Regards the import of the substances, one company for cadmium metal and one company for cadmium oxide were active in the field and were subject to the existing substances regulation.

In 2005, this picture has significantly changed. An overview is given here below.

#### Cadmium metal

The companies that stopped the production of cadmium metal/cadmium oxide and the approximate date are listed in **Table 2.6**.

Table 2.6 Production sites of metallic cadmium/CdO in the EU in the range 10 to > 1,000 t/y that stopped production

Company (and plant)	Country	Date/year of production stop
Asturiana de Zinc (now: Xstrata Zinc)	Spain	1998
Britannia Zinc Limited (in liquidation: 2003)	UK	2003
Espanola del Zinc S.A.	Spain	1991/1992
Metaleurop Nord S.A.S.	France	2003
Outokumpu Zinc OY (now: Boliden Kokkola)	Finland	2002
Ruhr-Zink GmbH	Germany	1998-1999
Union Minière Balen (now : Umicore)	Belgium	2002
Produits Chimiques Wiaux S.A.	Belgium	2000/2001

Former activities at Produits Chimiques Wiaux S.A.: limited to the conversion of massive cadmium metal into cadmium metal powder

The companies still manufacturing cadmium metal in 2005 are reported in **Table 2.7**. All companies produce the substance in massive form (e.g. plates, sticks, balls).

Table 2.7 Current producers of cadmium metal liable to the Regulation 793/93/EEC

Company (and site)	Country
Budel Zink (now: Zinifex Budel)	The Netherlands
Norzink (now: Boliden Odda A.S.)	Norway
Metal Europ Weser Zink (now: Xstrata Zinc GmbH)	Germany

Updated data on EU-16 production data are given in **Table 2.8**. No data are available on the situation in the EU-25.

Table 2.8 EU production, import, export and consumption data on primary cadmium metal in metric tonnes (Industry site specific questionnaire, 2004/2005)

Year	EU production	EU import	EU export	EU consumption
2002	1,114	n.d.	n.d.	n.d.
2003	1,207	n.d.	n.d.	n.d.

n.d. No data available

Based on the data of one producer 85% of the production volume is exported outside the EU-25. A second company mentions 100% export but it is not clear if this is meant as outside the EU or outside country where production is located.

The amount of secondary cadmium produced by recycling is given under Section 2.2.3.2.

The total volume of cadmium consumed within the old EU-16 (including Norway) and the new EU-25 territory is unknown.

### Cadmium oxide

Update information regards the producers of cadmium oxide is given in the **Table 2.9** and **Table 2.10**.

Table 2.9 Production sites of metallic cadmium in the EU in the range 10 to > 1,000 t/y that stopped production

Company (and plant)	Country	Date/year of production stop
Produits Chimiques Wiaux S.A.	Belgium	2000/2001

Former activities at Produits Chimiques Wiaux S.A.: limited to the conversion of massive cadmium metal into cadmium oxide

Table 2.10 Production sites of cadmium oxide in the EU with volume > 1,000 tonnes/year (reference year: 2002)

Company (and site)	Country
La Floridienne	Belgium

Information on the total production of cadmium oxide by La Floridienne was submitted for the reference year 2002. Since 1996 there is an increase of the production volume.

## **2.2 USES**

### **2.2.1 General overview**

#### Cadmium metal

Metallic cadmium is mainly used in the production of batteries, cadmium compounds (cadmium oxide and to a lesser extent cadmium hydroxide). Further also in coatings, alloys and other miscellaneous uses (see **Table 2.11** showing the industrial and use categories of cadmium). The two types of 'Main categories' for cadmium are characterised as non-dispersive use and use resulting into or onto a matrix.

Metallic cadmium is commercialised in different forms: powder, balls (3-5 cm diameter), plates (10-200-200 to 1.000mm) or sticks (200 to 240-10 to 12 mm) (IUCLID, 1997).

#### CdO production

An important proportion of the cadmium metal produced is subsequently used in the production of cadmium oxide powder. This substance has several applications and constitutes the (principal) raw material in the production of other cadmium compounds.

The CdO produced has a high purity (at least 99% CdO) resulting in a cadmium wt% of 87.25 to 87.5.

A short description of the uses of respectively cadmium metal and cadmium oxide and processes involved is given below (source: IcdA, 1997, unless specified otherwise).

### Cadmium metal

#### *Batteries*

See the batteries' related sections (see Section 2.2.2).

#### *Plating*

By plating of metals or alloys a coating is provided that is resistant to corrosion by alkalis, salt water and atmosphere. Furthermore these coatings are highly ductile and easily soldered.

Cadmium coatings have low coefficients of friction and maintain high electrical conductivity, and hence are used mainly in applications where both corrosion resistance and lubricity or good electrical conductivity are required (IcdA, com., 2003). Cd-Ti and Cd-Sn electroplated coatings are used to resist hydrogen embrittlement in high strength steel fasteners.

The coating can be realised by electrochemical reaction: cadmium is the anode in the cell formed with an iron substrate in water. Other technologies for coating are vacuum deposition (mainly cyanide baths), dipping or spraying<sup>10</sup>, or mechanical plating<sup>11</sup> with cadmium powder, where glass shot is used. Cadmium ion vapour deposition is another technique also used. For further details on the processes see the human health part of this report in a separate document.

Electrodeposition of cadmium on a metal substrate accounts for 90% of the cadmium used in plating. The remaining 10% is applied by vacuum deposition, metal spraying<sup>2</sup> or mechanical<sup>3</sup> plating.

Cadmium plating by electrodeposition uses an alkaline cyanide solution of the metal as starting material. The plating solutions can be purchased direct from chemical manufactures; alternatively they can be prepared on-site from cadmium metal or oxide. The plating solution normally contains 18-22 g/l Cd. Baths usually have cadmium bars or ball anodes, placed in steel anode baskets with a surface area of cadmium equal to the plating load. Barrel plating usually uses and electrolytes with less cadmium (15 g/l). After electroplating, and heat treatment if required, a chromate conversion coating is usually applied on a subsequent bath (IcdA, 1997).

Plating contains 99,95% cadmium (IUCLID, 1997).

#### *Alloys*

Cadmium has been a common component of many alloys which uses are related to their melting temperatures, e.g. tin-lead-bismuth-cadmium alloy joining metal parts which may be heat sensitive; silver-cadmium-copper-zinc-nickel alloy for joining tungsten carbide to steel tools. The EU use of cadmium as a constituent of alloys (mainly Cu-Cd and Ag-CdO) has declined in importance in the recent years (4% of total use in 1985, about 0.6% in 1996) as these have been

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<sup>10</sup> dipping and spraying are no longer used (ICdA, com., 2003)

<sup>11</sup> mechanical coating has declined significantly (ICdA, com., 2003)

substituted by cadmium free alloys with comparable characteristics of ductility and strength in the majority of uses.

Cu-Cd alloys are prepared by re-melting high conductivity copper in suitable furnaces and adding the necessary cadmium in the form of a copper-cadmium master alloy, or by 'side-casting' from holding furnaces fed by the large reverberatories of refineries.

During the manufacturing of the master alloys, drosses containing Cd are released. Usually, they are recycled internally or in other metal plants.

The normal form of the casting is a wire bar, which is hot rolled before drawing to wire. Normal practise is followed in drawing the rod to wire, using dies of suitable shape in the case of trolley wire. Limited quantities of sheet and strip are produced by rolling and of rod by extrusion and drawing (IcdA, 1997).

Cu-Cd alloys contain usually 0.2-0.8% cadmium. The production of these alloys occurs via pre-alloys (containing 49-51% cadmium) which are further processed by other industries to prepare the final Cu-Cd alloys (IUCLID, 1997).

Ag-CdO electrical contact alloys are produced by internally oxidising an Ag-Cd alloy. The percentage of Cd in Ag-CdO alloys is generally in the range of 5% to 15% (IcdA, pers. Com., 2003).

#### *Other uses*

Applications as reported by Farnsworth (1980): deoxidiser in nickel plating, in process engraving, in electrodes for cadmium vapour lamps, in photoelectric cells and in the photometry of ultraviolet sunlamps, in selenium rectifiers and Jones reducers and application of cadmium powder as an amalgam (1Cd:4Hg) in dentistry, are stated by Industry as no longer in use (IcdA, pers. Com., 2003).

#### Cadmium oxide

Cadmium oxide is used as starting material for a wide variety of other cadmium compounds (PVC heat stabilisers, pigments). Cadmium oxide has been used as a stabiliser for the cadmium sulphide and sulpho-selenide forms in glass<sup>12</sup>. In nitrile rubbers the substance improves heat resistance; in plastics, it improves high temperature properties.

Another field of (minor) applications is based on the catalytic properties of cadmium oxide. It catalyses reactions between inorganic compounds, as well as organic reactions such as oxidation-reduction, dehydrogenation, cleavage and polymerisation (use as vulcaniser). It sensitises photochemical reactions.

Other (former) uses included phosphors, semi-conductors, manufacture of silver alloys, and as nematocide-anthelmintic in swine and poultry.

A short description of the uses and processes involved is given below (source: IcdA, 1997, unless specified otherwise).

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<sup>12</sup> This use is not known by Industry (ICdA, pers. com., 2003)

### *Batteries*

Although cadmium metal is one of the principle raw materials, cadmium oxide is used in the manufacture of certain types of cadmium electrodes (IcdA, 1997). See the batteries' related sections (see Section 2.2.2).

### *Stabilisers*

Barium cadmium stabilisers can be manufactured in a number of ways. The starting materials are usually the metals or the metal oxide. They are combined with various organic compounds. Three general processes can prepare the salts:

- Direct dissolution of finely divided metal oxides in heated organic acids
- Precipitation from aqueous solution of metal salts (chlorides or nitrates) and alkali soaps
- Fusion of metal oxides with organic acids.

For liquid barium/cadmium stabilisers the production starts from metal oxides which are dissolved directly in the heated organic acids in the presence of solvents. The reaction water is removed and the finished product filtered.

Solid stabilisers are prepared by the precipitation process through the method of preparing metal soaps of natural fatty acids to give for example, cadmium laurate. Following precipitation the resultant slurry is filtered and dried (IcdA, 1997).

### *Pigments*

There is a number of proprietary manufacturing processes, which use either cadmium metal, or cadmium oxide as the essential raw material. In general the manufacturing process involves the preparation of a cadmium sulphate or nitrate solution; filtration to remove recoverable solids; addition of sodium sulphide and precipitation of cadmium sulphide, with simultaneous additions of other salts to alter colour characteristics; filtration to define precipitate and drying; calcination to convert crystal structure to more stable form; further rinsing, milling and blending followed by packaging (IcdA: compilation of Industry data, 1997).

Table 2.11 Industrial and use categories of cadmium in the EU (HEDSET, 1994)

Industrial category	EC No.	Use category	EC No.
Chemical industry: basic chemical	2		
Chemical industry: chemicals used in synthesis	3	Intermediates	33
		Laboratory chemicals	34
Electrical/electronic engineering industry	4	Conductive agents	12
		Batteries and cells...	
Personal domestic	5	see Product Register	
Metal extraction, refining and processing industry	8	Electroplating agents	17
		Others: Alloys	55
Paint, lacquers and varnishes	14	Reprographic agents	45
Others: Basic metal used in metal industry	15	Corrosion inhibitors	14

Table 2.12 Industrial and use categories of cadmium oxide in the EU (HEDSET, 1995; Product Registers, 1997 and 1998)

Industrial category	EC No.	Use category	EC No.
Chemical industry: basic chemical	2		
Chemical industry: chemicals used in synthesis	3	Intermediates	33
		Laboratory chemicals	34
		Raw material for the production of other cadmium chemicals	55
Electrical/electronic engineering industry	4	Conductive agents	12
		Electroplating agent	17
Polymers industry	11	Stabilisers	49
Paints, lacquers and varnishes industry	14	Colouring agents	10
		Fillers	20
		Reprographic agents	45
Others: Industrial : other = colours/frits	-	-	-
Other : Ceramic industry	15	Colouring agents	10
Other: Glass and related industry	15	Colouring agents	10

This Table reflects the information as reported by Industry falling under the HEDSET obligation and was further completed by information contained in the Product Registers.

#### Other data on uses of the substances: Product Registers

##### *Cadmium metal*

The Danish Product Register (1997) reports under the CAS number of metallic cadmium, in descending order of involved amount: construction industry and chemical industry (private household insignificant). In the same way, product types are listed: paints, lacquers and varnishes, construction materials and laboratory chemicals. With 31 out of 49 products containing 0-1% cadmium and 3 products with 80-100% cadmium content the total quantity used in products in 1997 was lower than 1 tonne for Denmark.

The register of 1998 gives a similar picture. The additional information concerns the content in the different product types: paints, lacquers and varnishes: 12 of the 26 products contain lesser than 1% of the substance; construction materials: all products contain maximum 1% cadmium; laboratory chemicals: two of the three products have a content of 80-100% cadmium; colouring agents: eight products of the twelve contain maximum 1% cadmium. The quantity for each major product type is smaller than 10kg and the overall quantity is less than 1 tonne/year.

The Swedish product register (15/09/97) reflects the presence of the substance - albeit at low concentration (< or = 10%) - in a range of products and trades. The largest number of products and highest volume are used in dyestuffs (pigments) and in fillers plastic, paints etc. The total volume in products did not exceed 1 tonne in 1996 (More details of the industrial and use categories can be found in **Annex F**).

When over viewing the information contained in the product registers it could be questioned if the entry with CAS-N° of cadmium metal (i.e. 7440-43-9) is not used also to report on cadmium in a (more) generic way.

### *Cadmium oxide*

The Danish Product Register (April 1997) reports 14 of the 25 products containing 1-10% cadmium oxide and two products with 80-100% of the substance. The major Industry implicated is the manufacturing of electronic equipment. Product types (in descending order of used substance's quantity): Laboratory chemicals and conductive agents. The total quantity in products is less than 1 tonne/year. For 1998 the Register is very similar. Nevertheless, here reprographic agents seem quantitatively most important, followed by conductive agents (11 products) and laboratory chemicals. The total quantity of the substance used in products is less than 1 tonne/year.

Details of the Swedish Register (1997: figures of 1996) are annexed (see **Annex G**).

#### The consumption pattern of cadmium (oxide and other cadmium compounds):

The world wide overall consumption pattern of cadmium (and its compounds) has been estimated by the International Cadmium Association (cited in Pearse, 1996) as follows: batteries (61%), pigments (20%), stabilisers (10%), plating (8%), alloys (3%) and other uses (4%).

For the Western World, Morrow came for the year 1996 to the following figures: batteries (69%), pigments (13%), stabilisers (8%), coatings (8%) and alloys and other (2%) (cited in: Morrow, 1998). In the context of the ESR Programme, Industry estimated the consumption pattern of cadmium (oxide) in Western Europe for the year 1996 as follows: batteries (60%), stabilisers (20%) and pigments (20%). Other uses are considered insignificant (IUCLID, 1997) and estimated to be less than 0.1% (IcdA, CollectNiCad, pers. Com., 2002). The figures were reviewed by Industry, refined and reported in the mass-balance (see **Figure 2.4**).

#### Use of Production, Consumption and Import/Export data

The data from the HEDSET/IUCLID, 1997 and the site specific Questionnaire (producers/importers of Cd (O)) provide the basis for the exposure assessment of these industrial sources.

The data from WS Atkins and underlying completed Questionnaires were used for the exposure assessment of pigments as well as stabiliser producers and users.

For plating an EU generic scenario is used (by lack of any site-specific exposure data) and based on the amount of cadmium estimated to be consumed in this application in the EU as a whole (estimation from IcdA, 1997).

Site-specific data (collated by the Questionnaires 1998, 2000 and 2001) are used for the exposure assessment of the batteries' producing and cadmium recycling companies.

Data on the cadmium flow related to batteries and recyclers (see the mass-balance updated for the year 2000) are used in the targeted risk assessment of cadmium (oxide) used in batteries, and in particular for estimating the emissions from waste disposal (see batteries' related Section 2.2.2).

Site-specific data collected via the Questionnaires (2004) are used to update the local assessment for all scenarios related to production and use of the priority substances for which new data were submitted (see Section 2.2.3). The reference year for the latter update was set at the year 2002.

## 2.2.2 Batteries

### 2.2.2.1 Used terminology on Nickel-Cadmium batteries

Electrochemical cells and batteries are identified as primary (non-rechargeable) or secondary (rechargeable), depending on their capability of being electrically recharged<sup>13</sup>. Within this classification different types of battery formats exist.

A battery can consist of only one cell or can be put together of several cells, which are connected among each other. There are cylindrical cells, button cells, prismatic batteries and battery packs available on the market (see **Table 2.13**) depending on application type, use, equipment.

Table 2.13 Overview of the different battery formats and chemistry

Product Group	Sub-groups		
Batteries type and geometry	Rechargeability	Format	System
	Primary <sup>14</sup> (non-rechargeable)	Button	Lithium: LiMnO <sub>2</sub> , Li(CF <sub>x</sub> ) <sub>n</sub>
			Others: AM, ZnO <sub>2</sub> , ZnAgO, ZnHgO
		Cylindrical	Lithium: LiMnO <sub>2</sub> , Li(CF <sub>x</sub> ) <sub>n</sub> , LiSOCl <sub>2</sub> , ZnO <sub>2</sub>
			Others: ZN, AM
		Prismatics	Lithium: LiMnO <sub>2</sub> , Li(CF <sub>x</sub> ) <sub>n</sub>
		Packs	Others: ZN (E-Block 9V, normal 4,5 V), AM (E-Block 9V)
	Secondary (rechargeable)	Buttons	NiCd, NiMH
		Cylindrical	NiCd, NiMH, AM, Pb-acid, Lithium: Li-ion
		Prismatics	NiCd, NiMH
		Packs	Pb-acid
Lithium: Li-ion			

LiMnO <sub>2</sub>	Lithium manganese dioxide	ZnO <sub>2</sub>	Zinc-air
Li(CF <sub>x</sub> ) <sub>n</sub>	Lithium polycarbonmonofluoride	ZnAgO	Zinc silver oxide
LiSOCl <sub>2</sub>	Lithium thionyl chloride		
AM	Alkali-manganese	ZnHgO	Zinc mercury oxide
ZN	Zinc-carbon	NiCd	Nickel-cadmium
NiMH	Nickel-metal-hydride	Pb-acid	lead-acid

Source: IOW, 1997

<sup>13</sup> Rechargeable batteries can be charged many times. After a certain amount of charge cycles they are no more rechargeable and must also be disposed of.

For information: the definition as set by the EC Battery Directive reads: Battery: any source of electrical energy generated by direct conversion of chemical energy and consisting of one or more primary battery cells (non rechargeable). Accumulator: any secondary battery cell or set of secondary battery cells (rechargeable).

<sup>14</sup>Cadmium has been used in some primary batteries in the past. There is no current application of cadmium in primary batteries (ICdA, pers. comm., 2000)

Ni-Cd batteries are generally viewed as high performance battery chemistries with good energy density and power density, especially suitable for high drain rate applications. Included in their best performance characteristics are their long useful life, wide temperature operating range, resistance to electrical/mechanical abuse and rapid charge/discharge characteristics. Disadvantages are low energy density, the so-called ‘memory effect’ and higher costs than lead-acid batteries. Nickel-cadmium batteries may readily be formulated into many different types, shapes and sizes of batteries designed to meet the specific requirements of many different applications.

The pocket-plate battery is the oldest and most mature of the various designs of nickel-cadmium batteries available and is manufactured in a wide capacity range, 5 to more than 1200 Ah and is used in a number of applications. Developmental work has been conducted continuously since the introduction of the pocket-plate nickel-cadmium battery to improve the performance characteristics and reduce battery weight. These innovations have resulted in the sintered-plate, fiber-structured and plastic-bonded or pressed-plate technologies (Evjes and Catotti, 2002). The sintered plate battery consists of a perforated mechanical substrate (e.g. nickel-plated steel or nickel-clad steel wire) coated with a highly porous sintered nickel matrix which is impregnated with nickel hydroxide (positive electrode) or cadmium hydroxide (negative electrode). The fiber (foam) structure technology uses a three-dimensional nickel-plated fiber matrix, which is highly porous.

Within these technologies a further distinction can be made between vented (open) and sealed cells. A functional vented battery generates a stoichiometric mixture of hydrogen and oxygen gases during overcharge and expels them normally from the cell into the battery container. Most often vented batteries have been used in industrial applications.

Sealed nickel-cadmium batteries incorporate specific battery design features to prevent a build-up of pressure in the battery caused by gassing during overcharge. As a result, batteries can be sealed and require no servicing or maintenance other than recharging.

Since both the term sealed and portable can be applied to some industrial batteries the term consumer batteries was initially used in the questionnaire sent to the Member States to indicate batteries with mainly domestic application. However, in general sealed, portable batteries not exceeding a weight limit (e.g. < 3 kg) irrespective of some other uses are referred to under this terminology.<sup>15</sup> Furthermore since household applications represent to date less than 20% of the market by weight (see **Table 2.27**) it is deemed more appropriate to use the term portable batteries in order to indicate that the figures presented in this report may include professional applications next to household applications.

A battery is made of cells assembled in series. Roughly Ni-Cd batteries can be divided into the following weight categories. Sealed cells: cell weight between 10 and 150 grams (maximum 500 g), usually assembled by 3 to 10 to make packs for portable applications. The most common are 3 and 4 cell packs. Larger batteries do exist for stationary industrial applications. Vented cells: cell weight between 1 and 70 kg (typically 3 to 10), usually assembled by at least 10 cells but up to several hundred. (CollectNiCad, personal communication, October 2002). A compilation of some of the different subtypes of Ni-Cd batteries and their specific characteristics is given in **Table 2.14**.

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<sup>15</sup> Definitions may differ within, between MSs, IND, OECD, etc; e.g. the weight limit by industry is/can be different from those applicable elsewhere e.g. by Member States

Table 2.14 Format, size and characteristics of Ni-Cd batteries

Product group	Subgroup					
	Format and size	IEC n° (US-Standard)	Weight (in g)	Nominal Voltage (in V)	Capacity (in Ah)	Cadmium content (in g per 100 g battery)
Portable batteries <sup>16</sup>	Button			1.2	up to 1 Ah	11-15 typical/average content = 13.8
	Cylindrical	R 20 (D)	145	1.2		
		R 14 (C)	75	1.2		
		R 6 (AA)	22	1.2		
		R 03 (AAA)	12	1.2		
		KR6	26	1.2	0.75	
Prismatics	9 V E-block		9.6 V			
	Packs		20-450			
Industrial/professional use <sup>17</sup>	Automotive vehicles		200 kg			8
	Safety and back-up systems		200 g to 1,000 kg			
	Aviation		20 kg (per battery) > 1 kg (per cell)			

Sources: Individual producers/recyclers (via Questionnaire 1998, 2000/2001)

### 2.2.2.2 Ni-Cd chemistry and composition

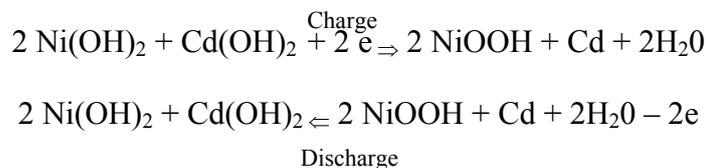
The nickel-cadmium (Ni-Cd) battery is a rechargeable battery system based on the reversible electrochemical reactions of nickel and cadmium in an alkaline potassium hydroxide electrolyte. The chemical compositions of Ni-Cd batteries can vary widely depending on the type and its specific application. For industrial batteries cadmium content may vary between 3 and 11%. For portable batteries values between 11 and 15% have been reported (battery questionnaire 2000). In addition, most Ni-Cd batteries contain significant amounts of nickel, iron, plastics and electrolytes and small amounts of metals such as cobalt and copper (Morrow and Keating, 1997).

Ni-Cd cells use a reversible electrochemical reaction between nickel and cadmium electrodes packed in an alkaline electrolyte (potassium hydroxide or sodium hydroxide and lithium hydroxide as an additive). The active materials are insoluble in the electrolyte, whose ions act only as a charge carrier and do not take part in the electrochemical charge/discharge reactions (Cornu, 1995). At the cadmium electrode during discharge, cadmium is oxidised by combining with two OH<sup>-</sup> ions to form cadmium hydroxide [Cd(OH)<sub>2</sub>] and releasing two electrons (US EPA, 1993, Gross, 1995). During charging the reverse happens. Hydrated nickel (III) oxide is reduced

<sup>16</sup> Since household applications represent to date less than 20% of the market by weight (see Table 2.27) it is deemed more appropriate to use the term portable batteries (instead of consumer batteries) in order to indicate that the figures presented in this TRAR may include professional applications next to household applications.

<sup>17</sup> For information: the definition as set by the draft EC Battery Directive 'industrial and automotive batteries and accumulators': any battery or accumulator use for industrial purposes, for instance as standby or traction power, emergency lighting, or for automotive starting power for vehicles. Remark: definitions may differ within and between MSs, IND, OECD, etc

to nickel (II) hydroxide at the other electrode (US EPA, 1993). The charge-discharge equation is as follows (Cornu, 1995):



The principal difference between the various types of Ni-Cd cells is the nature of the cell electrodes. The three primary types of positive electrodes used are pocket plate, sintered plate, and fiber plate. The hydrated nickel oxide electrode is usually in powder form and is held in pocket plates or suspended in a gel or paste and placed in sintered (perforated mechanical support) or fiber electrodes (US EPA, 1993).

The negative electrodes use pocket plate, sintered plate, fiber plate, foam or plastic banded supports to hold the cadmium (hydroxide) in place. Graphite or iron oxide is commonly added to improve the conductivity of both the nickel and cadmium hydroxide. Since the individual cells are recycled before assembling into batteries, it is not important whether the negative electrodes are originally impregnated with Cd(OH)<sub>2</sub> (the product of discharge reactions) or Cd metal (the product of charging reactions) (US EPA, 1993).

A typical chemical composition for a Ni-Cd cell is given in **Table 2.15**.

Table 2.15 Average chemical composition for a Ni-Cd battery

Material	Weight %	
	Portable <sup>a</sup> Ni-Cd battery	Industrial <sup>b</sup> Ni-Cd battery
Iron	35	48
Nickel	22	8
Cadmium <sup>c</sup>	13.8 <sup>c</sup>	8 <sup>c</sup>
Plastic	10	10
(OH) <sub>2</sub>	9	5
Water	5	16
Potassium hydroxide	2	5
Others	3.2	0
Total	100	100

Source of the figures: EPBA and EUROBAT product information (1997) in ERM (1997)

- a) Portable Ni-Cd battery, are batteries weighing between 10 g and 3 kg. Since household applications represent to date less than 20% of the market by weight it is deemed more appropriate to use the term portable batteries in order to indicate that the figures presented in this report may include professional applications next to household applications.
- b) Industrial Ni-Cd battery: large size batteries weighing over 3 kg in weight
- c) Latest update of information from industry i.e. manufacturers/recyclers (CollectNiCad,,2000)

Large, industrial-size batteries contain on average approximately 8% cadmium. Small, portable-type batteries contain approximately 13.8% cadmium. These figures refer to actual manufacturing and production data and have been confirmed by the information collected from

individual battery producers via the Battery Questionnaire 2000 and will be used in this report as representative for industrial batteries and portable batteries respectively.

### 2.2.2.3 Production, recycling and use

#### 2.2.2.3.1 Ni-Cd batteries manufacturing processes

Nickel-Cadmium batteries are widely used in many different applications where an autonomous energy source is required. Each application demands a different battery design, adapted to its performance requirements. For industrial applications different battery technologies are available: pocket plate cells, sintered plate cells, nickel fiber plate cells, plastic bonded plate cells.

Pocket plate batteries represent the conventional battery technology. Pocket plate electrodes contain the active materials in perforated steel pockets. This type of plates is mechanically very strong and the steel strip retains the active material during cycling, minimising swelling. In each cell a number of positive and negative electrodes are paralleled to form the plate group. Nickel-plated steel is used for connecting the elements and the terminals. The electrodes and separators are immersed in the alkaline electrolyte and the cell has a vented design.

A process flow diagram for the pocket plate batteries process is shown in **Figure 2.5**.

The reported emission/waste data represent site specific data (local worst case) from a pocket plate Ni-Cd batteries manufacturing plant (Industry Questionnaire, 2000/2001). The emission factors for air and water were calculated using the used Cd amount for the manufacturing of Ni-Cd batteries and the emissions to air/water. The sludge factor for cadmium in the WWTP sludge was calculated from plant supplied data (Cd content of sludge, amount of sludge, Cd used during manufacturing).

The emissions/wastes from the production of this type of battery include the following:

- a) Wastewaters containing cadmium. The sources of these wastewaters are the manufacturing of active materials, nickel strip manufacturing and the cell formation process. This wastewater is estimated to amount to 0.124 kg/tonne of Cd used in the battery manufacturing process ( $F_{ww}=1.24 \cdot 10^{-4}$ ).
- b) Air emissions occur during manufacturing of pocket plates and during assembling. For this specific plant no air emission data were reported. However for another pocket plate manufacturing plant, recycling its emissions to water, an air emission factor of 0.464 kg/tonne Cd used was reported.
- c) Sludges recovered from treatment of wastewaters (manufacturing of active materials, nickel strip manufacturing, cell formation process). These are estimated to contain 17.7 kg cadmium per tonne of Cd used. The sludge from the wastewater treatment plant is sent to an external recycling plant.
- d) Rejected battery cells from the test and package step: 118.8 tonnes/year. This waste is treated at a recycling plant.
- e) Other waste: raw material bags, substituted filters, cleaning materials and tools: 1.15 tonnes/year.

Nickel fiber batteries are characterised by the use of a nickel fiber mat as electrode support. The active materials are impregnated by mechanical or electrochemical methods. Average diameter

of the nickel fibers is around 20 µm. Porosity, pore size and electrode thickness can be adjusted as required for every application: lower porosity, smaller pores and thinner plates are adequate for high rate applications, while higher porosity, bigger pores and thicker plates are the choice for medium rate batteries. Thickness, porosity, pore size and the impregnation method are then adjusted to each specific application, in order to achieve the best electrical performance/battery cost ratio.

A process flow diagram for the nickel fiber plate process is shown in **Figure 2.6**.

The reported emission/waste data represent site specific data (local worst case) from a fiber plate Ni-Cd batteries manufacturing plant. The emission factors for air and water were calculated using the used Cd amount for the manufacturing of Ni-Cd batteries and the emissions to air/water. The emission factor for cadmium in the filter cake was calculated from plant supplied data (Cd content of filter cake, amount of filter cake, Cd used during manufacturing).

The emissions/wastes from the production of this type of battery include the following:

- a) Wastewaters containing cadmium. The source of this waste is the impregnation step. This wastewater is estimated to amount to 0.769 kg/tonne of Cd used in the battery manufacturing process. This wastewater is collected and recycled in an external recycling plant.
- b) Emissions to air occur during assembling are very small; 0.00027 g/tonne of Cd used.
- c) Filter cake recovered from formation process. This is estimated to contain 10.5 kg Cd/tonne of Cd used. The filter cake is recycled.
- d) Rejected batteries (no information)

Sintered plate batteries contain a cadmium anode, a potassium hydroxide electrolyte, and a nickel oxide cathode. For the electrodes, sintered plates containing the active materials are used. In one operation, the plates are made by impregnating sintered nickel substrates with nickel and cadmium nitrate salts. The nickel and cadmium nitrates are converted to hydroxides in sodium hydroxide solution. The plates are then washed thoroughly and dried in a hot oven. The impregnation cycle is repeated to deposit the desired amount of active material. The plates then go through a formation treatment, which removes impurities and brings the active materials to a condition similar to that existing in working electrodes. The cell is assembled into final form using an absorbent plastic separator and a nickel-plated steel case. With the addition of the alkaline electrolyte, they are ready for electrical testing, packing, and shipping.

There are currently three distinct manufacturing processes used for preparing the electrodes of the electrodes of the sintered plate batteries. The preceding paragraph described the worst case from an environmental standpoint of the three, due to the high concentration of cadmium and nickel compounds contained in the wash water. The other processes in use are:

- An electrolytic deposition process which deposits active materials directly on the sintered plates – this process produces wastewater containing nickel and cadmium compounds, though the amount is not as large as in the impregnation process described above; and
- A pressed powder process involving active materials mixed with binders in a dry powder form. The powder mix is pressed onto a wire mesh or expanded metal grid in a mold. This is a dry process and no wastewater is involved.

A process flow diagram for the impregnation-sintered plate process is shown in **Figure 2.7**.

The reported emission/waste data represent site specific data (local worst case) from a sintered-plate Ni-Cd batteries manufacturing plant. The emission factors for air and water were calculated using the used Cd amount for the manufacturing of Ni-Cd batteries and the emissions to air/water. The sludge factor for cadmium in the WWTP sludge was calculated from plant supplied data (Cd content of sludge, amount of sludge, Cd used during manufacturing).

The emissions/wastes from the production of this type of battery include the following:

- Wastewaters containing cadmium and nickel salts together with sodium hydroxide. The source of this waste is the washing step. This wastewater is estimated to amount to 0.048 kg per tonne of Cd used in the battery manufacturing process.
- Atmospheric emissions are stated not to occur since the process is merely wet.
- Sludges recovered from treatment of wastewater. These are estimated to contain cadmium (6.3 kg per tonne of Cd used) and nickel hydroxide. The WWTP sludges are land-filled (special landfill class I).
- Rejected batteries from the test and package step, together with other scrap, are externally recycled for cadmium.

Figure 2.5 Flowsheet manufacturing process pocket plate Ni-Cd batteries

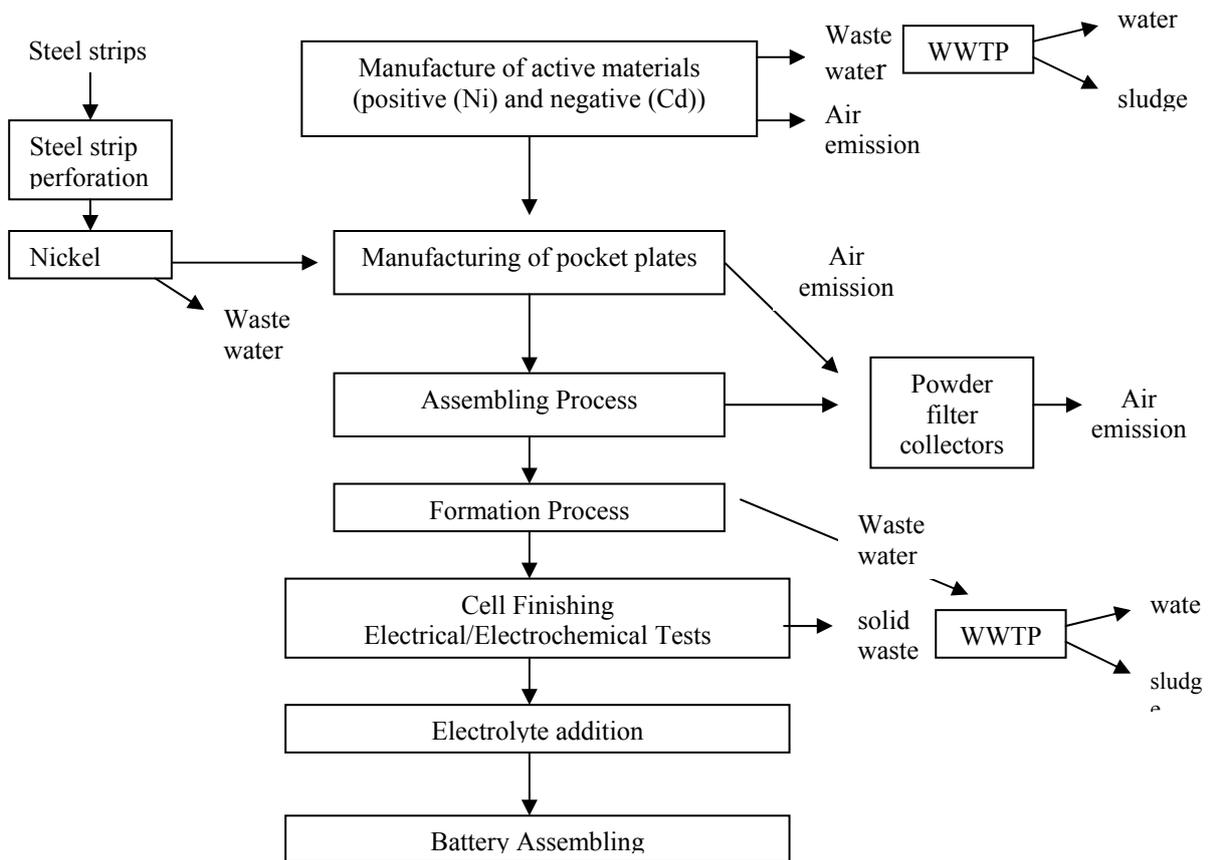


Figure 2.6 Flowsheet production process Nickel fiber plate Ni-Cd batteries

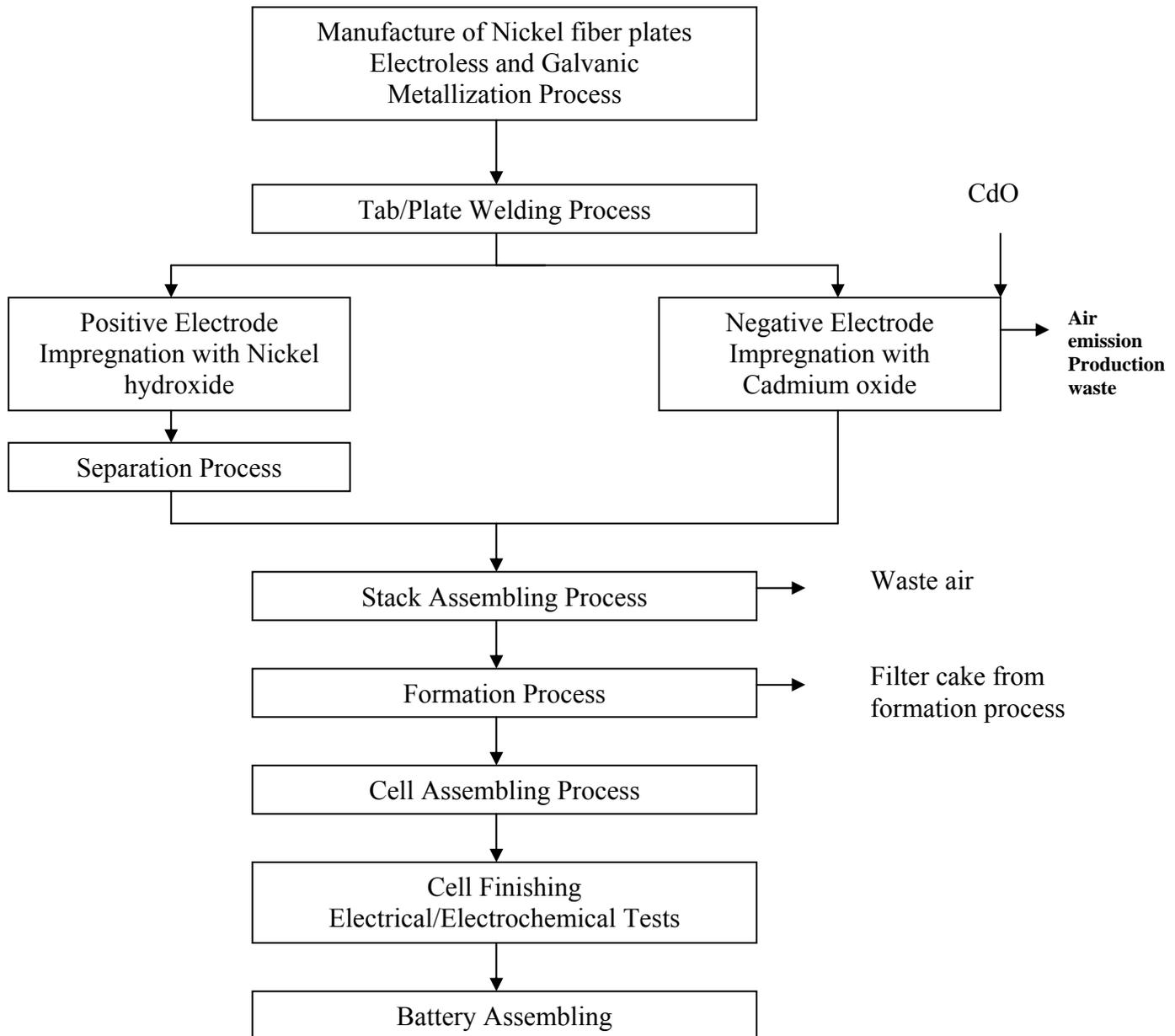
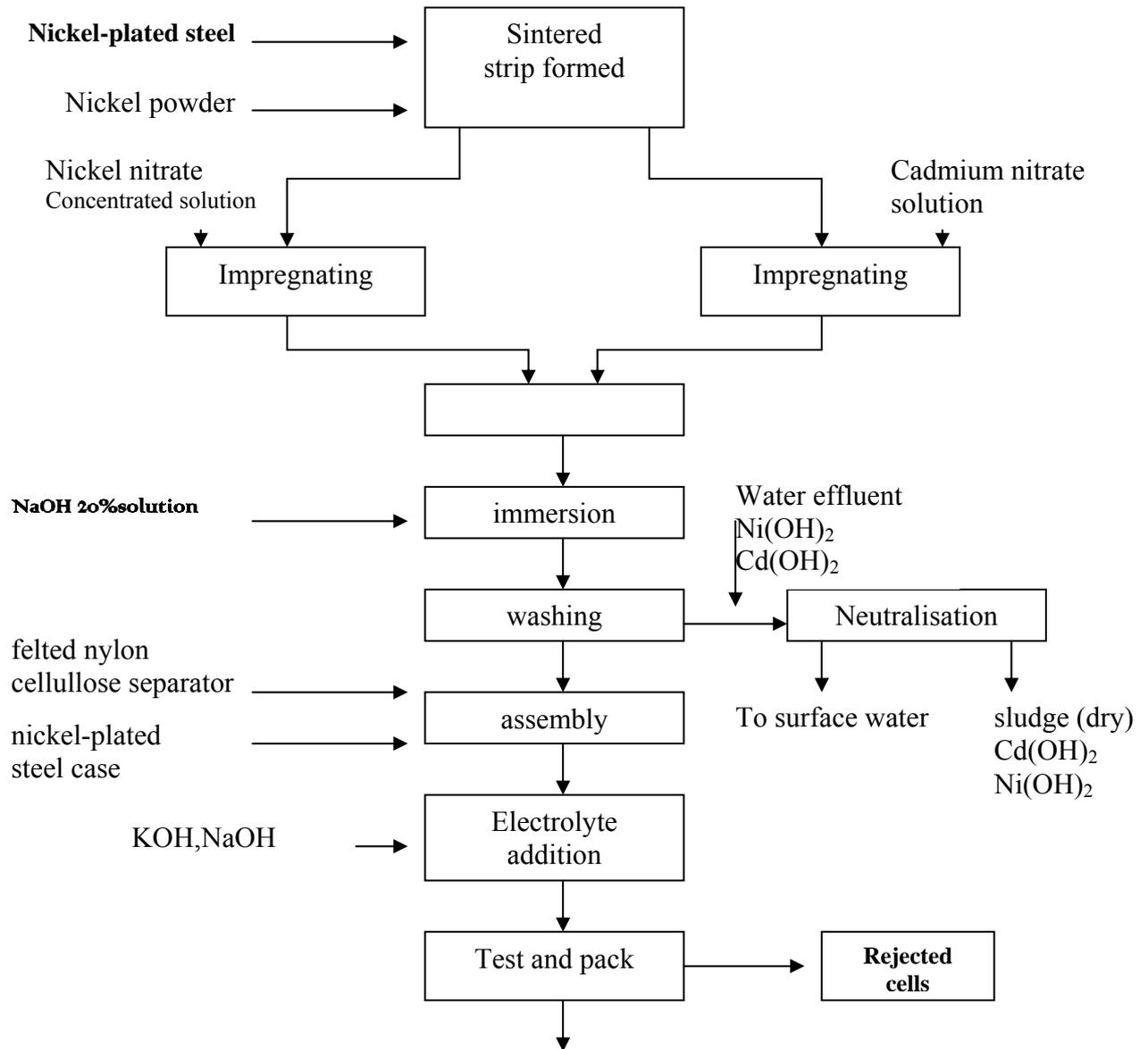


Figure 2.7 Flowsheet of major operations in sintered plate Ni-Cd batteries manufacture



### Recycling processes

Ni-Cd batteries might be recycled either pyrometallurgical (high-temperature) or hydrometallurgical (wet chemical) processes. Today, commercial Ni-Cd battery and manufacturing scrap-recycling systems are usually based upon pyrometallurgical (high temperature) processes. Hydrometallurgical (wet chemical) systems have also been designed and have reached the pilot plant stage, but no purely hydrometallurgical systems are utilised today to recycle Ni-Cd batteries. Some recycling systems may have elements of both pyrometallurgical and hydrometallurgical processes in their overall system. (Morrow, 1997).

In pyrometallurgical recycling processes, cadmium-containing wastes or used batteries are heated at a low temperature to drive off moisture and organic compounds, and then heated to above 800°C to volatilise the cadmium. The vapour is then condensed, either as cadmium oxide or metal, and collected for final processing into high purity material (> 99.99%) suitable for any re-use in industrial applications. In hydrometallurgical processes the cadmium containing wastes are dissolved in a suitable reagent, usually a strong acid, and then subjected to a series of wet chemical reactions designed to successively remove impurities. The final cadmium product is normally a cadmium sulphate, chloride or nitrate solution from which high purity cadmium may be electrochemically obtained. Ion exchange techniques have been utilised in some hydrometallurgical recycling schemes, depending on the nature of other impurities present. (OECD, 1996).

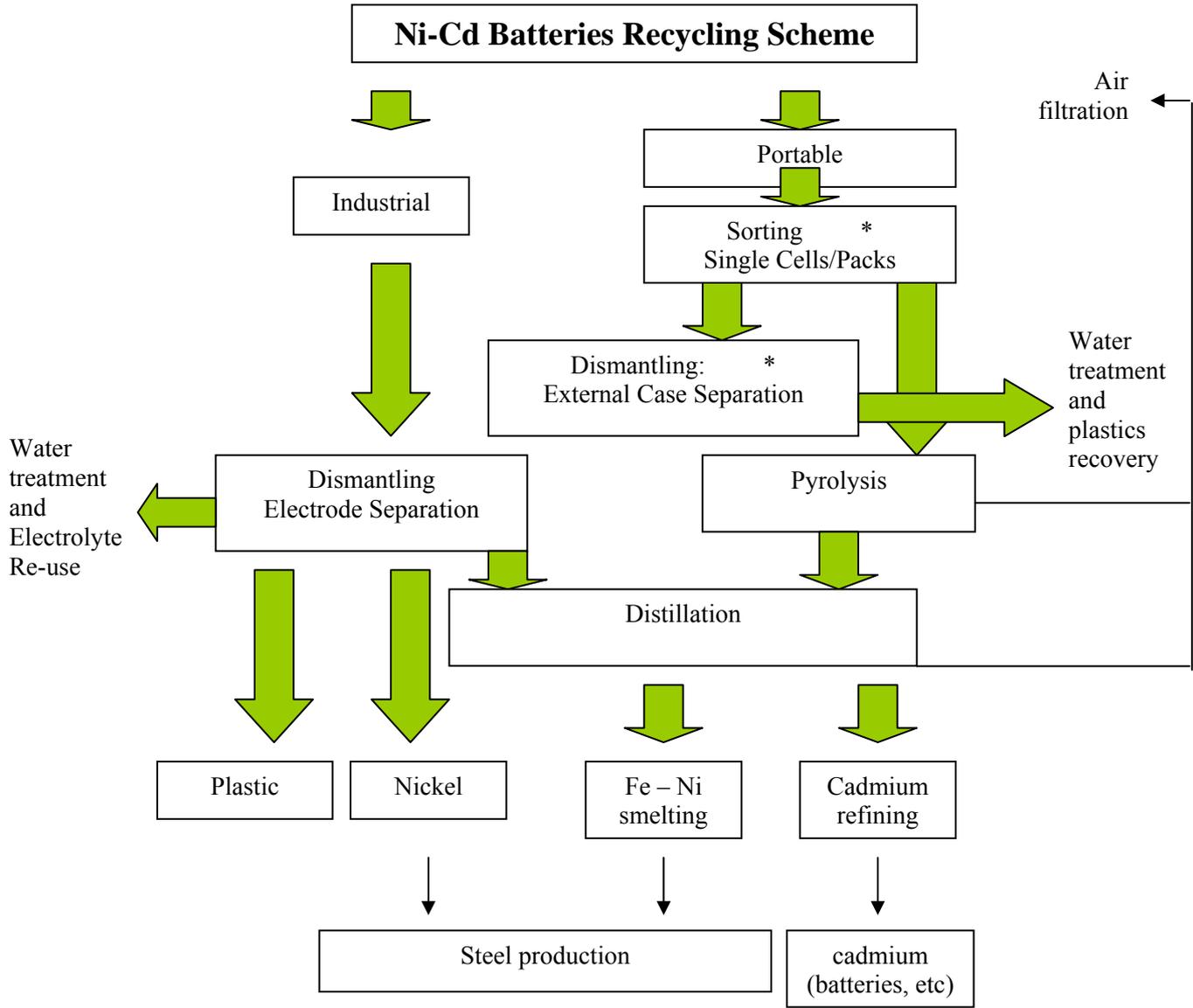
A schematic presentation of the recycling processes for industrial and portable Ni-Cd batteries is supplied in **Figure 2.8**.

The reported emission/waste data represent site specific data from a Ni-Cd batteries recycling plant. The emission factors for air and water were calculated using the recycled Cd amount from Ni-Cd batteries only and the emissions to air/water. The emission factor for cadmium in waste was calculated from plant supplied data (Cd content of waste, amount of waste, Cd recycled (from batteries only)).

The emissions/waste from the recycling of Ni-Cd batteries include the following:

- a) Wastewaters containing cadmium. The source of this waste is the dismantling step. This wastewater is estimated to amount to 0.32 g/tonne of Cd recycled (from batteries only).
- b) Emissions to air occur during pyrolysis and distillation; 4.7 g/tonne of Cd recycled (from batteries only).
- c) Waste:
  - plastic boxes from batteries: 0.0011 kg/tonne Cd recycled (batteries) (landfilled)
  - metallic boxes from batteries: 1.23 kg/tonne Cd recycled (batteries) (externally recycled)
  - Fe/Cd electrodes after treatment: 1,2 kg/tonne Cd recycled (batteries) (ext. recycled)
  - Conc. electrolytes: 5,7 kg/tonne Cd recycled (batteries) (ext. scrap treatment)
  - Process slag: 154 kg CdO/tonne Cd recycled (batteries) (internal treatment)
  - Air treatment dust: 61kg CdO/tonne Cd recycled (batteries) (internal treatment)
  - Used filters: 0.138 kg/tonne Cd recycled (batteries) (internal treatment)
  - Rainwater sludges: 0.0016 kg/tonne Cd recycled (batteries) (internal treatment)

Figure 2.8 Ni-Cd Battery Recycling (CollectNiCad, 2000b adapted)



\* Facultative step(s)

In **Table 2.16** a summary is given of the Cd processing facilities in the world along with their location, type and estimated processing capacity (Morrow, 1999).

Table 2.16 Worldwide Cd processing facilities

Company	Location	Type	Capacity (tonnes of Ni-Cd/year)
Accurec Gmbh	Germany	NiCd Recycler	1,000
INMETCO	USA	Stainless steel	3,000
Japan Recycle Center	Japan/Korea	NiCd recycler	3,000
Kansai Catalist	Japan	Zinc refinery	500
Mitsui Mining and Smelting	Japan	Zinc Refinery	1,800
SAFT AB	Sweden	NiCd Recycler	1,500
SNAM	France	NiCd Recycler	5,400*
Toho Zinc Co, Ltd	Japan	Zinc Refinery	1,700

\* SNAM St. Quentin stopped its recycling activities (2001), it has now become a battery sorting plant, all recycling capacity is transferred to the Viviez site.

The present capacities of the world's Ni-Cd battery recycling plants vary from 500 tonnes to 5,400 tonnes with a present total effective capacity of approximately 15,000 tonnes (Morrow and Keating, 1999). The total EU capacity is estimated at 7,900 tonnes.

The facilities located in the EU i.e. SAFT AB (Sweden), SNAM (France), and ACCUREC (Germany) are being considered in this report.

### 2.2.2.3.2 Mass balance

A complete overview of the mass balance for cadmium in the EU for the reference year 1996 is given in **Figure 2.4** (see Section 2.1.2.1). The production volume of cadmium in the EU in 1996 is estimated to be 5,808 tonnes/year. Corrected for import/export 5,528 tonnes/year is available for different applications. Approximately 2,733 tonnes/year is used for battery manufacturing which equals approximately 47% of the cadmium being produced in Europe. The EU regional consumption of cadmium reaches the value of 2,638 tonnes, which are distributed for 75.2% to Ni-Cd batteries, 14.9% to pigments, 5% to stabilisers and 5% into alloys and plating.

Table 2.17 Cadmium consumption in the Western World (1990 and 1994) or EU (1996) by application

Application	% of total consumption		
	1990 <sup>a</sup>	1994 <sup>a</sup>	1996 <sup>b</sup>
Ni-Cd batteries	55	60	75.2
Cadmium pigments	20	16	14.9
Stabilisers for PVC	10	12	5
Protective coatings	8	7	4
Cadmium containing alloys	3	2	0.9

Table 2.17 continued overleaf

Table 2.17 continued Cadmium consumption in the Western World (1990 and 1994) or EU (1996) by application

Application	% of total consumption		
	1990 <sup>a</sup>	1994 <sup>a</sup>	1996 <sup>b</sup>
Miscellaneous	4	3	< 0.1
Total	100	100	100
Total production in the Western world (in tonnes)	15,900 <sup>c</sup>	16,500 <sup>c</sup>	13,840 <sup>c</sup>

a) Source: Cadmium Association, OECD Risk Reduction Monograph N° 5 (1994);

b) Source: mass balance (see Section: 2.1.2.1), EU consumption only;

c) Source: World Bureau of Metal Statistics (2000), production in the Western world (does not include Central and Eastern European countries)

Updated (year 2000) and detailed mass balances for industrial and sealed/portable Ni-Cd batteries (Cd content) are presented in **Figure 2.9** and **Figure 2.10**.

Figure 2.9 Industrial Ni-Cd batteries mass balance (EU-16 + Switzerland, Year 2000) (Cadmium content) (CollectNiCad, 2002a, revised July 2002)

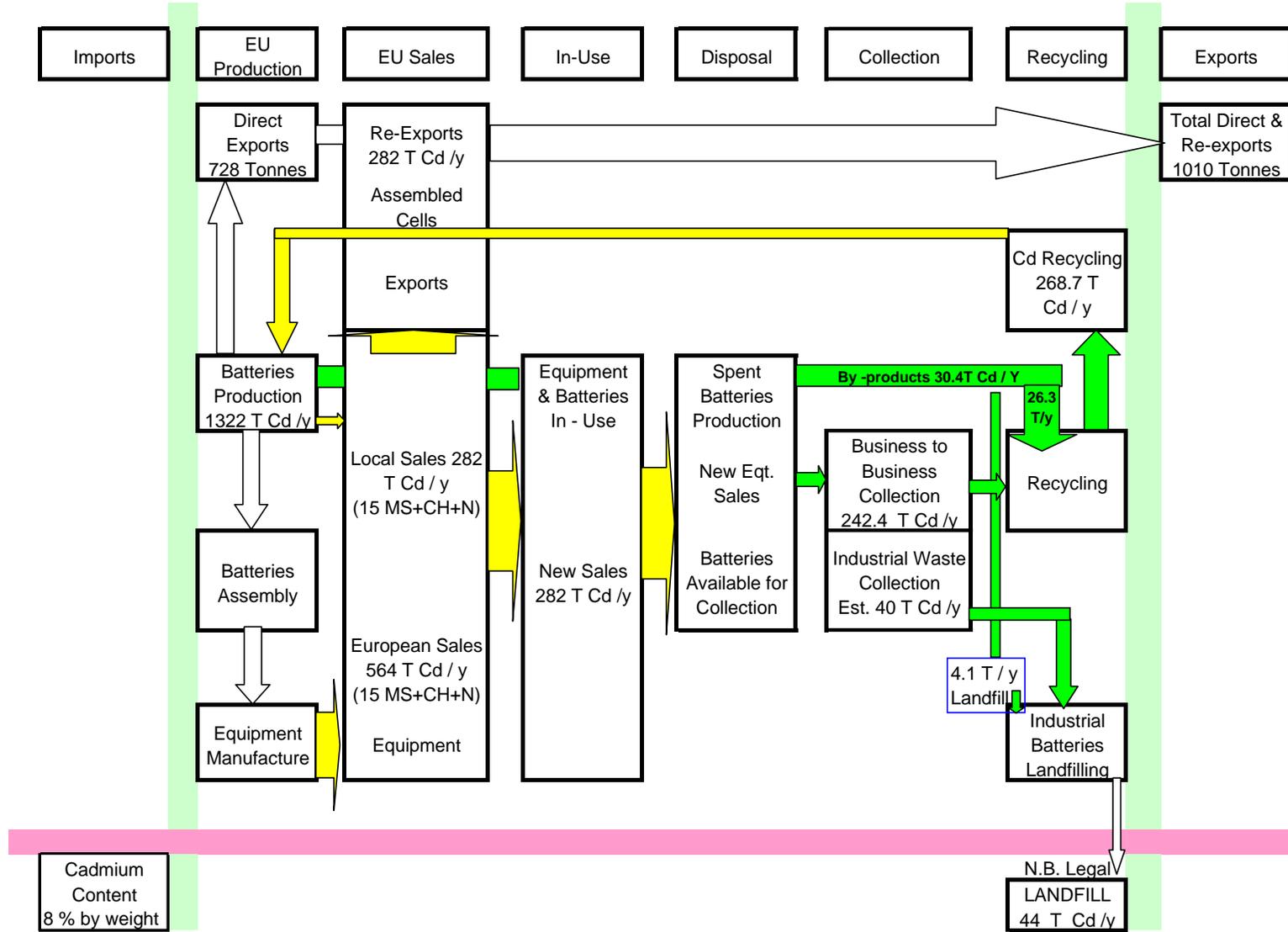
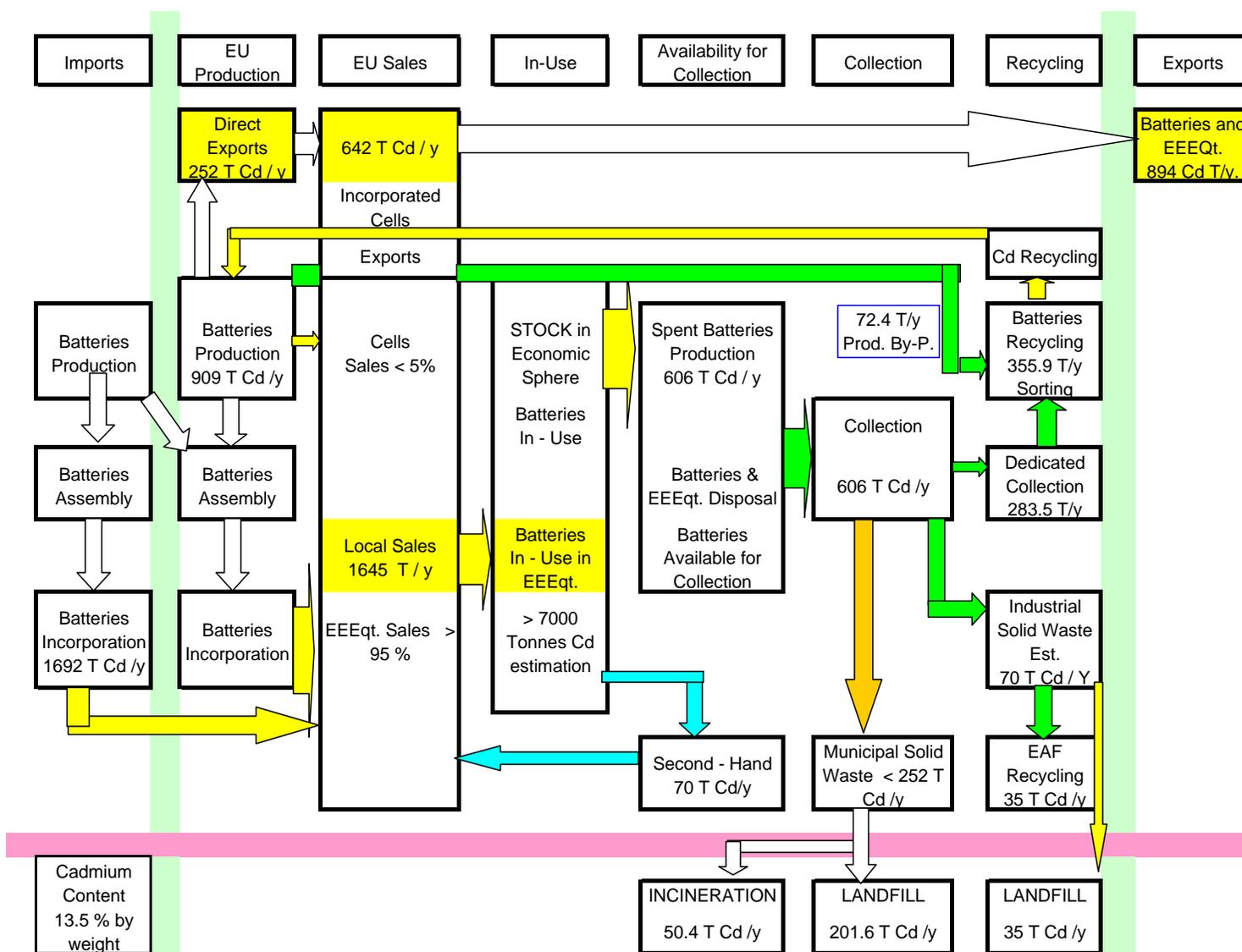


Figure 2.10 Portable Ni-Cd batteries mass balance (EU-16 + Switzerland, Year 2000) (Cadmium content) (CollectNiCad, 2002a, revised July 2002)



### 2.2.2.3.3 Ni-Cd batteries producing/recycling companies

In the current Risk Assessment Report the exposure data were generated by a number of companies that collaborated voluntarily in the data collection (Industry Questionnaire, 1998 and update questionnaire 2000/2001). The list of companies given in **Table 2.18** is considered as giving a complete overview of the Ni-Cd batteries producing/recycling companies.

Table 2.18 Companies producing/recycling Ni-Cd batteries in EU

Ni-Cd producers		
Country	Location	Company
France	Roulet St. Estephe	SAFT Nersac
	Bordeaux	SAFT Bordeaux
Germany	Duisburg	Friwo (EXIDE-group) <sup>c</sup>
	Brilon	Hoppecke
	Zwickau	GAZ (Zwickau)
Spain	Torrejon De Ardoz/ Madrid	EMISA (EXIDE- group) <sup>b</sup>
Sweden	Oskarhamn	SAFT-AB <sup>a</sup>
Ni-Cd recyclers		
Country	Location	Company
France	Viviez	SNAM
Germany	Mülheim	ACCUREC
Sweden	Oskarhamn	SAFT-AB <sup>a</sup>

- a) Production and recycling at the same site  
 b) EMISA stopped the manufacturing of Ni-Cd batteries in 2003, SAFT, May 2003.  
 c) FRIWO, production stopped (year?), ICdA, pers.com. 2005.  
 SNAM St. Quentin stopped recycling (2001) with transfer of recycling capacity to the site of Viviez; VARTA stopped production (end 2000); SANYO: no production of battery cells in the EU, only assembly of imported constituents, therefore not included under manufacturers (pers. comm. 2001); PHILIPS stopped manufacturing cells and shifted to assembly (of non-EU manufactured cells into packs) only since June 2001, Panasonic (former Philips), letter 30.09.02.

At world scale other major manufacturers are Sanyo, Panasonic, GP Batteries, BYD and many of them are importers of batteries incorporated in OEMs equipment<sup>18</sup>.

### 2.2.2.4 Market and sales data

#### 2.2.2.4.1 General

Portable rechargeable batteries are utilised for a wide variety of products and applications. The most important application fields are Cordless Power Tools (CPT), Emergency Lighting Units (ELU) and applications in various Electrical and Electronic Equipment (EEE). Industrial

<sup>18</sup> OEM= Original Equipment Manufacturer

applications of rechargeable batteries include military and space applications, transportation applications, power systems such as reserve power supply for industrial processes.

The nickel-cadmium portable battery market has been analysed in several different ways, in some cases according to geography, in others according to millions of cells sold, and yet in others in terms of the total sales value. In compiling these data, in particular those related to the historical market, EURAS has relied heavily on work done by Industry (e.g. CollectNiCad, 2000c).

#### 2.2.2.4.2 Portable Nickel-Cadmium batteries<sup>19</sup>

##### General

A compilation of the available data from different data sources on Ni-Cd battery sales in the EU is given in **Table 2.19**.

Table 2.19 Summary of the market data (million units) available on portable Ni-Cd batteries in the EU

Year	Market study						
	ERM <sup>a</sup>	EPBA <sup>b</sup>	Nomura <sup>c</sup>	SANYO <sup>d</sup>	SAFT <sup>e</sup>	CollectNiCad1 <sup>f</sup>	CollectNiCd2 <sup>f</sup>
1970					12.5		
1975					21		
1980					42		
1985	66	66					
1986							
1987					143		
1988					177		
1989			201				
1990	203	203	226.5				
1991		286	276				
1992			287				
1993			315	310			
1994		244	343	350			
1995	620	564	356	360			
1996		213	334	290			

Table 2.19 continued

<sup>19</sup> Since household applications represent to date less than 20% of the market by weight it is deemed more appropriate to use the term portable batteries (instead of consumer batteries) in order to indicate that the figures presented in this RAR may include professional applications next to household applications.

Table 2.19 continued Summary of the market data (million units) available on portable Ni-Cd batteries in the EU

Year	Market study						
	ERM <sup>a</sup>	EPBA <sup>b</sup>	Nomura <sup>c</sup>	SANYO <sup>d</sup>	SAFT <sup>e</sup>	CollectNiCad1 <sup>f</sup>	CollectNiCd2 <sup>f</sup>
1997		233	356	260			
1998		236	353	250			
1999			352	250		338	343

- a) ERM (1997)  
b) EPBA production sheets  
c) Nomura (1994) in CollectNiCad (2000c)  
d) Carcone (1998) in CollectNiCad (2000c)  
e) Eloy in CollectNiCad (2000c)  
f) CollectNiCad (2000c)

The results of the ERM study have been based on data provided by EPBA (European Portable Battery Association). While the presented results for the years 1985 and 1990 are in concordance with the results of the other studies the figure of 1995 is clearly out of scope. The main reason for this discrepancy is the assumption taken in the other market studies in deducing the EU share from the world market data. The EU market share in the ERM study mounts up to 40% of the world market in 1995, while the EU world market share in the other studies have been assumed to be respectively 25% in the Nomura and SANYO study and 20% for the SAFT study. The latest survey conducted by CollectNiCad (CollectNiCad, 2000c) supports these latter suppositions and will be discussed in more detail here below.

The European sales volume for the year 1999 for portable Ni-Cd batteries has been established) on the basis of data obtained from battery manufacturers and original equipment manufacturers O'EM's. Two different and independent methodologies have been used.

The first method (CollectNiCad. 1) calculates the total sales of Ni-Cd batteries from the number of cells used in the three major application areas: cordless power tools, emergency lighting, household equipment (shavers, dust busters, dental care etc.), telecommunications and the sales of single cells. In order to translate the number of cells into a weight estimate an average weight of 38.0 g of one cell has been assumed, calculated from the total number of cells introduced on the EU Countries market.

The second method (CollectNiCad 2) is based on production data (in number of cells and in tonnes of batteries) of all Ni-Cd battery manufacturers active in Europe and corrected for import/export ratios of cells and packs as well as of batteries incorporated in electrical and electronic equipment.

#### Data for portable Ni-Cd Batteries by market segments/applications (CollectNiCad. 1)

For the breakdown of the market data by application an in depth analysis was performed of the European sales of portable Ni-Cd batteries in the three major applications areas: cordless power tools, emergency lighting and household and 'electrical and electronic equipment' (EEE).

**Table 2.20** provides a summary of the market data by application. Those data show a total annual market of 12,700 tonnes in 1999.

Table 2.20 Portable Ni-Cd batteries EU market, sales by application (million cells/year) reference year 1999

Electrical and Electronic Equipment (EEE)		
Application	Average weight/cell (g)	Sales (million cells/year)
Household equipment	22	28
Dust buster	48	12
Toys	55	5
Audio-Video	26	10
Single cells and others	22	54
Cordless phones	14	50
Emergency lighting		
Application	Average weight/cell (g)	Sales (million cells/year)
Emergency light	120	26
Power tools		
Application	Average weight/cell (g)	Sales (million cells/year)
Cordless tool	41	138
Others		
Application	Average weight/cell (g)	Sales (million cells/year)
Medical	20	10
Military	40	5
Average weight/unit	37.8	
Total sales		338

Source: CollectNiCad (2000d)

The average weight of approximately 38 g for a portable Ni-Cd battery is used in the further calculations

#### Data for portable Ni-Cd Batteries based on production data (CollectNiCad 2)

The data obtained by the second method are presented in **Table 2.21**.

Table 2.21 Overview EU market corrected for import and export in 1999

	Local annual sales (millions of cells)	Domestic sales (%)	Export sales (%)	Import Europe (%)	Net EU market (millions of cells)
Japan	158	n.d.	50	30	23.7
Europe	324	65	35		210.6
North America	457	n.d.	15	50	34.3
Asia	530	n.d.	70	20	74.2
Total	1,469	n.d.	n.d.	n.d.	342.8

n.d. No data available

Those data indicate that a total market of approximately 1,4 billion of Ni-Cd cells have been reached in 1998 and 1999. To evaluate the market in the E.U. countries the import-export of Ni-Cd cells assembled into packs and of packs incorporated in EEE were taken into account (see

**Table 2.21).** The net EU market contribution for each country/continent was calculated with the following formula:

$$\text{Net EU market contribution} = \text{Local annual sales} \times \text{export (\%)} \times \text{import Europe (\%)}$$

According to **Table 2.21**, 342.8 millions of cells have been sold in 1999 within the 15 EU Member States corresponding to approximately 23.3% of the world market. The assumption of the EU market share of 20-25% is therefore confirmed and will be used to select data to build a historical market curve. In this respect the high ERM figure for 1995 is being rejected.

### Historical market development

In order to make any predictions on the amounts of batteries available for collection and/or disposal it is imperative to have a good picture of the historical market development. In **Table 2.22** the selected data for the portable consumer/sealed portable market are summarised. To express these market figures in tonnes/year these values have been multiplied with the estimated average unit weight of 38 grams. Missing values were extracted by interpolation.

Table 2.22 Overview of the historical reference data for portable Ni-Cd batteries

Year	Millions/cells	Tonnes/year	Year	Millions/cells	Tonnes/year
1980	42	1,596	1991	276	10,488
1981	n.d	<i>1,778</i>	1992	287	10,906
1982	n.d	<i>1,960</i>	1993	315	11,970
1983	n.d	<i>2,142</i>	1994	343	13,034
1984	n.d	<i>2,324</i>	1995	356	13,528
1985	66	2,508	1996	334	12,692
1986	n.d	<i>3,971</i>	1997	356	13,528
1987	143	5,434	1998	353	13,414
1988	177	6,726	1999	352	13,376
1989	201	7,638	2000	314	11,930
1990	226.5	8,607	2001	275	10,995

n.d. No data available

Figures denoted in italics are interpolated

#### **2.2.2.4.3 Industrial Ni-Cd batteries (CollectNiCad 2000c)**

The European market for industrial batteries can be split into a number of well-defined sectors as follows:

- Standby, or stationary, applications - safety, and back-up systems at airports, hospitals, power stations, offshore installations etc.
- Transportation - railways, metro cars, etc.
- Aviation - starting of engines, oil board safety systems, etc.
- Electric vehicles (EV)

The batteries within the two largest segments - standby and transportation - are used within a country's infrastructure. The need for batteries for new installations is the largest during this

infrastructure development phase. Batteries for standby applications are often purchased by equipment manufacturer (OEM) and delivered together with the equipment to the user. Many of these OEM's are situated in Western Europe while the users are situated in e.g. the Middle East and Far East. Thus, the batteries are purchased by and invoiced to a European customer, but they are very often re-exported to other parts of the world. In some of the Member states with important OEM'S, the re-export factor of standby batteries can be as high as 50%.

Batteries for transportation and aviation purposes are to a higher extent delivered directly to the end user and the re-export factor is lower (15%). The EV (Electric Vehicles) market is still at a low level. Main part of the EV nickel-cadmium is produced in EU and is used within EU.

The volumes of the different industrial Ni-Cd batteries for use within the EU market has been estimated from data of the three major suppliers (representing more than 95% of the market supply) with addition for an estimated volume of imported batteries and are listed in **Table 2.23**.

Table 2.23 Industrial Ni-Cd batteries EU market sales (tonnes/year)

Year	Industrial Ni-Cd battery (tonnes/year)
1995	3,242
1996	3,608
1997	3,625
1998	3,964
1999	3,697
2000	3,566

Sources Original references Saft, Exide and Hoppescke in CollectNiCad (2000c,2002)

From this table it is clear that the industrial batteries' market has reached a stable level of 3,500 to 4,000 tonnes/year. Cross-validation with the ERM study shows the same magnitude (4,000 tonnes in 1995).

#### 2.2.2.4.4 Country by country data

The data presented in this section are obtained mainly by two ways. The first was through the Questionnaire on Batteries sent out in 2000 by the MSR to the national authorities of the EU and Norway, the collector organisations as well as the EU associations of manufacturers (i.e. EPBA). The second series of data was compiled via the efforts run in parallel by Industry (CollectNiCad 2000d).

It needs to be mentioned that to date the information in this document is rather limited and no attempt was made to verify the correctness of each figure. Another remark concerns the fact that figures obtained via different sources are not necessarily independently generated (e.g. the data provided by the national collector organisations may be the only data available at the authority level). Finally the data obtained via different ways may in some case be 'complementary' to each other (e.g. the data on collection as provided by the collection organisation versus Industry's data obtained from the recyclers) and thus allowing for at least some approximate direct check by comparison.

### Data sources

Responders to the Questionnaire are indicated by a figure between brackets in the last column of the Tables and accompanied by details in a footnote, if needed. The figure (1) is used when data were obtained from the MS (national authority). The indication (1C) is used when Collection organisation(s) replied. The main primary generators of data in so far as these are known, are indicated under the corresponding subsections. Data compiled and submitted by CollectNiCad are indicated by the figure (2).

### Data errors and deviations

Besides the well known sources of errors e.g. reporting, (de)coding, transcription, etc deviation of data generated by different types of sources may be due to (a different degree of taking into account) stockpiling, as well as import and/or export of new, spent or recycled material or appliances containing batteries. On the other hand, differences in used definitions of e.g. 'portable', 'consumer' and 'industrial' but also 'marketing' and the specific sorting or not of Ni-Cds may cause divergences between figures generated by different MS, collector organisations and Industry. Finally, difficulties may arise due to the different units in which marketing figures versus collection amounts are expressed. The former are generally in units (or mAh) while the latter are reported in weight units. Together with the variation in battery weight, this may cause deviations.

### Portable Ni-Cd batteries

A summary of the available data is given in **Table 2.24** for consumer/sealed portable Ni-Cd batteries.

Table 2.24 Portable Ni-Cd battery market data (tonnes/year) for EU countries

Country	1994	1995	1996	1997	1998	1999	2000	2001	Reference
Austria				62	98	97 309	286	247	(1C)* (2)
Belgium			381	388	368	327	302	261	(1) (2)
Denmark	214 <sup>b</sup>	233 <sup>b</sup>	218-328 <sup>b</sup>	291	242	210 137	127	110	(1C) (2)
Finland <sup>a</sup>			250			134	124	107	(1) (2)
France						130 2,212	2,046	1,768	(1)* (2)
Germany	3,095	2,642	2,334	2,214	2,050	3,210 2,261	2,091	2,880 1,808	(1C) (2)
Greece						404	374	323	(2)
Ireland						233	216	186	(2)

Table 2.24 continued overleaf

Table 2.24 continued Portable Ni-Cd battery market data (tonnes/year) for EU countries

Country	1994	1995	1996	1997	1998	1999	2000	2001	Reference
Italy						1,567	1,449	1,253	(2)
Luxembourg						25	23	20	(2)
The Netherlands						652	603	521	(2)
Portugal						241	223	193	(2)
Spain						1,168	1,080	934	(2)
Sweden	486	338	333	328	190	175 249	230	199	(1) (2)
UK <sup>a</sup>	2,001	1,766	1,958	2,167	2,652	2,983 2,706	2,503	2,163	(1) (2)
Norway		199	187	124	175	215 125	116	100	(1) (2)
Total EU-16 <sup>a</sup>						14,005	11,793	11,265	
Switzerland						274	253		(2)
Total <sup>a</sup>						14,279	12,046		

- 1) Questionnaire Member States (2000). Primary sources: (B): BEBAT, (F): only SCRA members, (UK): ERM, (S): based on information from importers and manufacturers, updated '02: Ni-Cd batteries that have been put on the Swedish market, as reported to the Swedish EPA, (NO): sealed cells, separate or in appliances, in this table: with the assumption that all cells in appliances are totally attributed to consumer application.
- 1C) Questionnaire (2000) Collection organisations. (A) : only data via UFB (Incl. some industrial uses, DK: Danish Battery Association, (DE): Data provided by ARGE Batterien, data for 2001 submitted by UBA, 2002.
- \* Incomplete data-set(2): Industry Country by country data (CollectNiCad 2000d)
- a) Upper limit used and assuming average battery cadmium content of 13.8% see Table 2.2.5
- b) Miljøprojekt (2000)

For the data submitted by the authorities, the way the data are obtained/generated and the surrounding uncertainties are in general not explicitly specified. Industry (CollectNiCad) compiled data mainly through the information given by manufacturers and their commercial network (no primary data are available).

Six Member States have submitted their figures on the sales of portable<sup>20</sup> Ni-Cd batteries. Additional data for 17 countries were provided by CollectNiCad (2000f) for the year 1999. In general the latter figures are in concordance with the figures reported by the Member States. However, the market figures provided for France collated from the Member State Questionnaire are incomplete (130 versus 2,212 tonnes/year). In comparison with countries of a similar population size (UK, Italy) the industry's estimate seems a more realistic one. The industry's estimates for Denmark, Norway and Germany are approximately 30-40% lower than the figures provided by these countries. According to Industry the differences in the market data for Germany are mainly related to exports. A considerable amount is claimed to represent exported batteries, amount which is said by Industry to be neglected as such in the German data provided by the DE MS (neither primary data nor details from Arge Batterien were submitted to the Rapporteur).

Overall it can be concluded that approximately a maximum of 14,000 tonnes of portable Ni-Cd batteries is put on the EU-16 market (including Norway) for the reference year 1999.

<sup>20</sup> Those MSs replied to the Questionnaire under the section 'Consumer batteries'. Some MSs gave details related to the types and applications of batteries while others did not.

Recent data given by industry indicate a decrease in the weight volume introduced on the market with respectively 11,930 and 10,995 tonnes/year for the years 2000 and 2001.

### Industrial batteries

Very few countries replied on the Questionnaire 2000. The primary data sources for Industry's submitted data are in the first place the manufacturers. An overview of the present available data is given in **Table 2.25** for industrial Ni-Cd batteries.

Table 2.25 Industrial Ni-Cd battery market data (tonnes/year) for the EU Member States

Country	1994	1995	1996	1997	1998	1999	Reference
Austria						144	(2)
Belgium						97	(2)
Denmark				48-54 <sup>c</sup>		20	(2)
Finland <sup>a</sup>			23	121	104	68 87	(1) (2)
France						1,097	(2)
Germany						213? 251	(1*) (2)
Greece						230	(2)
Ireland							
Italy						243	(2)
Luxembourg						1	(2)
The Netherlands						80	(2)
Portugal						13	(2)
Spain						758	(2)
Sweden	250	200	200	200	150	150 142	(1) (2)
UK <sup>a</sup>	853	858	862	907	958	1,008 404 <sup>b</sup>	(1) (2)
Norway		95	104	119	84	57 1	(1) (2)
<b>Total EU-16<sup>a</sup></b>						<b>3,632</b>	
Switzerland						93	(2)
<b>Total<sup>a</sup></b>						<b>3,725</b>	

1) Questionnaire Member States (2000) Primary sources: (B): BEBAT, (F): only SCRA members, (UK): ERM, (S): SAFT

1C) Questionnaire (2000) Collection organisations (DE) : only data from VfW-REBAT (consumer/sealed portable + industrial): data from ZVEI not available

2) Industry Country by country data (CollectNiCad, 2000f)

\* Incomplete data-set on country basis

a) Upper limit used except for UK figure(s) that were corrected cfr text

b) UK + Ireland

c) Miljoproject (2000)

Four Member States have submitted market data on industrial Ni-Cd batteries. Additional data for 17 countries were provided for the year 1999 by industry. For the few cases where comparison is possible, the figures are in concordance with the figures provided by the Member States. Industry's estimate for the UK is much lower than the figure submitted by the UK-MS (DTI). ERM (on behalf of UK) provided this estimate based on sales information from SAFT and Exide ranging from 600-1000 tonnes. It was acknowledged by ERM that they did not correct for export that is estimated to be 50% (ERM, Pers. com., 2000). Applying the export rate gives an estimated figure for the UK market ranging from 400 to 670 tonnes (the figure '404' is used for calculating the totals for the year 1999).

Overall approximately 3,700 tonnes of industrial Ni-Cd batteries is put on the EU-16 market (EU including Norway) for the reference year 1999.

### Market trends

Most of the data related to market evolution come from Industry. The data submitted by CollectNiCad relate to the past and to semi-quantitative information on the application's market shares (see paragraph below). No precise information is (made) available on how the Ni-Cd battery market is likely to evolve in the future.

Ni-Cd batteries can be classified into four lines of products according to their market applications: industrial batteries, Emergency Lighting units (ELU), Cordless Power Tools (CPT) and applications in numerous Electrical and Electronic Equipment (EEE).

The largest application field for Ni-Cd batteries and a growing market have become the CPT applications (separated between the Professionals and Consumer market). The ELU market is under a slight growth rate with higher market shares in countries like France, United Kingdom, Italy and Spain, by opposition to Germany where centralised units powered by lead-acid batteries are used. The EEE market, which has been the largest market segment for Ni-Cd batteries during the first half of the nineties, is declining. From 1995, Ni-Cd batteries have gradually being replaced on the market by other types of batteries like the Nickel-Metal Hydride, the Lithium-Ion and the Lithium-Polymer batteries. Industrial Ni-Cd batteries are continuously in competition with lead-acid batteries but forms a stable market. A summary of the market shares for the different applications for the years 1999 and 2000 is given in **Table 2.26** and **Table 2.27**.

Table 2.26 Weight distribution in percent of the market share of Ni-Cd batteries by applications- reference year 1999

Industrial	Portable CPT
22% (Stable)	35% (growing)
Portable ELU	Portable EEE
18% (Stable)	25% (Declining)

Source CollectNiCad (2000e)

Table 2.27 Weight distribution in percent of the market share of Ni-Cd batteries by applications (reference year 2000)

Industrial	Portable CPT
24% (Stable)	35% (growing)
Portable ELU	Portable EEE
19% (Stable)	16% (Declining)
Specialities (Aviation, Industrial Comm. and Computing)	
6% and growing	

Source CollectNiCad (2002b)

From the information available it can be concluded that the Ni-Cd market has increased significantly in the 80's to reach a more or less stable level in the late 1990's of around 13,500 tonnes/year for consumer/sealed portable nickel-cadmium batteries and 3,500 to 4,000 tonnes/year for the industrial nickel-cadmium battery market.

To date, no market projections are available for the amount of portable Ni-Cd batteries, which will be put on the market in the future. A study by ERM (2000) employed a positive common growth rate for all types of portable secondary batteries. However, since the market evolution is stated to be mainly technology driven and, as there is confidential business implication, it is difficult to get any good specific estimate for the growth rate of Ni-Cd chemistry applications.

Between 1996 and 1999 the portable Ni-Cd battery market in the EU seems to be oscillating around 13,000 -14,000 tonnes<sup>21</sup>. Although recent figures for 2000 and 2001 indicate a decrease in sales, the figure of 13,500 tonnes has been chosen as a worst case scenario to forecast future battery waste arising. The industrial batteries remain at the level of 3,600 tonnes.

## 2.2.2.5 Collection/recycling data

### 2.2.2.5.1 Country by country data

#### Portable Nickel-cadmium batteries

Data on the Ni-Cd battery collection/recycling efforts for individual EU countries were collated from the Questionnaire 2000. In addition Industry (CollectNiCad) provided a second series of data for the year 1999 and 2000. The latter represent the amount collected and processed for recycling. An overview of the available data is given in **Table 2.28** for portable Ni-Cd batteries.

<sup>21</sup> The reference year 1999 has been chosen because this was the most recent year for which cross validation of the data provided by industry with those provided by the Member States was possible.

Table 2.28 Total weight (tonnes/year) of collected/recycled portable Ni-Cd batteries for the individual EU countries

Country	1994	1995	1996	1997	1998	1999	2000	2001	Reference
Austria	22.5	26.7	42.5	61.8	97	97	53	84	(2) (A)
Belgium	9	10	10	37 50	79 66	59 59	177 115	70	(1) (2) (B)
Denmark	34 34	54 54	9 --	94 103	80 78	66	59	108	(1C) (2) (Dk)
Finland		1	6		91 12	113 5	10	1	(1) (2)
France	33 60	50 35	65 70	95 105	100 92	140	140	182	(1) (2)
Germany	220	206	303	440	403	596	1,001 950	921	(1) (2) (GRS)
Greece							1	1	(2)
Ireland						9	11	5	(2)
Italy	1			2	1	25	33	36	(2)
Luxembourg					5	5	5	5	(2)
The Netherlands	10	29	35	75	119	150	210	160	(2) (NL)
Portugal							1	1	(2)
Spain		4				38	30	66	(2)
Sweden	111	112 108	113 110	141 142	144 143	170 169	142 147	167 167	(1) (2)
UK	18	63	72	94	50 46	106 75	78	93	(1) (2)
Norway		2	10	66	63	53 12	10	43	(1) (2)
Total EU-16 <sup>a</sup>	459	539	663	1,106	1,125	1,446	1,852	1,943	
Switzerland	34	96	46	21	114	48	194	198	(2)
Total <sup>a</sup>						1,494	2,046	2,141	(2)

1) Questionnaire (2000) Member States. Sources: (B): data from BEBAT figure of 2000 is still provisional: lower figure: amount of sorted batteries, upper figure: amount of recycled batteries during the year 2000, (F): Ministère de l'aménagement du territoire et de l'environnement, (UK): data as from SNAM, (S): data as from SAFT, (DE): data from UBA, comments 2002.

1C) Questionnaire (2000) Collection organisation. DK: Danish Battery Association: figure of '95 includes collection till 31 March '96

2) Industry Country by country data (CollectNiCad, 2000f and 2001a) (A) Rumpold AG, (B) BEBAT, (Dk) Battery Association Denmark, (GRS) Gemeinsames Rücknamesystem Batterien, (NL) STIBAT

a) Lower limit used

The primary data source for Member States is data on collection as obtained via governmental or private collection organisations. Additional verification procedures by external independent organisms may enhance the confidence in these figures. Industry (CollectNiCad) compiled its series of figures through information obtained via the recycling companies and/or collection organisations (primary data are not available to the Member States Rapporteur). The transboundary movement of spent Ni-Cd batteries is liable to the Basel Convention administrative rules and offers a means to trace back collected amounts on national basis.

For the few cases where comparison is possible, no large differences are observed between the data provided by industry and the Member States. Overall approximately 1,852 tonnes of portable Ni-Cd batteries has been collected in the EU-16 for the year 2000 and 1,943 tonnes for the reference year 2001. Countries for which no (or poor) data are available have most often not yet a dedicated Ni-Cd collection system in place. A short overview of the situation in the EU is given by CollectNiCad in **Table 2.29**. The information on existing Ni-Cd collection schemes and programs present in Europe gathered by the Questionnaire is limited (only DK, S, UK, F, FIN and NO) and mostly does not provide many further details than those already reported in other publications (ERM, 1997; EUPHEMET, 2000 and CollectNiCad, 2000f). More details are available in Annex I.

Table 2.29 Overview of Ni-Cd Collection programs running in various European countries

Country	Collection Ni-Cd	Collection all type (primary and rechargeables)	Start	NCRA <sup>a</sup>	Sorting	Financial system (€/kg)
Austria	Yes	Yes	1990	UFB	Yes	2
Belgium	Yes	Yes	1993	BEBAT	Yes	3
Denmark	Yes*		1996**	Ministry**	No*	16
Finland	Yes			Municipalities/ importers/retailers	Some	
France	Yes		1999	SCRA	Yes	2
Germany	Yes	Yes	1998	GRS	Yes	2
Greece						
Italy						
Luxembourg						
Portugal						
Spain	Yes-local	Yes-local	1999			
Sweden	Yes	Yes	1998	Municipalities	Yes	34
The Netherlands	Yes	Yes	1995	STIBAT	Yes	2
UK + Ireland	Partial		1994	REBAT		
Norway	Yes		1997	Batteriretur		
Switzerland	Yes	Yes	1990	BESO	Yes	3-5

Source CollectNiCad (2000g), adapted.

\* Will change in future: all batteries (primary and rechargeable will have to be collected);

\*\* Before that date: other in place e.g. Danish Battery Association

a) NCRA = National Collection and Recycling Association

### Industrial Nickel-Cadmium batteries

Data on the Ni-Cd battery collection/recycling efforts for individual EU countries were collated from the questionnaire 2000. In addition CollectNiCad provided data for the year 1999. An overview of the available data for industrial Ni-Cd batteries is given in **Table 2.30**.

Table 2.30 Total weight (tonnes/year) of collected/recycled industrial Ni-Cd batteries for the individual EU countries<sup>22</sup>

Country	1994	1995	1996	1997	1998	1999	2000	2001	Reference
Austria		91	115	173		148	304	134	(2)
Belgium	14	105	71	140	112	65	91	104	(2)
Denmark		3	5 14 <sup>b</sup>	3	1	7	11	34	(2)
Finland		41	47	70	70 98	160 131	82	188	(1) (2)
France	158 528	153 560	251 1,100	383 560	400 618	529	817	780	(1) (2)
Germany	935	1,074	987	1,124	1,295	998	799	826	(2)
Greece			3						
Ireland						20	8	8	(2)
Italy	31	103	131	151	41	125	194	190	(2)
Luxembourg				4	3		10	5	(2)
The Netherlands	83	127	261	185	172	150	146	124	(2)
Portugal									
Spain		12		41	181	160	94	154	(2)
Sweden	136	157 147	254 254	204 204	189 189	200	216	295	(1) (2)
UK	29	21	24	80	52 51	112 112	136	112	(1) (2)
Norway		53	53	57	20 34	32 67	55	84	(1) (2)
Total EU-16 <sup>a</sup>						2,677	2,963	3,038	
Switzerland	39	19	18	20	23	21	160	42	(2)

1) Questionnaire Member States (2000) Primary sources: (B): BEBAT, (F): Ministère de l'aménagement du territoire et de l'environnement, (UK): SNAM, (S):SAFT

2) Industry Country by country data (CollectNiCad, 2000), updated for the years 2000 and 2001 (CollectNiCad, 2002)

a) Lower limit used

b) Miljøprojekt (2000)

In the few cases where two sets of data are available, no large differences are observed between the data provided by industry and the Member States. Overall approximately 2,677 tonnes of industrial Ni-Cd batteries have been collected in 1999.

### 2.2.2.5.2 Collection rate/Collection efficiency

Data on the absolute amounts of Ni-Cd batteries being collected was obtained from a questionnaire submitted in 2000 to the EU Member States. In addition CollectNiCad provided country by country data for the year 1999. Collection percentages mentioned in the questionnaires are not given in the **Table 2.28** and **Table 2.30**. Any comparison of these numbers should be performed with caution since most often the rationale behind the calculation

<sup>22</sup> With update for 2000 and 2001, via CollectNiCad, 2002.

of collection rates are not the same for the various EU Member States. Typically, collection rates are being calculated as the percentage collected batteries of a base year sale. In that case the collected amount corresponds to only a small percentage of same years' sales of portable Ni-Cd batteries (e.g. UK). However, this kind of approach is difficult to apply for long life articles<sup>23</sup> such as Ni-Cd batteries for which no correlation can be found between the base year sales data and the collected quantities for that same year.

So, Industry as well as Member States developed a number of alternative calculation formulas. One of the most recent is the so-called 'collection efficiency' being defined by STIBAT as the ratio between the amount of Ni-Cd batteries collected over the maximally available amount for collection (STIBAT, Deauville, 1999) with the latter equalling the sum of the collected Ni-Cd batteries and the quantity of Ni-Cd batteries disposed in the municipal waste stream.

Calculating the collection efficiency

$$\text{Collection efficiency} = Q_{\text{Ni-Cd Coll}} = \frac{Q_{\text{Ni-Cd Coll}}}{Q_{\text{Ni-Cd Coll}} + Q_{\text{Ni-Cd MSW}}}$$

$Q_{\text{Ni-Cd Coll}}$  = Quantities of batteries collected separately

$Q_{\text{Ni-Cd MSW}}$  = Quantities of batteries eliminated with Municipal Solid Waste

Although this equation may have advantages (i.e. independent of present market volume and battery's lifetime) it needs to be mentioned that detailed studies dealing with the analysis of MSW are complex and for the moment limited to a few countries. Furthermore the amount of Ni-Cd batteries found in MSW might not be completely representative for all Ni-Cd batteries going into the waste stream. For example, replacement of batteries in emergency lighting units is not common. Therefore, the majority of end-of-life Ni-Cd batteries in emergency lighting become waste during building refurbishment and are generally disposed of as mixed industrial and some as municipal waste (ERM, 2000). For pure conceptual and mathematical reasons the use of a collection ratio, defined as a simple percentage of the total amount of used Ni-Cd batteries coming available for collection and that will effectively be collected for recycling, is preferred. By subtraction, the remaining amount of batteries arriving into the waste stream is obtained.

Since not all European countries have a (Ni-Cd) battery collection system in place two collection ratio's are considered further in this report:

- 10% collection of the Ni-Cd batteries coming available for collection: representative for a country with a collection system with low efficiency;
- 75% collection of the Ni-Cd batteries coming available for collection: considered by Industry as representing an EU-wide realistic target (CollectNiCad, Pers. com., July 2002) and chosen to be representative for a country with a collection system with a high efficiency.

The span of 10-75% is believed to cover all possible combinations in the EU (limited to waste management options). Hence, in this regard the development of country specific scenarios are not deemed necessary.

<sup>23</sup> Long life articles are defined in the revised TGD as articles having a service life longer than one year

## 2.2.3 Updated data (reference year 2002)

### 2.2.3.1 Introduction

Quantitative update information regards the use of the substances in the different applications is fragmentary.

Consumption volumes are updated for the uses in batteries, in pigments and in stabilisers for those companies that participated in the updating exercise (see **Table 2.31**).

Furthermore some producers provided tentative data regards the break-down of the quantities cadmium metal and cadmium oxide: the uses of cadmium oxide expressed as percentages of the production in 2002 are estimated as follows: batteries: 83.5%, stabilisers: approximately 27% pigments: 1.5% and others: 4%. This latter information is substantially different from the data provided by the processors/users of the substances.

No update consumption data are available for Cd plating, alloys and others.

Table 2.31 Consumption data on cadmium metal and cadmium oxide for the major use applications (amounts in metric tonnes and expressed as elemental cadmium)

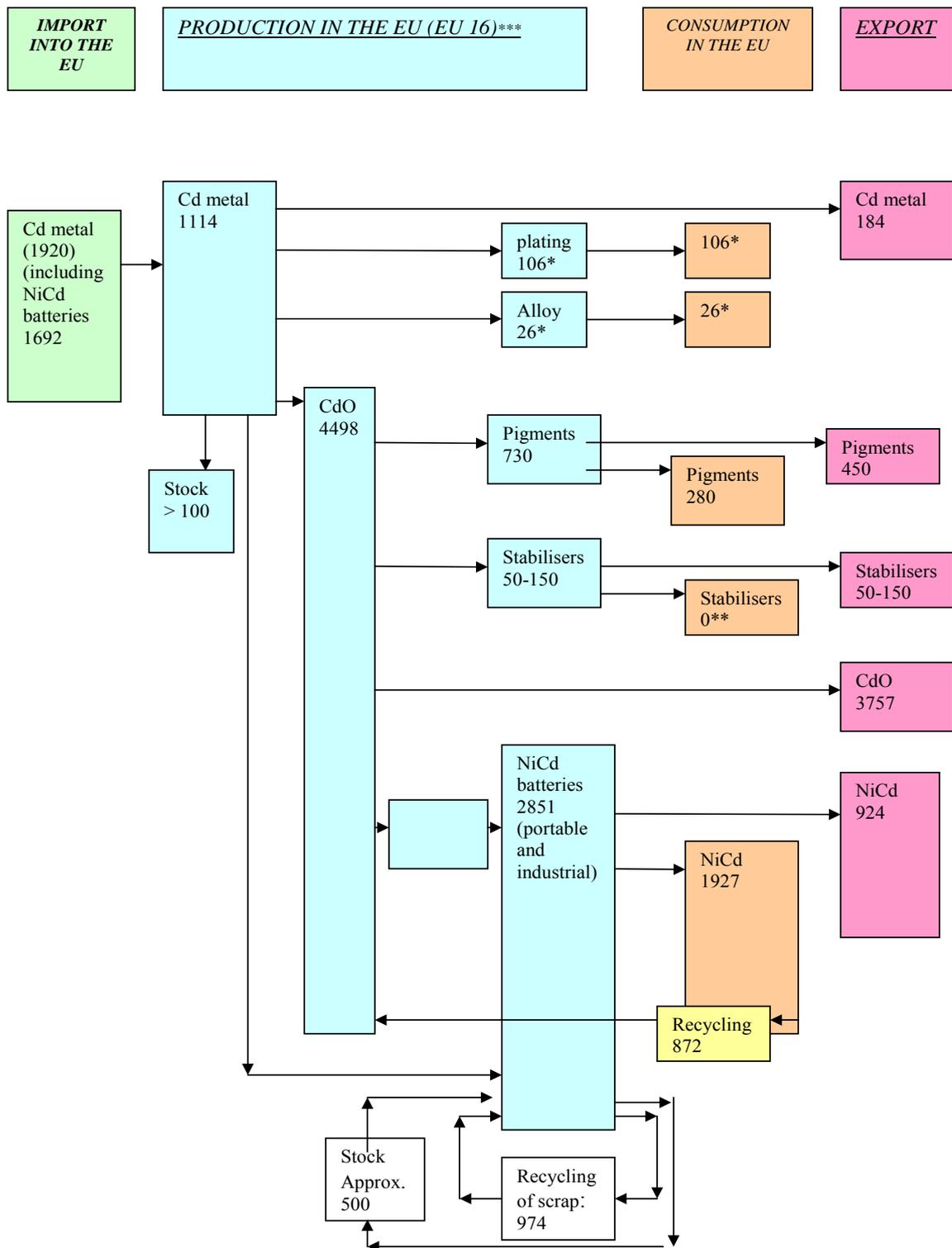
Year	Batteries	Pigments	Stabilisers
2002	1634.6*	n.d.	in the range 50 to 150
2003	1725*	299	in the range 50 to 120

n.d. No data available;

\* Figures based on the information provided by 3 companies

Recently, an update of the mass-balance of cadmium in the EU (year 2000-2002) was provided by industry (see **Figure 2.11**). The production volume of cadmium in the EU in 2000-2002 is estimated to be 1,114 tonnes/year. Corrected for import/export 2,850 tonnes/year is available for different applications.

Figure 2.11 Cadmium mass balance flow in the EU for the reference year 2000-2002 (mass balance drawn up by ICdA, IZA-Europe and Recharge)



\* Data refers to 1996. No update in figures was received

\*\* Due to the Vinyl 2010 Commitment

\*\*\* Not included is cadmium contained in imported raw materials (zinc, copper and lead ores). For zinc ores the estimated amount of cadmium in the EU-16 is 5,000 tonnes/year. Most of this cadmium is stated to be separated in the production processes, stabilised and disposed of in authorised hazardous waste disposal sites. Estimated amount is 5,000 tonnes for EU zinc industry.

### 2.2.3.2 Ni-Cd Batteries

Since the previous update of information in 2002/2003, the number of companies producing Ni-Cd batteries has further decreased. **Table 2.32** mentions those companies that ceased the production of these batteries. Current producers are given in **Table 2.33**.

Table 2.32 Companies formerly producing Ni-Cd batteries and date/year of ceasing production

Company (and plant)	Country	Date/year of production stop
Friwo (EXIDE-group)	Germany	p.m. date to specify
EMISA (EXIDE- group)	Spain	2003

Table 2.33 Current producers of Ni-Cd batteries in EU\*-16

Company (and location)	Country
SAFT Nersac	France
SAFT Bordeaux	France
Hoppecke	Germany
GAZ (Zwickau)	Germany
SAFT-AB	Sweden

Table 2.34 Current recyclers of Ni-Cd batteries in EU\*-16

Company (and site)	Country
SNAM	France
ACCUREC	Germany
SAFT-AB	Sweden

The amount of cadmium (metal and oxide) used by three out of seven (for the year 2002) and five (for the year 2003) companies is approximately 1,635 metric tonnes for the year 2002. A slightly higher amount is reported for the year 2003 (see **Table 2.31**).

The volume of secondary cadmium produced in the EU-16 by the recycling of batteries, production scrap and other sources, was about 974 tonnes for the year (of which 56% batteries) 2002 and 10,23 tonnes for the year 2003 (of which 52% batteries). These figures are based on the information provided by 2 out of the 3 recycling companies (data of the company with highest capacity are included).

### 2.2.3.3 Cd containing Pigments

Compiled update information from the producers of cadmium containing pigments was submitted to the Rapporteur. Currently only three companies are producing these pigments in the EU-16. General Chimica and Degussa ceased production respectively in 2003.

Compiled data on the mass-balance of cadmium in pigments for the year 2003 was provided by the pigment producing companies and is given in **Table 2.35**.

Table 2.35 Mass-flow of cadmium within pigments for the year 2003 (in metric tonnes)

	Cd in pigments	Cd content
Production	1,216	730
Exports outside EU-16	750	450
EU-16 sales	466	280
Imports outside EU-16	33	20
EU-16 consumption	499	299

Note The calculation of the consumption figures assumes that the volumes of export and import of coloured articles are the same

#### 2.2.3.4 Cd containing stabilisers

The production of stabilisers containing cadmium (compounds) decreased significantly since the end nineties in view of the Vinyl 2010 commitment. It should be noticed that any production of stabilisers by the companies adhering to this agreement, is destined solely for export and cannot be sold in the EU-15. The number of producers in the EU-16 dropped to only a few. Currently only 2 companies (three sites) acknowledged to the Rapporteur that some production still took place at their sites in Italy and Germany.

Only two of these use the priority substances as starting material in their process.

The consumption data of cadmium metal and cadmium oxide for this use are given as a range: between 50 and 150 tonnes in 2002. Somewhat lower values are given for the year 2003 (see **Table 2.31**).

Any EU production of stabilisers is for export and cannot be sold in the 15 original EU countries that are part of the Vinyl 2010 commitment.

#### 2.2.3.5 Alloys, plating and other uses

No update information was submitted to the Rapporteur for these uses.

### 2.3 LEGISLATIVE CONTROL MEASURES

#### 2.3.1 EU legislation

Cadmium (and its compounds) is a multi-regulated substance: in the EEC several directives have been adopted spread over the whole spectrum of risk reduction legislative instruments actually in use in the EU i.e. limitations in the marketing and use, environmental quality standards (emission and immission standards, protection of natural resources (groundwater, drinking water)), workplace (OEL's, etc) and consumer.

The directives, regulating at the source, are the Council Directive 76/769 (10<sup>th</sup> amendment; 91/338/EEC) relating to the restrictions on the marketing and use (see **Table 2.36**), and the Council Directive 91/157/EEC on batteries and accumulators. The latter directive establishes a marketing ban on batteries and accumulators with high mercury content as well as an obligation for Member States to undertake steps to ensure the separate collection of batteries with a view to their recovery or separate disposal. The latter obligation concerns spent batteries and accumulators containing certain amounts of cadmium, lead or mercury.

Table 2.36 Limitations and prohibitions on the marketing and use of Cadmium and its compounds (Directive 76/769/EEC, amendment Dir. 91/338 and Dir. 99/51/CE)

<p>Cd and its compounds 91/ 338/EEC</p>	<p><b>1. May not be used to give colour to finished products</b></p> <p><b>1.1. Manufactured from the substances and preparations listed below:</b></p> <ul style="list-style-type: none"> <li>▪ polyvinyl chloride (PVC) [3904 10] [3904 21] [3904 22]</li> <li>▪ polyurethane (PUR) [3909 50]</li> <li>▪ low-density polyethylene (LDPE), [with the exception of low-density polyethylene used for the production of coloured master batch] [3901 10]</li> <li>▪ cellulose acetate (CA) [3912 11] [3912 12]</li> <li>▪ cellulose acetate butyrate (CAB) [3912 11] [3912 12]</li> <li>▪ epoxy resins [3907 30]</li> <li>▪ melamine-formaldehyde (MF) resins [3909 20]</li> <li>▪ urea-formaldehyde (UF) resins [3909 10]</li> <li>▪ unsaturated polyesters (UP) [3907 91]</li> <li>▪ polyethylene terephthalate (PET) [3907 60]</li> <li>▪ polybutylene terephthalate (PBT)</li> <li>▪ transparent/general purpose polystyrene [3903 11] [3903 19]</li> <li>▪ acrylonitrile methacrylate (AMMA)</li> <li>▪ cross-linked polyethylene (VPE)</li> <li>▪ high-impact polystyrene</li> <li>▪ polypropylene (PP) [3902 10]</li> </ul> <p>In any case, whatever their use or intended final purpose, finished products or components of products manufactured from the substances and preparations listed coloured with cadmium may not be placed on the market if their cadmium content (expressed as cadmium metal) exceeds 0.01% by mass of the plastic material.</p> <p>EXCEPTED for products to be coloured for safety reasons</p> <p><b>1.2. May not be used in paints.</b></p> <p>However if the paints have a high zinc content, their residual concentration of cadmium must be as low as possible and at all events not exceed 0.1% by mass.</p>
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Table 2.36 continued overleaf

Table 2.36 continued Limitations and prohibitions on the marketing and use of Cadmium and its compounds (Directive 76/769/EEC, amendment Dir. 91/338 and Dir. 99/51/CE)

Cd and its compounds 91/ 338/EEC	<p><b>2. May not be used to stabilise:</b></p> <p><b>2.1. The finished products listed below manufactured from polymers or copolymers of vinylchloride:</b></p> <ul style="list-style-type: none"> <li>▪ packaging materials (bags, containers, bottles, lids)</li> <li>▪ office or school supplies</li> <li>▪ fittings for furniture, coachwork or the like</li> <li>▪ articles of apparel and clothing accessories (including gloves)</li> <li>▪ floor and wall coverings</li> <li>▪ impregnated, coated, covered or laminated textile fabrics</li> <li>▪ imitation leather</li> <li>▪ gramophone records</li> <li>▪ tubes and pipes and their fittings</li> <li>▪ swing doors</li> <li>▪ vehicles for road transport (interior, exterior, underbody)</li> <li>▪ coating of steel sheet used in construction or in industry</li> <li>▪ insulation for electrical wiring</li> </ul> <p>In any case, whatever their use or intended final purpose the placing on the market of the above finished (components of) products is prohibited if their cadmium content (expressed as Cd metal) exceeds 0,01% by mass of the polymer.</p> <p>EXCEPTED for products using cadmium based stabilisers for safety reasons.</p> <p><b>3. May not be used for cadmium plating metallic products or components of the products used in the sectors/applications listed below:</b></p> <ul style="list-style-type: none"> <li>▪ Equipment and machinery for: <ul style="list-style-type: none"> <li>▪ food production</li> <li>▪ agriculture</li> <li>▪ cooling and freezing</li> <li>▪ printing and book-binding</li> </ul> </li> <li>▪ Equipment and machinery for the production of: <ul style="list-style-type: none"> <li>▪ household goods</li> <li>▪ furniture</li> <li>▪ sanitary ware</li> <li>▪ central heating and air conditioning plant</li> </ul> </li> </ul> <p>and the manufactured products as listed in this subsection</p>
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Table 2.36 continued overleaf

Table 2.36 continued Limitations and prohibitions on the marketing and use of Cadmium and its compounds (Directive 76/769/EEC, amendment Dir. 91/338 and Dir. 99/51/CE)

Cd and its compounds 91/ 338/EEC	In any case, whatever their use or intended final purpose the placing on the market of cadmium plated products or components of such products used in the sectors/applications listed and of the products manufactured in the sectors listed is prohibited.  EXCEPTED sectors: aeronautical, aerospace, mining, off shore and nuclear whose applications require high safety standards and in safety devices in road and agricultural vehicles, rolling stock and vessels.  EXCEPTED electrical contacts, in any sector of use, on account of the reliability required of the apparatus on which they are installed.
99/ 51 /EC	Exemptions for Austria and Sweden, already applying stricter provisions than the aforementioned, are granted until 31 December 2002, time by which the European regulations will be reconsidered and adapted to technical progress. See in this context the study reports by WS Atkins (1999a, b) and RPA Ltd (2000), on the risks to health and the environment by cadmium contained in certain products (i.e. used as a colouring agent or as stabiliser in polymers and for metal plating), as commissioned by the EC (DG Enterprise).

In addition to Dir. 91/338/EEC, toys should also comply to Directive 88/378/EEC ('Safety of Toys Directive') thus fulfilling the daily limit value for cadmium for the bioavailability resulting from the use of toys i.e. 0.6 µg per day (EC, 2003). Consumer protection is further also aimed at through the establishment of regulatory standards (e.g. European Standard EN 71 part 3) in circumstances where prevention from exposure is of particular importance, i.e. in toys and articles which come into contact with food (ICdA, 1997).

Commission Regulation EC 466/2001 sets maximum levels for certain contaminants in foodstuffs.

Table 2.37 Commission Regulation (EC) 466/2001: Maximum levels of Cd in food from aquatic sources (Official Journal L 077 , 16/03/2001)

Product	Maximum level (mg/kg wet weight)
Muscle meat of fish, excluding fish species listed below	0.05
Muscle meat of <i>Dicologlossa cunneata</i> , <i>Anguilla anguilla</i> , <i>Engraulis encrasicolus</i> , <i>Luvarus imperialis</i> , <i>Trachurus trachurus</i> , <i>Mugil labrosus labrosus</i> , <i>Diplodus vulgaris</i> , <i>Sardina pilchardus</i>	0.1
Crustaceans, excluding brown meat of crab	0.5
Bivalve molluscs	1.0
Cephalopods (without viscera)	1.0

(information extracted from EC Working document EQS for cadmium, 2003)

End of pipe EEC directives concern putting limits to discharges/emissions of cadmium in the different environmental compartments (air, water, sewage sludge for agricultural use).

Quality objectives have been adopted for the workplace as well as for different environmental compartments.

### Water

Standards for surface freshwater intended for the abstraction of drinking water, and for water intended for human consumption have been fixed through the Council Directives 75/440/EEC

(will be repealed in December 2007 by Dir 2000/60/EC; the Water Framework Directive) and 80/778/EEC.

Table 2.38 Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States

Standard in mg/l	Details	Source
0.005 mg/l	Permissible level; $\geq 95\%$ of samples Guidance levels for several water parameters pH, zinc, max. Susp. matter etc.	O.J. L 194 , 1975
Standards adopted in Member States		
n.d.	n.d.	n.d.

Table 2.39 Directive 80/778/EEC and Directive 98/83/EC on water for human consumption

Standard in $\mu\text{g/l}$	Details	Source
5 $\mu\text{g/l}$	MAC; min. total hardness 60mg/l Ca (or analogous cations)	O.J. N° L 229, 1981 O.J. N° L 330, 1998
Standards adopted in Member States		
n.d.	n.d.	n.d.

(MAC: max. admissible concentration, GL: Guide Levels, MRC minimum required concentration). The reference detection method in this medium is given: i.e. atomic absorption.

Council Directive 80/68/EEC for groundwater comprises cadmium compounds in List I for which MS must prohibit the direct and avoid the indirect introduction to the groundwater. The directive shall be repealed in 2013 due to 2000/60/EC. Specific measures to prevent and control groundwater pollution will be adopted within the implementation of Art. 17 of 2000/60/EC.

In Council Directive 78/659/EEC on the quality of fresh water for fish and Council Directive 79/923 on shellfish waters, no specific cadmium concentration is given. The latter Directive only stipulates that no harmful effects on shellfish and larvae should occur and aim good quality of shellfish products. Atomic absorption spectrometry preceded if needed by concentration and/or extraction, is indicated as the reference detection method.

Council Directive 76/160/EEC concerning the quality of bathing water specifies cadmium but has yet not specified a 'Guide value' or 'Mandatory value'.

Council Directive 76/464/EEC on pollution by certain dangerous substances, and its daughter directive, Council Directive 83/513/EEC on the limit values and quality objectives for cadmium discharges, require Member States to set up an (prior) authorisation system for discharges of cadmium.

For most industrial discharges, with the exception of industrial plants manufacturing phosphoric acid and/or fertilisers, emission limit values are laid down. By way of alternative, Member States may base their authorisations on the quality objectives laid down for different types of waters.

Reference methods of measurement and monitoring procedures for cadmium in water, sediments and shellfish (i.e. AAS preceded by appropriate conservation and treatment of the sample) are laid down in Annexe III, of the directive including details on accuracy, precision and flow of the effluent.

Table 2.40 Directive 76/464/EEC: on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Directive 83/513/EEC, the so-called Cadmium Discharges Directive)

Limit values* for zinc mining, refining lead and zinc and production of non-ferrous metals and metallic cadmium	Details	Source
0.2mg cadmium/l effluent	monthly mean measurements (limits for mean of daily measurements = 2-fold)	O.J. N° L 129, 1976
Limit values for the production of cadmium (compounds)	Details	
0.2mg cadmium/l effluent	mean of one month; total cadmium concentration	
0.5g cadmium/kg processed cadmium		
Minimum standards for the protection of aquatic life		
≤ 5 µg/l	in surface water; total cadmium conc	
≤ 5 µg/l	estuaries; dissolved cadmium	
≤ 2.5 µg/l	in marine territorial waters, coastal waters; dissolved cadmium	
Quality objective (target value)**		
≤ 1 µg/l	in surface water; total cadmium conc	
≤ 1 µg/l	estuaries; dissolved cadmium	
≤ 0.5 µg/l	in marine territorial waters, coastal waters; dissolved cadmium	
and no significant increase of concentration of cadmium in sediments or in shellfish and mollusca (e.g. <i>Mytillus edulis</i> )		
Standards adopted by Member States		
0.06	NI; max. permissible conc.; dissolved	van Hout, 1994; in Pearse, 1996
0.01	NI; target value; dissolved	van Hout, 1994; in Pearse, 1996

\* To be considered as 'emission limit value' under the Dir. 2000/60/EC

\*\* To be considered as 'environmental quality standards' under Dir. 2000/60/EC

The Water Framework Directive 2000/60/EC (O.J. L 327, 22.12.2000, p.1-73) aims at the establishing of a framework for the protection of surface, transitional, coastal waters and groundwater which prevents further deterioration and protects and enhances the status of the aquatic ecosystems and depending terrestrial ecosystems and wetlands; promotes sustainable water use; aims at enhanced protection and improvement of aquatic environment through specific measures for the progressive reduction of discharges, emissions and losses of priority substances and the cessation of phasing-out of discharges, emissions and losses of priority hazardous substances, pollution; contributes to mitigating the effects of floods and droughts. Herewith the objectives of relevant international agreements including those which aim to prevent and eliminate pollution of the marine environment with the ultimate aim of achieving

concentrations of priority hazardous substances near the background values for naturally occurring substances (e.g. cadmium) and close to zero for man-made synthetic substances.

The list of priority substances (Annex X of Directive 2000/60/EC) has been established by Decision N° 2455/2001/EC, as has specified cadmium as a Priority Hazardous Substance.

This implies (art. 16 of 2000/60/EC) that the European Commission has to submit proposals for progressive reduction of discharges, emissions and losses, but also, as cadmium is listed as Priority Hazardous Substance, cessation or phasing-out of discharges, emissions and losses within 20 years after adoption of the proposals.

The proposals must at least cover quality standards, for water, sediment or biota, and emission controls for point sources, and also review the Cadmium Discharges Directive (83/513/EEC). If no agreement on the proposals is reached at Community level by 2006, Member States have to establish themselves quality standards and controls on the principal sources.

As the quality standards are part of the surface water status, these would have to be reached at the latest by 2015.

### *Air*

Waste Incineration Directives: 89/369 and 89/429 set emission limit values to air based on BAT for new and existing municipal waste incineration plants (new = exploitation permit delivered after December 1, 1990). For new installations (with a nominal capacity of at least 1 tonne waste/hour) the emission value for cadmium and mercury is fixed at 0.2 mg/Nm<sup>3</sup> off-gas. Old installation with minimal 6 tonnes/hour nominal capacity must apply to this value at the latest by December 1, 1996.

The hazardous waste incineration Directive (94/67) controls emissions of heavy metals by prior authorisation procedure of plants. Emission limits in flue gas for existing installations (before December 31, 1996): the sum of cadmium (compounds), expressed as cadmium and thallium(compounds) must be lower than 0.1 mg/m<sup>3</sup>. For new installations, the corresponding limit is fixed at 0.05 mg/m<sup>3</sup>.

In addition to Directive 75/442/EEC, Directive 2000/76/EC on the incineration of waste sets stricter emission limit values, in particular for cadmium to air (the total emission limit value of 'Cd + Tl' = 0.05 mg/(Nm)<sup>3</sup> as daily average value suitably standardised depending on the type of combustion; air emission limit value for cadmium and its compounds: all average values over sampling period of a minimum of 30 minutes and a maximum of 8 hours: expressed as cadmium: total: 0.05 mg/m<sup>3</sup>; exemption until January 1, 2007 for existing plants and certain conditions, hazardous waste incinerators only), water (the emission limit value for the discharges of waste water from the cleaning of exhaust gases, mentions for cadmium and its compounds, expressed as cadmium and in mass concentration for unfiltered samples: 0.05 mg/l). These emission limit values should be met by means of stringent operational conditions and technical requirements of the installations (existing plants as from December 28, 2005; for new plants as from December 28, 2002).

Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management (O.J. L 296, November 11, 1996, p. 5-63) aims to define the basic principles of a common strategy to define and establish objectives for ambient air quality (AAQ i.e. related to outdoor air excluding workplaces) in the Community designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole; assess the ambient air quality in the MSs on the basis of common methods and obtain adequate information on the issue and

ensure its public accessibility (e.g. by means of alert thresholds) maintain AAQ where it is good and improve it in other cases. Cadmium is mentioned in the list of atmospheric pollutants to be taken into account in the assessment and management of AAQ (for cadmium, an air quality standard of 5 ng/m<sup>3</sup> has been proposed).

### Soil

Council Directive 86/278/EEC concerns the protection of the environment and in particular of the soil when sewage sludge is used in agriculture. Limit values concentrations have been set of the substance in soil, in sludge for the agricultural use and for the maximum amounts of cadmium which may be add annually to the agricultural land.

Table 2.41 Directive 86/278/EEC: on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (Annex IA)

Annex IA		
Limit values in soils in mg/kg	Details	Source
1 up to 3		O.J. N° 181, 1986
Standards adopted by Member States (COM(97) 23 final)		
1 up to 3	BE; Flanders: sandy soil: 1 clay soil: 3; Wallonia: 1	
1 up to 3	ES: pH < 7: 1; pH > 7: 3	
2	FR	
1 up to 4	PT: pH < 5.5: 1; pH 5.5 < 7: 3; pH > 7: 4	
3	UK	

Remark: for DE: limit values: 1.5 mg/kg (or 1 mg/kg dry weight) at pH > 5 and < 6 (UBA, comments 2000).

Table 2.42 Directive 86/278/EEC: on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (Annex IB)

Annex IB		
Limite values in sludge (mg/kg)	Details	Source
20 to 40		O.J.
Standards adopted in Member States (COM(97) 23 final)		
10 and 12	BE; Flanders: 12; Wallonia: 10	
20 up to 40	ES: pH < 7: 20; pH > 7: 40	
20 and 40	FR: reference value: 20; limit value: 40	
20	PT	

Remark: here there are no data for UK; for SE: A charge of 30 SEK per gram of cadmium exceeding 50 g/tonne P (changed to 5 g Cd/tonne P) was introduced in Sweden in 1994 and was changed to a tax in July 1995 (KEMI, comments 2000); for DE: limit value: 10 mg/kg (or 5 mg/kg dry weight) at pH > 5 and < 6 (UBA, comments 2000).

Table 2.43 Directive 86/278/EEC: on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (Annex IC)

Annex IC		
Limit values for the introduction of metals in arable soils in kg/ha/year		
0.15		
Standards adopted by Members States (representative for the p'riod '91 - '94) (COM(97) 23 final)		
0.012 and 0.024	BE: Flanders: grassland: 0.012; culture land: 0.024	
0.15	ES	
0.06	FR	
0.15	PT	
0.15	UK	

Remark: for DE: limit value: maximum 0.017 kg Cd/ha/annum (based on the limit value in sludge and the max. sludge application), maximum sludge application of 5 tonnes/ha/3 years (UBA, comments 2000).

The Fertiliser Directive (76/116/EEC) is currently under revision. In that framework, extensive work has been done by Member States in performing national risk assessment reports and by the EC (see ERM, final reports of January 2000 and June 2001, commissioned by DG Enterprise). The aim of the exercise is to review the data on the exposure of risk groups and on environmental conditions in the Member States to judge whether or not cadmium in fertilisers presents an unacceptable risk and thus to harmonise the situation within the EU (Austria, Finland and Sweden have a derogation<sup>24</sup> from Article 7 of the Directive in so far it concerns cadmium i.e. these MS may prohibit the marketing of fertilisers containing cadmium at concentrations in excess of those which were fixed nationally at the date of Accession) and to adopt EU-wide risk management measures related to the cadmium (content) in fertilisers, if needed so. In that context several Member States have implemented national regulations limiting the maximum cadmium concentration in fertilisers, the cadmium input in and/or the cadmium concentration in agricultural soil. A non-exhaustive overview of these figures is given in the environmental part of the Risk Assessment Report (see separate document).

### Waste

Council Directive 78/319/EEC on toxic and dangerous waste determined cadmium and its compounds as requiring priority consideration in the control, prevention, recovery and recycling of any waste containing or contaminated by the substance.

The packaging and packaging waste Directive (i.e. Dir. 94/62/EC of 20 December 1994; Commission Decisions 1999/177/EC and 2001/171/EC) aims to reduce the impact of these materials (and waste arisings) by limiting the total quantity that may be put on the market, by enhancing re-use and recycling and by setting limits to hazardous substances. The sum of the concentrations of four heavy metals (lead, cadmium, mercury and hexavalent chromium) in packaging which are not to be exceeded at different points in time, are: 600 ppm (July 1998); 250 ppm (July, 1999) and 100 ppm (July 2001). Exemptions are included in the Directive (e.g. packaging made entirely of lead crystal glass) and following COM decisions (for recycled

<sup>24</sup> Council Common Position (EC) No 62/98 adopted on 13 October 1998, O.J. of 14.12.98, C 388, p. 1 – 3.

material used in closed product loops and controlled chain i.e. plastic crates and pallets, and for glass packaging).

The Directive on 'End of Life Vehicles' (Dir. 2000/53/EC) aims at the prevention of waste from vehicles and at re-use, recycling and other forms of recovery of end-of life vehicles and their components so as to reduce the disposal of waste as well as at the improvement in the environmental performance of all economic operators involved and especially those directly involved in the treatment of end-of- life vehicles. Limitations of the use of hazardous substances in vehicles are encouraged and the use of heavy metals (lead, mercury, cadmium and hexavalent chromium) in materials and components of vehicles put on the market after July 2003 are prohibited, with exemptions (e.g. cadmium in batteries for electrical vehicles) foreseen in Annex II under the specified conditions (at least until 1 January 2003).

Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (EEE) requires the substitution of various heavy metals (incl. Cadmium) and other chemicals in new EEE put on the market from 1 July 2006. Exempted is Cd plating except for applications banned by Directive 76/769/EEC. The Directive 2002/95/EC should apply without prejudice to other Community legislation in particular the Batteries Directive (91/157). Directive 2002/96/EC on waste electrical and electronic equipment aims at the prevention of the waste of EEE (EEE: including large and small household appliances, IT and telecommunications equipment, tools, toys, medical devices, etc) by promoting re-use, recycling and other forms of recovery. The list of materials and components of WEEE that should be selectively treated (i.e. removed) mentions 'batteries'.

### 2.3.2 National legislation

Nordic countries have been even more comprehensive in regulating cadmium and its compounds resulting in a stricter legislation than that on community level (Nordiske Seminar- og Arbejdsrapporter, 1992). Since the early eighties the use of the substance in pigments, in stabilisers (and in plating) has been banned in Denmark (since 1983) and Sweden (since 1982). All Nordic countries have strictly regulated the content of the substance in fertilisers and in sewage sludge since 1992 at the latest. Regulations on batteries did exist years before the adoption at EEC level of a directive with similar objectives.

A non-exhaustive overview of the Danish legislation focusing in particular to issues related to the environment, is given as to exemplify the extent of regulation in Nordic countries (DEPA, Pers. comm.. 2001).

Table 2.44 Danish environmental legislation on cadmium (Danish EPA, Pers. com., 2001).

Regulation	Content
<a href="#">No. 223 of April 5, 1989</a> Statutory order from the Ministry of the Environment on the content of cadmium in phosphorus-containing fertilisers	The phosphorous fertilisers are regulated on the content in phosphorous containing fertilisers sets the maximum content of cadmium relative to phosphorus in fertilisers containing $\geq 1\%$ phosphorus be weight. The order does not cover manure, compost, sludge or other waste products they are added phosphorous manufactured from raw phosphate.  After 01.07.1998 the maximum content of cadmium in phosphorous fertilisers are 100 mg Cd/kg P.

Table 2.44 continued overleaf

Table 2.44 continued Danish environmental legislation on cadmium (Danish EPA, Pers. com., 2001)

Regulation	Content
<p><a href="#">No. 1199 of December 23, 1992</a> Statutory order from the Ministry of Environment and Energy on the prohibition of sale, import and manufacture of cadmium-containing products</p>	<p>Importation, sale and manufacture of cadmium-containing products are prohibited.</p> <p>For the purpose of this Order cadmium-containing products means products in which cadmium is used either as surface treatment agent (cadmium plating), colour pigment or plastic stabiliser with more than 75 ppm in the homogeneous components of the product.</p> <p>Irrespective of the prohibition in subsection 1 above, manufacture, importation and sale of cadmium-containing products are permitted for the purposes specified in the Annex to this Order, within the stated deadlines.</p>
<p><a href="#">No. 93 of February 22, 1996</a> Statutory order from the Ministry of Environment and Energy on collection of hermetically sealed nickel-cadmium accumulators (closed nickel-cadmium batteries) and remuneration for collection and disposal for recycling</p>	<p>Remuneration may be paid for environmentally sound collection and disposal for recycling of hermetically sealed nickel-cadmium accumulators (closed nickel-cadmium batteries).</p> <p>Remuneration may be paid to private persons and public enterprises, associations, municipalities etc. collecting and delivering or being in charge of delivery of closed nickel-cadmium batteries for recycling.</p> <p>In this Statutory Order recycling means recovery of the cadmium and possibly the nickel content of closed nickel-cadmium batteries.</p>
<p><a href="#">No. 130 of February 10, 1997</a> Statutory order from the Ministry of Environment and Energy on provision of information by export of certain used production plants</p>	<p>This Order lays down rules on the duty to provide information on export of used production plants from heavily polluting enterprises (listed activ-ties - including wastewater containing cadmium), including non-complete plants, located in Denmark.</p> <p>The rules apply to categories of production plants which have been installed in the types of enterprises listed in Annex IA, and which meet one or more of the criteria listed in Annex IB.</p> <p>The duty to provide information applies no matter whether the used plant is exported for the purpose of final mounting and operation in the receiving country, or with a view to resale only.</p> <p>The disposer of a plant listed in Annexes IA and B of this Order shall notify the supervision authority of agreements made for export of the plant. Notification may take place before the final agreement is concluded, when the question of importing country and receiving party is decided.</p>

Table 2.44 continued overleaf

Table 2.44 continued Danish environmental legislation on cadmium (Danish EPA, Pers. com., 2001)

Regulation	Content
<p><a href="#">No. 298 of April 30, 1997</a> Statutory order from the Ministry of Environment and Energy on certain requirements for packaging</p>	<p>This Statutory Order lays down provisions for essential requirements for the manufacture, composition, and utilisation of packaging, as well as limit values for the content of heavy metals (including cadmium) in packaging.</p> <p>The provisions of the Statutory Order apply to all packaging, including packaging containing products. Roads, railways, ships, and airfreight containers are outside the scope of this Statutory Order.</p> <p>This Statutory Order shall apply without prejudice to existing quality requirements for packaging, including requirements for health, protection of health and hygiene for the packed products, or existing requirements for the transport of hazardous goods.</p> <p>Between 30 June 1999 and 30 June 2001, packaging and packaging components may only be placed on the market in Denmark provided the sum of concentration levels of lead, cadmium, mercury, and hexavalent chromium does not exceed 250 ppm by weight.</p> <p>After 30 June 2001 packaging and packaging components may only be placed on the market in Denmark provided the sum of concentration levels of lead, cadmium, mercury, and hexavalent chromium does not exceed 100 ppm by weight.</p>
<p><a href="#">Statutory order no. 1065 of November 30, 2000</a> Statutory order from the Ministry of Environment and Energy on classification, packaging, labelling, sale and storage of chemical substances and products.</p>	<p>This Order applies to chemical substances and products.</p> <p>Chemical substances means chemical elements and their compounds in the natural state or obtained by any production process, including any additive necessary to preserve the stability of the substance and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition.</p> <p>Dangerous chemical substances and products shall be classified in one or more of the following danger categories: explosive, oxidising, extremely flammable, highly flammable, flammable, very toxic, toxic, harmful, corrosive, irritant, sensitising, carcinogenic, mutagenic and toxic to reproduction as well as (for substances only) dangerous for the environment.</p> <p>Dangerous chemical substances and products shall be assigned danger symbols and indications of danger risk indications (R-phrases), and safety advices (S-phrases).</p>
<p><a href="#">No. 594 of June 6, 2000</a> Statutory order from the Ministry of Environment and Energy on cosmetic products</p>	<p>This Order shall apply to cosmetic products, which are marketed and to substances used in such products.</p> <p>According to this order cadmium and its substances may not be used in cosmetic products.</p>
<p><a href="#">No. 1044 of December 16, 1999</a> Statutory order from the Ministry of Environment and Energy on certain batteries and accumulators containing dangerous substances</p>	<p>Import and sale of batteries and accumulators containing:</p> <p>more than 0.025% cadmium by weight, shall not take place unless the battery or accumulator is marked with one of the symbols indicated in Annex I to this Order, with a view to separate collection and subsequent recovery or disposal.</p>

Table 2.44 continued overleaf

Table 2.44 continued Danish environmental legislation on cadmium (Danish EPA, Pers. com., 2001)

Regulation	Content
<u>No. 1042 of December 17, 1997</u> Statutory order from the Ministry of Environment and Energy on regulation of sale and usage of some dangerous chemicals and products to some specific purposes	Use of cadmium in paints and varnishes is forbidden. Use of cadmium in foodstuffs and stimulants is not allowed The cadmium content in glazing and decorative paintings is not allowed to be more than 0,002 percent.
<u>No. 733 of July 31, 2000</u> Statutory order from the Ministry of Environment and Energy on the list of dangerous substances.	Classification of dangerous substances including cadmium compounds.

## 2.4 VOLUNTARY CONTROL MEASURES

On the Swedish food market, voluntary cadmium-limits are already imposed on products through initiatives taken by producer associations as well as retailing companies. These limits, which are stricter than the legally imposed criteria, have been set as a response to the perceived consumer demands. Also the tax on cadmium reduces the profitable level of cadmium in phosphorus fertiliser substantially below the allowed limit.

As an example, the co-operatives supplying the farmer with fertilisers, the Swedish Farmers Regional Selling and Purchaser Associations (sw: Lantmännen) have introduced its own limit value for soil, 0.30 mg/kg, for its most important trademark. If the top soil of a single field contains more Cd, the farmer may proceed to the second step, which consists of an analysis of the cadmium content in the wheat grains. If this level is below 0,100 mg Cd/kg, the crop can be sold under the trademark, otherwise not (KEMI, 2000, as derived from Drake and Hellstrand, 1998, The economics of the Swedish Policy to Reduce cadmium in Fertilisers, Kemi PM 2/98).

The voluntary commitment of the European PVC Industry aimed – amongst other targets – to phase out the use of cadmium in all stabilisers systems placed on the EU market (i.e. by ESPA members). This target was achieved in March 2002 (Vinyl 2010, The Voluntary Commitment of the PVC Industry, Progress Report 2002).

## 2.5 OTHER SUPRANATIONAL INSTRUMENTS

Cadmium is included in several international declarations and programmes on reduction of micropollutants.

The OECD started in 1990 a Risk Management Programme on five chemicals, one of them cadmium, for which Risk Reduction Monographs were published. The OECD programme on Cadmium actually recommends collection and recycling of Ni-Cd batteries as a means of reducing risk.

Cadmium falls under the UN-ECE-LRTAP Protocol for Heavy Metals, the aim of which is the reduction of heavy metal emissions due to human activity (at stationary sources) and with the potential of causing harmful affects at long distance from the source via transport trough the atmosphere.

The WHO air quality guideline value for cadmium is 5 ng/m<sup>3</sup> (this value was established to prevent any further increase of cadmium in agricultural soils that could increase the dietary

intake of future generation, given that no reliable unit risk could be derived to estimate the excess lifetime risk for lung cancer in the general population).

In 1998, the Ministerial Meeting of the OSPAR Commission in Sintra identified Cadmium (among other substances) as a substance for priority action under its Hazardous Substances Strategy. A Background document on Cadmium was prepared and adopted in 2002.

Several PARCOM Recommendations have been adopted related to the substance i.e. Rec. 92/3 concerning New secondary steel production and rolling mills, and Rec. 92/4 relating Electroplating industry. Cadmium is one of the substances that should be substituted in the latter field of uses.

The Rhine Commission has adopted a Ministerial declaration on heavy metals (with cadmium included) that have to be banned.

In 1998, the Helsinki Commission (HELCOM) Recommendation 19/5 was adopted including cadmium on the list of substances for priority action.

Cadmium also appears on the list of candidate-substances to include in the next extension of the monitoring programme of the International Commission for Protection of the river Scheldt.

The substance is also identified within the North Sea Conference framework (1990), and is one of the substances that 'cause a major threat to the marine environment' for which 'reductions between 1985 and 1995 of all inputs of the order of 70% or more - provided that the use of BAT or other low waste technology measures enable such reductions' - should be achieved. Atmospheric emissions by 1995, or by 1999 at the latest, should be significantly reduced (by 50% or more). Within that framework, harmonised quantification and reporting procedures for chemicals were developed. One of these procedures concerns Cadmium.

## **3 ENVIRONMENT**

### **3.1 ENVIRONMENTAL EXPOSURE**

#### **3.1.1 Methods and definitions: added Cd, natural background and ambient concentrations**

The environmental exposure to Cd is calculated based on all known current anthropogenic emissions of Cd, i.e. Cd that is emitted by the Cd/CdO producers and processors and Cd in diffuse sources such as fertilisers, steel production, traffic, waste incineration, landfills etc. Local exposure assessment is based on emissions from Cd/CdO producers and processors. Regional and continental exposure assessment is based on all anthropogenic Cd emissions, including diffuse emissions. Actual Cd concentrations in the environment (ambient concentrations) are furthermore determined by the natural background of Cd (from geological origin or from natural processes) and Cd that was added to the environment in the past by man (historical pollution).

The natural Cd and Cd from historical pollution determine the background Cd concentrations in the environment. The predicted environmental concentrations (PEC's) are based on predicted added (anthropogenic) concentrations plus the background concentrations. The background Cd in surface water and air is assumed to be the natural background. The residence time of Cd in these two compartments is less than one year (see Section 3.1.3.4.1) and historical pollution should, therefore, not affect actual Cd concentrations. Background Cd in air originates from natural processes such as volcanic eruptions, bush fires etc. and, therefore, these diffuse Cd sources are not included in the anthropogenic emission inventory. Background Cd in surface water originates from runoff, leaching and atmospheric deposition of Cd from natural origin. Again, none of these processes are included in the anthropogenic emission inventory. Runoff and leaching of Cd added by man are, however, included in the anthropogenic emissions to water. The natural background in surface water and air is estimated in Section 3.1.3.4.3 and is added to the continental anthropogenic Cd concentrations, yielding the PEC<sub>continental</sub>. This PEC<sub>continental</sub> is then used in the PEC<sub>regional</sub> and PEC<sub>local</sub> according to standard procedures of the TGD. The approach is different for soils and sediments where the residence time of Cd is at least several decades (see Section 3.1.3.4.1). The historical Cd emissions by man affect ambient Cd concentrations in soils and sediments, even far away from point sources such as smelters (see Section 3.1.3.4.3 and the human health part of this Risk Assessment Report, in separate document). Therefore, the actual background of Cd in soils and sediments exceeds the natural background. Background Cd concentrations in soils and sediments are estimated from the ambient Cd concentrations in areas away from point sources (see Section 3.1.3.4.3). That background Cd is added to the predicted added anthropogenic Cd concentration, yielding the PEC<sub>continental</sub> which, in turn, is used for the PEC<sub>regional</sub> and PEC<sub>local</sub>.

The standard TGD procedure to calculate the PEC<sub>regional</sub> in soil appears not adequate for various reasons (see Section 3.1.3.4.1 and 3.1.3.4.2). Because soil Cd is an important compartment in Cd risk assessment, an alternative model for the TGD protocol was developed (see Section 3.1.3.4.2). This model predicts future trends in soil Cd based with a more detailed Cd input/output balance than the TGD model.

The metallic Cd and the CdO powder are less harmful in the environment than soluble Cd<sup>2+</sup>. However, the metallic Cd and the CdO powder transform in the environment to the toxic Cd<sup>2+</sup>. Details on the extent of transformation in water and in soil are given in Section 3.1.3, 3.2.1.1.2

and 3.2.2.1.2 of this report. The source of Cd (from the Cd/CdO producers and processors, from the diffuse sources or from the background) is not taken into account in the environmental risk assessment. Releases to the aquatic compartment by the producers and processors are often based on measurements in effluents after the sewage treatment plant (STP). Most Cd/CdO particles are retained in the STP and the Cd in the effluent is mainly present as dissolved Cd. Atmospheric losses are deposited onto soil where the metal or metal-oxide readily transforms to a species with the same fate as soluble Cd<sup>2+</sup> (see Section 3.2.2.1.2). Arguments for similar bioavailability of soil background Cd and recently added Cd are given in human health part of this Risk Assessment Report (see separate document) where soil-plant transfer of Cd is discussed.

No attempt was made to express environmental Cd concentrations as bioavailable concentrations, with the exception of Cd concentrations in water where only the dissolved fraction is considered. The bioavailability of Cd is known to vary with properties of the compartment (see Section 3.2). Unfortunately, there are no standard procedures to correct for that variance. This variance is however accounted for in the effect assessment where PNEC values are calculated as a function of properties of the compartment. Predicted total concentrations are then compared with the properties specific PNEC's for risk characterisation.

### **3.1.2 Environmental releases**

#### **3.1.2.1 Releases during production and use (excluding batteries' related scenarios)**

##### **3.1.2.1.1 Source of data**

In this section, input of cadmium into the environment of the EU is calculated. Major anthropogenic sources of cadmium into the environment are associated with Cd-production and -processing, with iron and steel production, with cement manufacturing, with combustion of fossil fuels, with the use and disposal of Cd containing products and with the use of Cd containing fertilisers.

Emissions from the Cd and CdO producing industry are based on plant information submitted by the Cd-producing industries of the EU and Norway (further denoted as EU-16). These emissions are annual averages. This information was collated from a questionnaire submitted in 1997 to all Cd and CdO producing plants in EU-16. Data of two plants that are dedicated Cd recycling plants also provided emission data. Information on Cd losses associated with processing of Cd in pigments and in stabilisers is based on detailed data reported by WS Atkins (1998). The data are those for 1996. In Corden et al. (2001) some more recent data are available. Information on Cd losses at EU-level from plating processes is also based on the WS Atkins report. More general information is provided by the IPPC report on the surface treatment of metals (2004). This reports indicates that in this sector process waters are often treated on-site and then discharged usually to municipal (urban) waste water (sewage) treatment plants, or if the effluent is treated to a suitable standard (i.e. in compliance with the national/regional limit values for the discharge of waste water: for the metal treatment sector: in general the regulatory limit value (in total Cd) varies between 0.2 mg L<sup>-1</sup> and 0.6 mg L<sup>-1</sup> although lower limits are provided by law for some areas), directly to surface waters.

No accurate information on Cd emissions during processing of Cd in alloys was found. Estimated total EU emission data from processing of Cd in alloys reported by ERL (1990) and ICdA (1998) were used for the atmospheric compartment. Calculation of local PEC's from processing of Cd in plating and alloys was done by treating the emission at EU-level as point sources and by using standard values (see Section 3.1.2.3). No emission data to the aquatic compartment were available for Cd alloy processing sites. The default emission factor to water (A-table) is 0.5 and which is a large value compared to all other emission factors (see **Table 3.1**). Therefore, emission factor for alloy production was selected based on data obtained for the Cd plating sites (2360 g t<sup>-1</sup> processed). This value is 30-fold larger than the worst-case scenario proposed for Zn alloy processing sites (80 g Zn t<sup>-1</sup>) in the Zn RAR (2004).

The Cd emission during use and disposal of Cd containing products and from other sources such as iron and steel production, cement manufacturing, municipal waste incineration, fuel combustion and use of Cd containing fertilisers are calculated in two ways. The first way is based on calculations according to the TGD (1996) with Cd emission data at the EU-level (including Norway) (see Section 3.1.3.4.1). The second approach consists of alternative calculations, only made for agricultural soils for which measured (or estimated) emissions are collated for different European countries (see Section 3.1.3.4.2). Sewage sludge application as a source of Cd is included in the diffuse source inventory described in that section. Country average fluxes are used in this assessment and not the fluxes in the restricted number of soils where sludge is applied. Sewage sludge is a minor source of Cd for soils on an average basis; however it is a major source of Cd in soils where sludge is applied. This RAR does not assess the risks of Cd on these soils where sludge is applied. Sludge borne Cd has a different fate and effect than Cd added through fertiliser or atmospheric emissions. The lower bioavailability of sludge born metals soil is conserved on the long-term, even if most of the sludge organic carbon has decayed (Brown et al., 1998 and references therein). Therefore, the assessment of effects and the transfer to the food-chain are different between sewage sludge treated soils and soils enriched by inorganic Cd sources. The Cd fluxes through sludge vary widely and depend on local restrictions on the use of sludge in agriculture. Legislation in EU-16 countries is either based on maximal Cd concentrations in sludge (i.e. 1.2-10 mg Cd/kg) or maximum Cd fluxes (e.g. 3-15 g ha<sup>-1</sup>y<sup>-1</sup>). Some countries restrict a cumulative load (OECD, 1994). Total Cd input from sludge in the EU-16 is estimated to be at least 11.6 tonnes y<sup>-1</sup> (see **Table 3.156**).

There are no specific use scenarios described in this RAR. The main use of Cd/CdO is in NiCd batteries and emissions during the whole life-cycle (incl. disposal) are described in the TRAR/batteries' related (sub)sections. Current worst case Cd disposal scenarios are predicted to increase Cd emission to the environment in the future and the effect of the predicted future emissions on the PEC's are described in Section 3.1.3.4 as an illustration. In the present document, the risk characterisation is made using actual Cd emission.

The Cd emission, from Cd/CdO production and processing industry are presented in **Table 3.1** and **Table 3.2**. The total EU-16-emission to the aquatic environment from Cd/CdO -producing and -processing plants in 1996 is 1,504 kg y<sup>-1</sup> with 81% originating from the Cd producing industry. In general, industrial effluents are treated in a sewage treatment plant (STP) before being discharged into surface waters. Unless mentioned in the table, all data refer to concentrations measured after the STP. Five of the Cd producing plants emit their effluents to the sea or a bay. These plants (which are indicated in italics in the corresponding tables) emit 497 kg Cd y<sup>-1</sup> or 33% of the total amount emitted to the aquatic environment. Plant number 9 produces only minor amounts of Cd. Its Cd-emission is mainly due to the production of Zn.

The total EU-16-emission to the atmospheric compartment in 1996 from Cd-producing and processing plants is 4,646 kg y<sup>-1</sup> with 83% originating from Cd producing plants.

There are no direct local emissions to the soil compartment (i.e. local disposal) originating from Cd- and CdO-producing plants. Wastes from production are recycled or disposed off to controlled industrial landfill sites (IZA-Europe, pers. communication). No such information is available for the Cd processors. However, much of the waste produced (e.g. sludge) from process activities is likely to be classified as hazardous (for the surface treatment of metals, see IPPC, 2004; EU legislation in: EC, 1991; EC, 2000) and therefore excluded from the use in agricultural soil practices.

Emissions during the conversion of Cd to CdO are very low. According to the emission data from two CdO-producing plants in Belgium, there are no emissions to water as the production of CdO from Cd is a dry process. Water -mainly cleaning water- containing Cd and CdO is recycled. Emissions to air are very low -2.16 kg y<sup>-1</sup>- due to installation of air filters. Cadmium and CdO retained in the filters are recycled as is the waste containing Cd and CdO. During a monitoring program of a CdO-producing plant, Cd concentrations were measured in the ambient air at 150 to 200 m from the emission point. An average value of 7.6 ng Cd m<sup>-3</sup> was recorded (Industry Questionnaire, 1997). However, at the same site, Zn-chemicals are produced, another emission source of Cd to the environment. The emission data represent losses from both production processes together and it is not possible to distinguish which part is due to the production of CdO. The same comments apply to the other CdO-producing plant where besides CdO also Cd-powder is produced.

It needs to be mentioned that during the last years (in particular since 2001) a significant number of Cd metal producers stopped the cadmium production (some with, others without stopping the refining of the primary metal zinc/copper/lead). The same occurred in the area of CdO production (see Section 2.1.2.1 and see Section 2.1.2.2).

A very recent update provided by Industry (ICdA, com., 2003) reveals that from the initial list of cadmium production plants in Europe (drawn in 1997 on the basis of data from 1996) to date only three, possibly four remained active in the field of cadmium production. However, further details (i.e. on current production, import, export and exposure data) were not submitted for more recent years.

Table 3.1 Aquatic emissions from Cd-producing and -processing plants in the EU-16

Use-Category	Plant N°	Production/ consumption volume	Production emission <sup>fl</sup>	Processing emission <sup>fl</sup>	Emission factor	Conc. in effluent <sup>(c)</sup>	Number of production days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Flow receiving water <sup>(a)</sup>	Year
		tonnes y <sup>-1</sup>	kg y <sup>-1</sup>	kg y <sup>-1</sup>	g tonnes <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	
Cd-producers <sup>(e)</sup>	1	683	23.9 <sup>(g)</sup>		35	M (T)	365	0.045	1,440	16,000	1996
	2	510	614		1,204	M (T)	365	0.44	3,823	1,204,245	1996
	3*	596	15.7		91	M (D)	70	0.01	7,476	-*	1996
	4*	14.7	21.6 <sup>(g)</sup>		1,469	M (D)	15	0.12	4,000	-*	1996
	5	208	77.8 <sup>(f)</sup>		374	M (D)	243	0.16	2,000 <sup>(b)</sup>	18,000 <sup>(d)</sup>	1996
	6	262	0.18 <sup>(g)</sup>		0.69	M (T)	105	0.00068	1,320	39 10 <sup>6</sup> <sup>(h)</sup>	1996
	7 <sup>cl</sup>	274	70		255	M (T)	365	0.06	3,196	-*	1998
	8	378	11		19	M (T)	151	0.03	1821	1,700,000 <sup>(h)</sup>	1996
	9*	0.696	29.4 <sup>(g)</sup>		42,241	M (T)	365	0.0058	13,820	-*	1999
	10	1,579	0		0	(1)	316	(1)	(1)	(1)	1996
	11	32	0		0	(2)	32	(2)	(2)	(2)	1996
	13*	307	372		1,212	M (D)	123	0.17	17,790	-*	1996
	CdO-producers	11	1,256		0	0	(2)	251	(2)	(2)	(2)
12		1,280		0	0	(2)	256	(2)	(2)	(2)	1993
Cd-stabilisers	F			0.03		M(T)	20	0.001	1,490	725,760	1996
	G			0.5		M(T)	48	0.013	749	18,000 <sup>(d)</sup>	1996
	H			0.78		M(T)	60	0.008	2571	259,200	1996
	I			0.1		E(T)	13	0.0004 <sup>(3)</sup>	2,000 <sup>(b)</sup>	18,000 <sup>(d)</sup>	1996

Table 3.1 continued overleaf

Table 3.1 continued Aquatic emissions from Cd-producing and -processing plants in the EU-16

Use-Category	Plant N°	Production/ consumption volume	Production emission <sup>†</sup>	Processing emission <sup>†</sup>	Emission factor	Conc. in effluent	Number of production days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Flow receiving water <sup>(a)</sup>	Year
		tonnes y <sup>-1</sup>	kg y <sup>-1</sup>	kg y <sup>-1</sup>	g tonnes <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	
Cd-stabilisers	J			0		M(T)	13	0	0	0	1996
	K			4.1		E(T)	12	0.017 <sup>(3)</sup>	2,000 <sup>(b)</sup>	18,000 <sup>(d)</sup>	1996
	L			0		M(T)	155	0	0	0	1996
	M			0		M(T)	155	0	0	0	1996
	window manufacturer			0		M(T)	350	0	0	0	1996
Cd-pigments	A	237		0.6	3	M(T)	230	0.02	131	6,000	1996
	B	82.5		4.02	49	M(T)	231	0.002	5,112	504,5760	1996
	C	186		5.9	32	M(T)	276	0.08	200	135,000	1996
	D	283		0.9	3	M(T)	230	0.022	130	32,739	1996
	E	66		13.4	203	M(T)	85	0.044	3,618	89,856,000 <sup>(h)</sup>	1996
Cd-plating	EU	106		250	2360	E (T)	155	0.081	2,000 <sup>(b)</sup>	18,000 <sup>(d)</sup>	1996
Cd-alloys	EU	26		61.3	2360	E (T)	62	0.05	2,000 <sup>(b)</sup>	18,000 <sup>(d)</sup>	1996

n.a. Not available;

\* Emission to the sea;

<sup>†</sup> Annual averages;

(1) No water emissions: waste waters are recycled;

(2) No water emission: dry process;

(3) Value based on 90% elimination in sewer;

(a) Mean annual; (b) default value: 2,000 m<sup>3</sup> d<sup>-1</sup>;

M Measured value,

E Estimated value,

D Dissolved concentration,

T Total concentration;

(d) Default value: 18,000 m<sup>3</sup> d<sup>-1</sup>;

(e) Emissions included these from Cd recycling;

(f) Emission of Cd from Pb and Zn production; no waste water related to Cd-production;

(g) Emission of Cd from Zn or Zn and Pb production;

(h) Emission to big river;

<sup>‡</sup> Emission data are reported to have decreased in more recent years to average concentration of 0.038 mgCd/L in effluent water for the year 2003 (Industry/company information, 2004)

Table 3.2 Atmospheric emission from Cd-producing and -processing plants in the EU-16

Use-Category	Plant N°	Production/consumption Volume	Production Emission amount <sup>†</sup>	Processing Emission amount <sup>†</sup>	Emission Factor	Year
		tonnes y <sup>-1</sup>	kg y <sup>-1</sup>	kg y <sup>-1</sup>	g tonnes <sup>-1</sup>	
Cd-production	1	683	54 <sup>(b)</sup>		80	1996
	2	510	1,683 <sup>(b) (e)</sup>		3,300	1996
	3	596	800 <sup>(b)</sup>		4,598	1996
	4	14.7 <sup>(d)</sup>	3.03		206	1996
	5	208	946 <sup>(b)</sup>		4,548	1996
	6	262	6.24 <sup>(b)</sup>		23.8	1996
	7	274	200 <sup>(b)</sup>		730	1996
	8	378	28.6		76	1996
	9	648	110		170	1996
	10	1579	3.32		2.1	1996
	11	32.2	1.61		50	1996
	13	307	24.6 <sup>(a)</sup>		80	1996
	CdO-producers	11	1,256		0.30	0.24
12		1,280		0.31 <sup>(c)</sup>	0.24	1996
Cd-stabilisers	F			0.09	n.a.	1996
	G			0.8	n.a.	1996
	H			0.5	n.a.	1996
	I			0.1	n.a.	1996
	J			0.7	n.a.	1996
	K			0.04	n.a.	1996
	L			n.a.	n.a.	1996
	M			0	n.a.	1996
	Window manufacturer				n.a.	n.a.
Cd-pigments	A	237		1.15	4.9	1996
	B	82.5		2.37	29	1996
	C	186		3.6	19	1996
	D	283		5.8	21	1996
	E	66		0.2	3.0	1996

Table 3.2 continued overleaf

Table 3.2 continued Atmospheric emission from Cd-producing and -processing plants in the EU-16

Use- Category	Plant N°	Production/consumption	Production	Processing	Emission	Year
		Volume	Emission amount†	Emission amount†	Factor	
		tonnes y-1	kg y-1	kg y-1	g tonnes-1	
Cd-plating	EU			0	n.a.	1996
Cd-alloys	EU			770	n.a.	1996

n.a Not available

† Annual averages

(a) Estimated from a typical emission factor

(b) Cd emission from whole plant (including Zn and/or Pb production)

(c) 1996 value extrapolated from 1993 emission factor

(d) Production volume in 1991

(e) Pyrometallurgical processes

Previous estimates of total Cd inputs to the EU environment from Cd producing- and processing plants (Hutton, 1982; Jensen and Bro-Rasmussen, 1992; OECD, 1994 and EUPHEMET, 2000) are much higher than those given in the current RAR (see **Table 3.3**).

Table 3.3 Total, direct emissions in the EU (tonnes y<sup>-1</sup>). A comparison of different studies

	To Air (tonnes y <sup>-1</sup> /tonnes y <sup>-1</sup> )		To Water (tonnes y <sup>-1</sup> /tonnes y <sup>-1</sup> )	
	Cd-producing plants	Cd-processing plants	Cd-producing plants	Cd-processing plants
Hutton, 1982	19.5	8.8	50	107
Jensen and Bro-Rasmussen, 1992	22.8	12.2	17.3	45
OECD, 1994	/	4.05	/	1.6
EUPHEMET, 2000	< 15	~ 15	~ 15	< 3
RAR-Cd, 2002 <sup>(1)</sup>	3.9	0.8	1.2	0.3

<sup>(1)</sup> Data from the EU and Norway

Data in the Hutton report are based on estimated emission data and emission factors of the end of 1970's. Data in the report of Jensen and Bro-Rasmussen (1992) are based on the ERL-study (1990) which, in turn, is based on estimated emission data and emission factors of the end of 1980s. The emission results reported in the OECD report (1994) are based on the same production data but emission factors were adapted with some more recent estimates. The assessments of EUPHEMET (2000) are based on previous generic calculations and reported results based on production data, as well as on the conclusions of a previous version of this report (RAR CdO, 1999). The RAR Cd/CdO (2002) data are based on actual production and measured emission data of the mid 1990's, and therefore, at the moment, closer to reality than the EUPHEMET (2000) report.

The comparison in **Table 3.3** indicates a general decrease in the Cd emission from the Cd-producing and processing industry. Since the end of the 1970's emissions to air decreased more than 80%, while emission to water decreased more than 97%. This trend, based on measured data, confirms earlier performed estimates. Elgersma et al. (1992) studied the change in

the industrial Cd discharge to the River Rhine basin from 1970 to 1988. Emissions from primary Zn winning decreased from 2 tonnes  $y^{-1}$  in 1970 to 0.05 tonnes  $y^{-1}$  in 1988. The trend was the consequence of increasing regulatory pressure on Cd emitting industry and the consequent implementation of wastewater treatment plants in the seventies. The North Sea Conference report (1995) mentions a decrease in the Cd emission to water of about 50% over the period 1985-1995.

In Belgium a small decrease in Cd emission to water from non-ferrous-metal industry from 0.5 tonnes  $y^{-1}$  in 1980 to 0.4 tonnes  $y^{-1}$  in 1995 was recorded and further estimated to 0.2 tonnes in 2000 (BMM, 1997 and 2001). In Germany a decrease was calculated from 0.5 tonne/ $y^{-1}$  in 1990 to 0.2 tonnes  $y^{-1}$  in 1994 for the same sector (Barbier, 1996). Pacyna et al. (1991) estimated a 60% decrease of Cd emission to air in Europe between 1975 and 1982. The North Sea Conference report (1995) mentions a decrease in the Cd emission to air in EU between 50% and 70% over the period 1985-1995. In Belgium, Cd emission to air from non-ferrous-metal industry decreased from 6.9 tonnes  $y^{-1}$  in 1980 to 2.1 tonnes  $y^{-1}$  in 1995 and a further reduction to 0.36 tonnes  $y^{-1}$  for 2000 is estimated (VMM, 1997; BMM, 2001). Cadmium emission to air from the German non-ferrous-metal industry decreased from 1.1 tonnes  $y^{-1}$  in 1990 to 0.9 tonnes  $y^{-1}$  in 1994 (Barbier, 1996).

This general decreasing trend is also reflected in the measured Cd-levels in air and water (see Section 3.1.3.4 and the human health part of this Risk Assessment Report (in separate document). Recent trends of Cd in air, water and sediments are given in **Annex J**. The reductions are most likely the result from increasing environmental regulations in the EU, which prompted the implementation of technologies abating Cd losses.

### **3.1.2.1.2 Emission reduction during production and use**

Various types of measures and initiatives on national and international level are being taken to reduce Cd emissions from the Cd producing- and processing industries to the environment.

#### Emission reduction during production

##### *Water*

Wastewater treatment at Cd-producing and -processing plants involves filtration and precipitation. Liquid effluents from the different stages during production and processing of Cd are collected and treated with sodium carbonate at alkaline pH to precipitate Cd. Filtration aids and flocculating agents are added. The sludge is then filtered from the solution. The filtrate is neutralised prior to discharge to the environment. At industrial non-ferrous metal producing sites and waste water treatment plants (WWTP) a cadmium removal efficiency of at least 90% is reported based on physico-chemical techniques only, to achieve total cadmium concentrations within the range 1 – 0.1 mg  $L^{-1}$  (IPPC report, 2000). EUSES calculations give a corroborating removal rate (WS Atkins, 1998 and RPA, 2001): the Simple Treat model run with the  $K_p$  value of 130,000 l/kg yields the following distribution in the waste water treatment plant: 90% in sludge and 10% in water.

However, for municipal STP in practice, the average removal efficiency can vary widely from > 80% (based on measurements of influent and effluent cadmium concentrations and the water

flows; VMM, pers. com. 2002) to 60% (CUWVO, 1986; in: CBS/Milieucompendium, 2000). The latter, lower figure will be used in this RAR.

### *Air*

The major categories of available control techniques for Cd emission abatement to air are primary measures such as raw material substitution and low-emission process technologies, and secondary measures such as fugitive emission control and off-gas cleaning. In the case of particle-bound emission of Cd, dust-cleaning devices are used such as fabric filters, dry and wet electrostatic precipitators and scrubbers. In the pyrometallurgical production process, furnaces can be provided with a double bell furnace top. The dust collected in the filters is recycled within the production process. When scrubbing is applied, Cd is removed as slurry after sedimentation in a settling tank. These slurries can be further processed or land-filled.

To reduce fugitive emissions from discharging, handling, and stockpiling of raw materials or by-products, these activities are removed to completely enclosed buildings, which may be equipped with ventilation and dust filters or spray systems.

### *Land*

Slugs and ashes formed during the melting process can be recycled when it contains sufficiently high Cd content. If the material meets the requirements of regulatory leaching tests, it may be used for road construction. All solid wastes from the production of NiCd batteries are recycled to recover the Cd and other metals.

Emissions of leachates of modern landfills are reduced to a minimum through the installation of containment, collection and attenuation practices. Basins are lined with plastic or impervious clay. Leachates are controlled and neutralised or recirculated. In order to minimise the quantities of residues to be land-filled, recycling and prevention campaigns of wastes are promoted by regulations.

### Emission reduction during use and end-of-life

Since the 1980's restrictions exist in several OECD-countries on the use of Cd in pigments, stabilisers and plating. This has led to a significant decrease of Cd consumption in these products.

#### **3.1.2.2 Releases due to batteries' related scenarios**

Releases to the environment have been estimated for different life cycles stages of Nickel-Cadmium batteries (see **Table 3.4**).

Table 3.4 Overview of the main life cycle stages of NiCd batteries<sup>25</sup>

Life cycle stages	Phase
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<sup>25</sup> The cadmium emissions during the production of battery raw materials have been covered by the Section 3.1.2.1 issuing from the previously separate overall RAR on Cd/CdO and are not repeated here.

1. Production/manufacturing of NiCd Batteries and/or Battery Packs	Production
2. Incorporation into Battery-Powered Devices and Applications (EEE) <sup>a b</sup>	
3. Use, Recharging and Maintenance by End Users <sup>a</sup>	Use/Useful life
4. Recycling Collection Sorting Processing Recovery	Waste-Management
5. Disposal Incineration Land-filling	

- a) Life cycle stage 2 and 3 are not deemed relevant for the RA of the substance under study  
b) Life cycle stage 2 is a facultative step not relevant for individual cells or batteries put on the market

### 3.1.2.2.1 Life cycle stage 1: Manufacturing of NiCd batteries and/or battery packs

The emissions to air and water from the NiCd battery manufacturers are presented in **Table 3.5** and **Table 3.6**. Site specific information on the local Waste Water Treatment Plant (i.e. quantity of sludge produced, Cd content, destination of sludge) is presented in **Table 3.7**. Information on waste -other than sludge- is given in **Table 3.8**. The data for 1999/2000 were obtained from Industry Questionnaire, 2000/2001.

It must be noted that plant 2 is a producer and recycler; since no distinction could be made between emissions from production/recycling, the company is listed with NiCd producing companies.

All plants except 1 (i.e. plant 2) release Cd to freshwater (surface water). Plant 2 emits to the marine environment. The total EU-emission to the aquatic environment from NiCd batteries producing plants in 1999/2000 is 62 kg year<sup>-1</sup>. Emission factors to surface water varying between 1.1 and 48 g tonne<sup>-1</sup> Cd used (average: 18.7 g tonne<sup>-1</sup> Cd used) are calculated. In comparison with emission data from 1996 (presented in Annex IV), very similar emission factors are obtained for water (1.6-145 g tonne<sup>-1</sup> Cd used and on average: 29.5 g tonne<sup>-1</sup> Cd used respectively). The large variation in emission factors cannot be explained by distinguishing between consumer/sealed portable batteries (plant 4 (partly)) and industrial batteries producers (other plants). On the basis of the information available on electrode production processes for the sites no conclusions can be formulated with regard to differences in emission factors due to different production processes (see **Table 3.5**).

The processing emission of plant 1 decreased substantially from 9.6 kg year<sup>-1</sup> (in 1996) to 2.1 kg year<sup>-1</sup> in 2000. In 1999 still 4.9 kg year<sup>-1</sup> was emitted. The reduction in cadmium emission is due to the implementation of a new treatment plant (fully operational mid 2001) and the changing in the production process (since January 2000, no further details available) and cleaning method (from wet to mainly dry cleaning).

In general industrial effluents from the plants are treated in an on-site Waste Water Treatment Plant (WWTP) before being discharged into surface waters unless mentioned otherwise. All data refer to concentrations measured after the WWTP. Plant 1 and plant 5 discharge after on-site treatment into the public sewer system. These discharges will undergo an extra dilution before entering the surface water. Plant 6 and 7 reports that the wastewater is collected separately and treated off-site (external recycling). Since no additional information concerning the Cd content of influents of the local treatment plant was provided by industry, the emissions to wastewater and sludge could not be specified. However, in the questionnaires, specific information was requested with regard to quantity, Cd content and destination of waste generated (including WWTP sludge). This information reveals that the total amount of sludge produced by the companies is 730 tonnes  $y^{-1}$  with an average Cd content varying between 1.7 and 12.5%. The total quantity of generated WWTP sludges is sent to recycling plants (see **Table 3.7**).

The total EU emission to the atmospheric compartment in 1999/2000 from NiCd batteries producing plants is 51 kg year<sup>-1</sup>. The calculated emission factors to air for the different plants are situated between 0.27 and 464 g tonne<sup>-1</sup> Cd used (on average: 23 g tonne<sup>-1</sup> Cd used). Data from 1996 (Annex II) showed higher emission factors between 1.16 and 901 g tonne<sup>-1</sup> Cd used (average: 31.45 g tonne<sup>-1</sup> Cd used). Reductions in air emissions can be explained by improvements in air treatment systems. On the basis of the information available no conclusions can be drawn with regard to differences in emission factors between industrial/ portable battery producing sites and different electrode production processes (see **Table 3.6**). No data regarding emissions to air could be provided for company 1 and 3. However, plant 3 stated that since it concerns wet processes, the Cd emissions are mainly through effluents. It should be noted that plant 7 -processing less than 5% of total Cd amount- emits 28.99 kg year<sup>-1</sup> to air, that corresponds with 57% of the total air emissions of all NiCd batteries manufacturing plants.

The total amount of waste –apart from on-site WWTP sludge- generated by the NiCd batteries producing industry is 2,353 tonne/year. It should be noted that this waste includes packaging material, NiCd batteries material (plates, cells, electrolytes), cakes and filters from off-site wastewater treatment. The majority (91.7%) of this waste is recycled; the other fraction (8.3%) is disposed in a landfill. 2,091 tonnes of this waste is sent to an external recycling plant, 66 tonnes is internally recycled.

In analogy with the Cd/CdO producing plants the receiving environmental compartments for the emissions of the NiCd batteries plants are water and air. The total amount of cadmium released to the environment during manufacturing of NiCd batteries in 1999/2000 is 116 kg year<sup>-1</sup>. The total use of cadmium for the production of batteries is 2,166 tonnes (based on individual plant data for 1999/2000).

Table 3.5 Aquatic emissions from NiCd batteries producing plants in the EU (UC 12: Conductive agents)

Plant N°	Battery type	Electrode production process	Consumption volume	Processing emission	Emission factor	Conc. in effluent <sup>b</sup>	Number of production days	Concentration in effluent	Effluent flow	Flow receiving water <sup>a</sup>	Year
			tonnes y <sup>-1</sup>	kg y <sup>-1</sup>	g tonne <sup>-1</sup>			mg L <sup>-1</sup>	m <sup>3</sup> day <sup>-1</sup>	m <sup>3</sup> day <sup>-1</sup>	
1	Industrial	Pocket plate	39.5	4.9	124	M (T)	225	0.43 (P90)	127 (P90)	External to municipal STP	1999
2 <sup>b</sup>	Industrial	Pocket plate - vented	395 (production only) (507) (total, inclusive recycling) (Cd from batteries: 85)	7.3	18.5	M (T)	330	0.12 (P90)	367 <sup>c</sup> (P90)	432,000	2000
3	Industrial	Sintered and PBE	635	30.5	48	M (T)	315	0.12 (P90)	960	13 10 <sup>6</sup>	2000
4	Portable	Sealed cylindrical shaped/ sintered and PBE	842	21.9	26	M (T)	330	0.13 (P90)	771 (P90)	5.4 10 <sup>5</sup>	2000
5	Industrial	Fiber and (Pocket plate: imported)	59.7	<0.07	<1.1	M (T)	230	< 0.03	5	External to municipal STP	2000
6 <sup>f</sup>	Industrial	Fiber plate	132.7	0 <sup>d</sup>	0 <sup>d</sup>	N/A	250	N/A	N/A	N/A	1999

Table 3.5 continued overleaf

Table 3.5 continued Aquatic emissions from NiCd batteries producing plants in the EU (UC 12: Conductive agents)

Plant N°	Battery type	Electrode production process	Consumption volume	Processing emission	Emission factor	Conc. in effluent <sup>b</sup>	Number of production days	Concentration in effluent	Effluent flow	Flow receiving water <sup>a</sup>	Year
			tonnes y <sup>-1</sup>	kg y <sup>-1</sup>	g tonne <sup>-1</sup>			mg L <sup>-1</sup>	m <sup>3</sup> day <sup>-1</sup>	m <sup>3</sup> day <sup>-1</sup>	
7 <sup>g</sup>	Industrial	Pocket plate - vented	62.5	0 <sup>e</sup>	0 <sup>e</sup>	N/A	300	N/A	N/A	N/A	1999
			Total amount of Cd used during production of batteries (tonnes y <sup>-1</sup> )	Total Cd emission to water (kg y <sup>-1</sup> )	Emission factor (g/ on Cd used)						
			2,166	65	31.1						

N/A Not applicable;

M Measured value;

T Total concentration;

a Minimum flow rate;

b Company 2 emits to the marine environment;

c If cadmium emissions via storm water are included the effluent flow increases to 424 m<sup>3</sup>;

fd All process wastewater is collected and sent to recycling company, no emissions to water;

g Emissions to water from cleaning operations are disposed in alkaline solution and externally recycled, no emissions to water; PBE: Plastic Bonded Electrode.

Table 3.6 Atmospheric emissions from NiCd batteries producing plants in the EU (UC 12: Conductive agents)

Plant	Battery	Electrode	Production/consumption	Processing	Emission	Year
N°	type	production process	volume	emission amount	factor	
			tonnes y <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
1	Industrial	Pocket plate	39.5	n.d. <sup>a</sup>	n.d. <sup>a</sup>	1999
2	Industrial	Pocket plate -vented	395 (production only) (507) (total, inclusive recycling) (Cd from batteries: 85)	1.6	4.1	2000
3	Industrial	Sintered and PBE	635	n.d. <sup>a</sup>	n.d. <sup>a</sup>	2000
4	Portable (emergency lighting)	Sealed cylindrical shaped/ sintered and PBE	842	13.5	16	2000
5	Industrial	(Pocket plate: imported) and fiber	59	7	119	1999
6	Industrial	Fiber plate	132.7	0.036	0.27	1999
7 <sup>a</sup>	Industrial	Pocket plate -vented	62.5	28.99	464	1999
			Total amount of Cd used during production of batteries (tonnes y <sup>-1</sup> )	Total Cd emission to air (kg year <sup>-1</sup> )	Emission factor (g tonne <sup>-1</sup> Cd used)	
			2,166	51	23	

a No data. However, it is noted that it concerns a wet process, so the emissions of Cd are mainly through effluents;

PBE Plastic Bonded Electrode;

It should be noted that plant 7 -processing less than 5% of total Cd amount- emits 28.99 kg year<sup>-1</sup> to air, that corresponds with 57% of the total air emissions of all NiCd batteries manufacturing plants.

Table 3.7 On-site Waste Water Treatment Plant (WWTP) and sludge information (UC 12: Conductive agents)

Plant N°	Type of WWTP	Efficiency (% removal)	Amount of sludge produced (t/y)	Cd Content (%)	Destination sludge	Year
1	Physico-chemical treatment	n.d.	17.5	2-4 (<30% water)	External recycling plant	1999
2 <sup>a</sup>	Flocculation and filtration facility	99.7%	128.7	2 (water content: 55%)	(On-site) recycling plant	2000
3	Flocculation, flottation, filtration	99.2%	244	1.7 (water content: 57%)	Landfilled	2000
4	Flocculation and filtration facility	99.9%	330	9.7 (water content: 50%)	External recycling plant	2000
5	Filtration	n.d.	10	n.d.	External recycling plant	1999
6 <sup>b</sup>	No emissions to water (recycled)	/	/	/	/	1999

Table 3.7 continued overleaf

Table 3.7 continued On-site Waste Water Treatment Plant (WWTP) and sludge information (UC 12: Conductive agents)

Plant N°	Type of WWTP	Efficiency (% removal)	Amount of sludge produced (t/y)	Cd Content (%)	Destination sludge	Year
7 <sup>c</sup>	No emissions to water (disposed of)	/	/	/	/	1999
			730.2/y			

a Producer and recycler;

b All process wastewater is collected and sent to recycling company;

c Emissions to water from cleaning operations are disposed in alkaline solution and externally recycled;

n.d. No data available.

Table 3.8 Waste information (UC 12: Conductive agents)

Plant N°	Type of waste produced	Quantity of waste (tonnes y <sup>-1</sup> )	Cd content	Waste disposal type	Year
1	Industrial battery cells	118.8	< 3% (overall average content)	External recycling plant (98 %) Landfill (2 %)	1999
	Raw material bags	0.4			
	Substituted filters	0.25			
	Cleaning materials and tools	0.5			
2 <sup>a</sup>	Barium sulphate	194	< 0.001%	Land-filled	2000
	Used filters <sup>b</sup>	66	< 0.1%	External recycling plant	
3	Scraps	380	17.4%	External recycling plant	2000
4	Plates (neg.)	46	50%	External recycling plant	2000
	Cells	181	11%		
5	Pocket plate	6.2	30-40%	External recycling plant	1999
	Dust	3.3	45%		
	Batteries	8.1	3-10%		
	Electrolyte	126.4	0.2%		
6	Used KOH from formation process	852	Trace conc	External recycling plant	1999
	Wastewater from impregnation	102	1 g/L	External recycling plant	
	Filter cake from wastewater formation process	7	20%	External recycling plant	
7	Electrode overlefts	52.66	n.d.	External recycling plant	1999
	Old alk. Sol.	208			

a Producer and recycler;

b After Cd and Ni dust removal (dust is on-site recycled);

n.d. No data available.

Since the manufacturing activities of NiCd batteries are restricted to a small number of sites in a limited number of EU countries (i.e. Sweden, France, Germany, Spain and Belgium<sup>26</sup>), and

<sup>26</sup> Belgian manufacturer has stopped manufacturing cells and shifted to assembly (of non-EU manufactured cells into packs) only since June 2001, Panasonic (former Philips), letter 30.09.02.

hence are not equally distributed over the EU territory, it is not possible to apply the 10% rule for estimation of the regional emissions. In that case it is recommended to use the EU volume as input for the region and to apply another percentage or to use specific values as input for the regional model (e.g. emissions from the largest emitter). In this case the emissions from the largest emitter to air and water were allocated to the region. (EC, 1998).

Table 3.9 Summary emissions from production of NiCd batteries (life cycle stage 1)

Compartment	Total	Regional	Continental
	kg year <sup>-1</sup>	kg year <sup>-1</sup>	kg year <sup>-1</sup>
Air	51	28.99	22.01
Wastewater	4.97	4.9	0.07
Surface water	60	30.5	29.5
Soil, urban/ind	0	0	0
Total	116	64.4	51.6

### 3.1.2.2.2 Life cycle stage 2: Incorporation into battery-powered devices and applications

No emissions of the substance under study are expected.

### 3.1.2.2.3 Life cycle stage 3: Use, recharging and maintenance by end user

No direct emissions of cadmium of the substances under study are expected from the use of batteries, except possibly in the cases of battery corrosion or destruction of the battery. The number of batteries affected in these ways is expected to be small. The indirect cadmium emissions (generation of electric power, e.g. combustion of coal) associated with recharging of batteries have not been considered in this report. Lankey (1998) estimated an average total energy consumption of  $286 \pm 222$  MJ/kg for the use phase (1,000 charge cycles over the life of the battery). These figures are deemed negligible in comparison with the overall energy consumption and related indirect cadmium emissions.

### 3.1.2.2.4 Life cycle stage 4: Recycling

The emissions to air and water during the recycling of batteries are presented in **Table 3.10** and **Table 3.11** (Industry Questionnaire, 2000/2001). From the questionnaires it is also clear that information concerning on-site wastewater treatment is lacking (plant 1). Information on waste quantities generated – other than on-site WWTP sludge-is presented in **Table 3.12**.

Plant 2 stated that there are no “open treatment steps” at their site. As a consequence they do not emit Cd to either compartment. The wastewater produced is collected and treated off-site. The sludge produced during this process is land-filled. One company that is both producer and recycler is reported as a NiCd producer (see Section 3.1.2.2.1), since a split up of emissions was not feasible.

The total Cd emission to the aquatic compartment from Cd recyclers in the EU is based on information from 1 plant only and is  $0.126 \text{ kg year}^{-1}$ . The accompanying emission factor for that plant is  $0.16 \text{ g tonne}^{-1}$  Cd recycled. In comparison with emission data from 1996 (presented in

Annex IV), a very similar emission factor of  $0.19 \text{ g tonne}^{-1}$  Cd recycled is obtained. No emission factor was calculated for recycling plant 2 since the on-site operating processes are zero emission processes. In general industrial effluents from the plants are treated in an on-site Waste Water Treatment Plant (WWTP) before being discharged into surface waters. However, plant 2 collects its wastewater for off-site treatment. Since no additional information concerning the Cd content of influents of the local treatment plant was provided by industry, the emissions to wastewater and sludge could not be specified.

The total EU emission to the atmospheric compartment in 1999/2000 from Cd recyclers producing plants is  $1.77 \text{ kg year}^{-1}$  (based on plant 1 only). The calculated emission factor to air for plant 1 is  $2.21 \text{ g tonne}^{-1}$  Cd recycled. Data from 1996 (Annex IV) showed a higher emission factor of  $9.7 \text{ g tonne}^{-1}$  Cd recycled. Reductions in air emissions can be explained by improvements in air treatment systems. No emission factor was calculated for recycling plant 2 since the operating processes are zero emission processes.

The total amount of waste –including the off-site treated wastewater from plant 2- generated by the Cd recycling industry is  $1,045 \text{ tonnes y}^{-1}$ . It should be noted that this waste solely includes Cd containing material. The majority of this waste is sent to an external recycling plant (66.3%) internally treated (8%) or sent to a specialised landfill (25.6%). Taking into account the Cd content of this waste, it can be concluded that in total  $< 907 \text{ kg Cd}$  is externally recycled,  $134 \text{ kg Cd}$  is internally treated and  $0.4 \text{ kg Cd}$  is land-filled.

The overall Cd emission to the environment is only  $1.9 \text{ kg year}^{-1}$ . 93% of this emission is directed to air. Since  $842,300 \text{ kg year}^{-1}$  is produced by the Cd recycling plants a very low total emission factor of 0.0002% can be calculated.

Table 3.10 Aquatic emissions from Cd recycling plants in the EU (Cd recycled from batteries, production scrap and other sources)

Plant N°	Production/ Consumption volume	Processing emission	Emission factor	Conc. in effluent <sup>b</sup>	Number of production days	Concentration in effluent	Effluent flow	Flow receiving water	Year
	tonnes y <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>			mg L <sup>-1</sup>	m <sup>3</sup> day <sup>-1</sup>	m <sup>3</sup> day <sup>-1</sup>	
1 <sup>a</sup>	800.5 (376.8 batteries: 47.1%)	0.126	0.16	M(T)	350	0.45 (P90) Average: 0.17	6.1 (P90) Average: 3.8	11,500	2000
2	41.8 (37.6 batteries :89.9%)	0 <sup>c</sup>	0	N/A	240	N/A	N/A	N/A	1999
<b>TOTAL</b>	<b>842.3<sup>b</sup></b> <b>(414.4 from batteries )</b>	<b>0.126</b>							

- a) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown of the submitted figures between the producing process and the recycling process was not feasible. For this reason this company has been listed with the other producers;
- b) This total amount represents not only the cadmium recycled from NiCd batteries (414.4 t (256.3 tonnes portable batteries; 158.1 tonnes industrial batteries)) but includes also other Cd containing waste (production scrap: 286.4 t/y, other sources (not specified): 141.5 t/y). On average 81% of the batteries recycled are EU batteries; 19% is imported (Industry Questionnaires, 2000/2001; information from SNAM & SAFT). On the other hand, the recycled amount of Cd produced by the third recycler (115 t (battery fraction: 85t)) is not included in the given figure;
- c) No "open" treatment steps; no emissions. Wastewater is collected and treated off-site. No further information is provided. Sludge is land-filled;
- M (T) Measured total concentration after WWTP i.e. Cd concentration virtually equal to dissolved Cd concentration;
- N/A Not applicable.

Table 3.11 Atmospheric emissions from Cd recycling plants in the EU (Cd recycled from batteries, production scrap and other sources)

Plant	Production/consumption	Processing	Emission	Year
N°	Volume	Emission amount	Factor	
	tonne/year	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
1 <sup>a</sup>	800.5 (376.8 batteries: 47.1%)	1.77	2.21	2000
2	41.8 (37.6 batteries: 89.9%)	0 <sup>c</sup>	0	1999
TOTAL	842.3 <sup>b</sup> (414.4 from batteries)	1.77		

- a) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown of the submitted figures between the producing process and the recycling process was not feasible. For this reason this company has been listed with the other producers;
- b) This total amount represents not only the cadmium recycled from NiCd batteries (414.4 t (256.3 tonnes portable batteries; 158.1 tonnes industrial batteries)) but includes also other Cd containing waste (production scrap: 286.4 t/y, other sources (not specified): 141.5 t/y). On average 81% of the batteries recycled are EU batteries; 19% is imported. (Industry Questionnaires, 2000/2001; information from SNAM & SAFT). On the other hand, the recycled amount of Cd produced by the third recycler (115 t (battery fraction: 85t)) is not included in the given figure;
- c) No "open" treatment steps; no emissions. Wastewater is collected and treated off-site. No further information is provided. Sludge is land-filled.

Table 3.12 Waste information for Cd recyclers in the EU

Plant N°	Type of waste produced	Quantity of waste(tonnes y <sup>-1</sup> )	Cd content	Waste disposal type	Year
			mg kg <sup>-1</sup>		
1 <sup>a</sup>	Batteries plastic boxes	268	1.5	Special landfill	2000
	Batteries metallic boxes	231	< 2,000	External recycling	
	Fe/Cd electrodes after treatment	221	< 2,000	External recycling	
	Concentrated electrolytes	216	10,000	External scrap treatment	
	Process slag	58	Pure CdO	Internal treatment	
	Air treatment dust	23	Pure CdO	Internal treatment	
	Used filters	2.6	20,000	Internal treatment	
	Rainwater sludges	0.2	3,000	Internal treatment	
2	Plastic waste	Small	< 0.005% Cd	n.d.	1999
	Wastewater condensed with vacuum treatment furnace	25	n.d.	External treatment, Sludges are land-filled	

- a) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown in the submitted figures between the producing process and the recycling process was not feasible. For this reason this company has been listed with the other producers;
- n.d. No data available.

Since the recycling activities of NiCd batteries are restricted to a small number of sites in a limited number of EU countries (i.e. Sweden, France and Germany), and hence are not equally distributed over the EU territory, it is not possible to apply the 10% rule for estimation of the regional emissions. In that case it is recommended to use the EU volume as input for the region and to apply another percentage or to use specific values as input for the regional model (e.g. emissions from the largest emitter). In this case the emissions from the largest (and only) emitter to air and water were allocated to the region. (EC, 1998).

Table 3.13 Summary emission from recycling of NiCd batteries (life cycle stage 4)

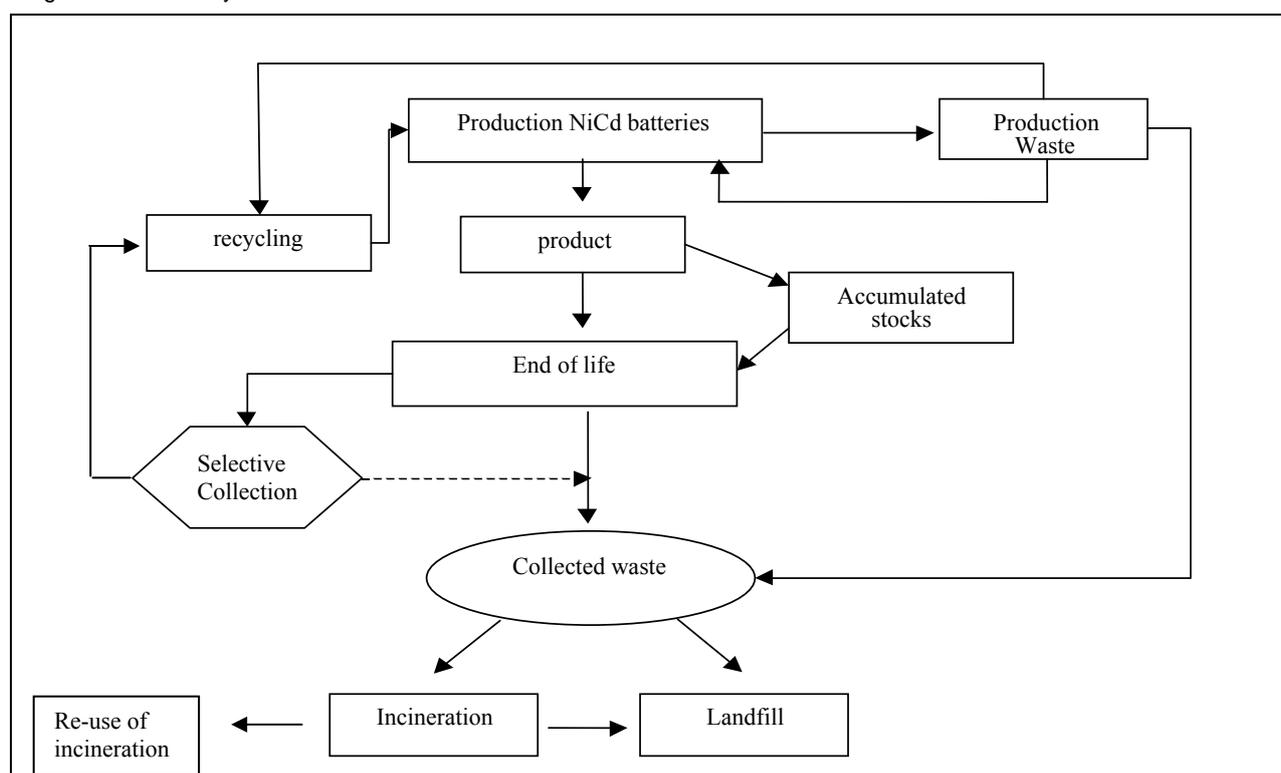
Compartment	Total	Regional
	kg year <sup>-1</sup>	kg year <sup>-1</sup>
Air	1.77	1.77
Wastewater	0	0
Surface water	0.13	0.13
Soil, urban/ind	0	0
Total	1.9	1.9

### 3.1.2.2.5 Life cycle stage 5: Disposal

#### Scope definition

At the end of their technical lifetime batteries or equipment containing NiCd batteries may end up in the waste stream or in private or municipal collection points. The end of life management of batteries consists of collection, recycling, landfills and incineration. A schematic overview of the cadmium flows related to the life cycle of NiCd batteries is given in **Figure 3.1**.

Figure 3.1 The life cycle of NiCd batteries



The size of the battery waste stream is related to the amount of batteries sold/used in previous years. In the case of NiCd batteries there is a considerable time lapse between the end of service life for the product and the occurrence of emissions from the waste treatment processing. The delay between marketing and emissions is mainly governed by (1) the service life-span (2) possible intermediate storage (stockpiling/hoarding) and (3) the transformation/transportation processes in landfills or incineration residues. As a result, current emissions probably may not be representative for the potential future emissions that are expected to take place several decades after production and processing of a substance have ceased.

In this regard this report addresses both the instantaneous cadmium emissions because of waste treatment (e.g. incineration) and the cumulative cadmium emissions of landfills. Guidance on how to estimate the emissions from the waste disposal stage is not provided within the Technical Guidance Document (TGD, 1996). The revised TGD includes some sections on waste disposal and has been taken as the starting point for the proposed approach as outlined here below.

Both the current and future cadmium emissions will be assessed albeit in a semi-quantitative way. Current emissions will initially be estimated based on an overall European situation. However, since waste management strategies may differ considerably between the Member States, due consideration will be given to these differences by means of including several scenarios (with the extremes: 100% land-filling and 100% incineration). Main emissions of cadmium from incineration of waste are expected to occur through air if no adequate flue gas treatment is in place and the disposal and/or re-use of incineration residues. However, neither the delayed cadmium emissions of the re-use of incineration residues nor the impact of future expected increase in cadmium content of bottom ash and fly ash on the re-usability of these incineration residues have been quantified. The major environmental concerns associated with metals in landfills are usually related to the generation and eventual discharge of leachate into the environment. Therefore the aforementioned emissions will be the focal point of this report. However, the impact of a future change in the MSW composition on the composition of the leachate of a landfill could not be judged based on the current lack of knowledge and methodology. Emissions of recycling are taken into account in this report at the manufacturing phase in Section 3.1.2.2.4.

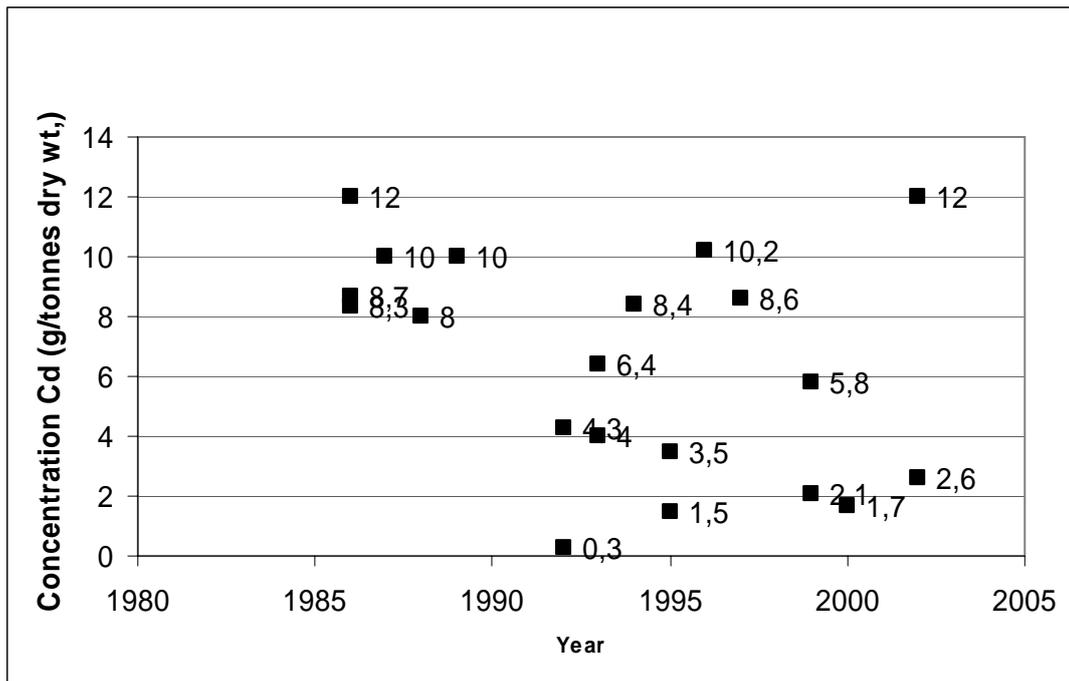
#### Contribution of NiCd batteries to the cadmium content of Municipal Solid Waste: current situation

MSW consists of vast array of materials discarded after their useful life and is very heterogeneous of nature. Reported total concentrations of cadmium in MSW are summarised in **Table 3.14** and visualised in **Figure 3.2** and range between 0.3-12 g Cd/tonne<sub>dry wt.</sub> The observed differences are due to the heterogeneity of the Municipal Solid Waste stream, the methodology used to estimate the total cadmium concentration and possible pre-treatment steps. For example the study of Maystre (1994) calculated the total flow of cadmium as a result of the individual cadmium content in a given type of material and the fraction of this material in the total amount of MSW. The obtained total cadmium concentration of 6 g tonne<sup>-1</sup><sub>dry wt.</sub> does not include the contribution of NiCd batteries. Brunner and Mönch (1986) and Brunner and Ernst (1986) reported total Cd values of 8.7-12 g tonne<sup>-1</sup><sub>dry wt.</sub> These values were calculated from the analysis of the composition of the incineration products. Direct waste analysis (Otte, 1995; ADEME, 1988 and 1993) revealed similar figures.

Table 3.14 Total cadmium concentrations ( $\text{g tonne}^{-1}$  dry wt.) in MSW

Country	$\text{g tonne}^{-1}$	Methodology used	Reference
Finland	0.3-4.3	Direct Waste Analysis	Assmuth (1992)
Switzerland	8.7 12	Analysis incineration products	Brunner and Mönch, (1986) and Brunner and Ernst (1986)
Switzerland	8.6		Titalyse (1997)
Germany	10	Not specified	Horch (1987) cited in Reimann (1989)
Germany	10	Not specified	Reimann (1989)
Germany	12	Not specified	Reimann (2002)
The Netherlands	3.5	Direct Waste Analysis	Otte (1995)
The Netherlands	6.4	Not specified	Rijkema (1993b) cited in Bernard et al. (2000)
The Netherlands	2.6	Direct waste analysis after sorting	Wiaux (2002)
The Netherlands	10.2	Not specified	Rijkema (1996) cited in Mersiowsky (2002)
The Netherlands	8.4	Analysis incineration products	Krajenbrink and Eggels (1997) (MSW of 1994)
UK	1.7	Direct Waste Analysis	(Ross et al., 2000)
UK	Average 0.8 P50: 0.7 P90: 1.5	Direct Waste Analysis (data 1992-1993)	NETC (1995)
Sweden	2.1-5.8	Direct Waste Analysis	Flyhammer and Hakansson (1999)
Sweden	8.3	Not specified	Statens Energiverk (1986) (cited in Flyhammer et al., 1998)
France	6 <sup>a</sup>	Mass Flow	Maystre (1994)
France	8	Direct Waste Analysis	ADEME (1988) in SFSP (1999)
France	4	Direct Waste Analysis	ADEME (1993)

a) Batteries were not included

Figure 3.2 Evolution of Cd concentration ( $\text{g tonne}^{-1}_{\text{dw}}$ ) in MSW

In general there seems to be a slight tendency that higher cadmium concentrations in the MSW have been found in the past ( $8\text{--}12 \text{ g tonne}^{-1}_{\text{dry wt.}}$ ) than at present ( $0.3\text{--}8 \text{ g tonne}^{-1}_{\text{dry wt.}}$ ) (see **Figure 3.2**: Since data are scarce and a large uncertainty surrounds the reported figures all data were, however, pooled together. Based on the pooled data the average Cd content of MSW is  $6.2 \text{ mg kg}^{-1}_{\text{dry wt.}}$  (median =  $P50 = 6.4 \text{ mg kg}^{-1}_{\text{dry wt.}}$ ). In the EU-16, 160,058 ktonnes of MSW is generated (see subsection “Waste management strategies in Europe” under Section 3.1.2.2.5). The moisture content of MSW is typically on average 30% (Van der Poel, 1999, Mersiowsky, 2001; DTU, 2001) yielding 112,041 ktonnes of MSW (dry weight). The reasonable worst case total cadmium content of MSW on a dry weight basis is derived as the 90<sup>th</sup> percentile and equals  $10 \text{ g Cd/tonne}_{\text{dry wt.}}$ . This value is taken forward in the calculations of the emissions (see Section 3) and equals a cadmium load of 1.1 ktonnes.

Only a fraction of this total cadmium content originates from NiCd batteries. **Table 3.15** illustrates the typical average metal concentrations of MSW constituents.

Table 3.15 Average concentration ( $\text{mg kg}^{-1}_{\text{dry wt.}}$ ) of metals in MSW components (Maystre et al., 1994 adapted)

Types of Materials	Cu	Zn	Cd	Hg	Pb
Plants and Food	28	74	3	< 1	235
Meat waste	24	96	4	< 1	82
Natural Fibers	58	104	< 2	< 1	24
Synthetic Fibers	9	43	2	< 1	19
Leather	75	437	5	< 1	372
Aluminium	2	17	53	< 1	84
Non Ferrous	1,792	46,827	10	< 1	30,010
Electronic Equipment	30,333	17,689	509	< 1	29,805

Table 3.15 continued overleaf

Table 3.15 continued Average concentration (mg kg<sup>-1</sup> dry wt.) of metals in MSW components (Maystre et al., 1994 adapted)

Types of Materials	Cu	Zn	Cd	Hg	Pb
Plastic foam	155	283	8	< 1	288
Rubber	28	7,028	8	< 1	197
Moulded Plastic Bodies	19	39	138	< 1	259
Primary Batteries Zn-C	2,725	95,305	5	72	102
Paper	280	35	8	< 1	399
Cardboard	84	60	2	< 1	43
Dust Bin Bags	200	363	6	86	470
Paper and Paraffine	210	77	4	< 1	263
Nickel-Cadmium Batteries <sup>a</sup>	-	< 100	130,000	< 1	1.0

- a) In the study of Maystre (1994) Nickel-Cadmium batteries were not reported as a specifically identified type of material entering the composition of Municipal Solid Waste but for the purpose of Comparison. They have been added in Table 3.15.

It is obvious that NiCd batteries have the highest concentration of cadmium when compared to other types of materials. The final contribution, however, to the overall cadmium content is of course dependent on the weight distribution of the different waste components.

Different studies attempted to estimate the specific contribution of NiCd batteries to the overall cadmium load in MSW. Reported estimates of the amount of cadmium in the MSW originating from NiCd batteries vary widely from 10-85% (EPA, 1989, Walker, 1995, Chandler, 1995, STIBAT 1998 and 2000, SCRELEC, 1999, Lemann, 1995). The reason for this large variation is among other things related to the relative small sample volumes, the heterogeneity of the municipal waste stream and the method that is used to quantify the amount of NiCd batteries in MSW.

Roughly two approaches can be distinguished. The first approach tries to predict the MSW composition indirectly through a material flow analysis. In the second approach MSW is being sorted and the cadmium concentration of the constituents are directly analysed. Typically, a material flow analysis is based on the collection of product historical data on the quantity of cadmium consumed in the production of a product. Finally, after correction for import and export the time it takes for the cadmium to reach the waste stream is projected by estimating the life time of the product and assuming that the product will be discarded at the end of this period. These estimates of gross discards are adjusted for materials recovery (recycling) and the remaining portion is the estimate of the net discard in MSW. In the available mass flow studies on NiCd batteries hoarding has not been taken into account resulting in an overestimation of the contribution of NiCd batteries to the overall cadmium emissions in MSW in Europe. The Lemann study (1995) indicating the highest contribution (85%) of NiCd batteries was considered unreliable after a critical evaluation of the data presented. In this study an element and material balance of the Municipal Solid Waste incinerator Hagenholz was conducted in 1995 in parallel with a detailed slag analysis. The results revealed that only 3.64 tonnes NiCd scrap/year could be recovered. This figure was approximately 4 times lower than the estimated mass flow of NiCd batteries reaching the incineration plant, based on FOEFL statistics on the use of batteries in 1992 (11.5 tonnes y<sup>-1</sup> on average). The authors of the study explained these conflicting results by the simple fact that more than three-quarters of the batteries decompose completely during the incineration process and are therefore unrecognisable in the crude slag. Based on the latter assumption the FOEFL statistics of 1992 were still used (the data from 1992 were compared with

the analysis from March 1995 because the average life time for NiCd batteries were estimated to be between 1-3 years). Since the total cadmium load for 1994 was estimated to be 2,437 tonnes  $y^{-1}$  it was concluded that NiCd accumulators caused 85% of the cadmium input in the Hagenholz incinerator. However, if the measured discard of 3.64 tonnes of NiCd is used only 20% is attributable to NiCd batteries (assuming an average Cd content of 13.8%).

Another method of estimating cadmium in MSW is to examine actual concentrations of cadmium found in municipal refuse samples and to scale these concentrations to the overall waste stream. The analysis of the cadmium content of MSW offers the advantage of being a direct approach circumventing the above mentioned constraints. However, waste composition data are uncertain, and the proportions of individual components typically vary considerably from sample to sample. Sample numbers and waste quantity analysed should be sufficient high to develop a statistically reliable picture of composition. At present, while some data are available from various countries in waste quantities and component distribution, data that consider the chemical composition of the various components in the waste stream is limited. Three major campaigns for sorting portable batteries from M.S.W. streams have been realised in the Netherlands and France, during the last years<sup>27</sup>. The results of those campaigns are presented in **Table 3.16**. They indicate that the fraction of primary battery is found in the weight fraction range of 150 to 170 ppm. The rechargeable batteries' fraction, composed mainly of consumer/sealed portable NiCd batteries, are in the range of 4 to 9 ppm (on a wet weight basis). As such it can be concluded that NiCd batteries as a percentage of all battery types found in MSW is in the range of 2.6-6.6% (see **Table 3.16**). Similar figures have been reported by the Witzenhausen Institut (Witzenhausen, 2001) with NiCd contributions ranging from 3.5-8.4%. A weighted average of 6% has been reported by Witzenhausen Institut (2004). Taken into account that on average a portable sealed NiCd battery contains 13.8% of Cd and contains 5% water (see **Table 2.15**) a lower limit of 0.5 g Cd/tonne<sub>wet wt.</sub> ( $4 \cdot 0.138 \cdot 0.95 = 0.52$ ) and an upper limit of 1.2 g Cd/tonne<sub>wet wt.</sub> can be calculated ( $9 \cdot 0.138 \cdot 0.95 = 1.17$ ). The moisture content of MSW is typically on average 30% (Mersiowsky, 2001; DTU, 2001). Based on this the above figures can be converted to a dry weight basis and a lower and upper limit of 0.7 and 1.7 g Cd/tonne<sub>dry wt</sub> is obtained.

Table 3.16 Fraction of Batteries found in MSW: Primary and sealed portable NiCd batteries in various European countries

Country	Year	Primary Battery Weight Ratio In M.S.W.(ppm)	NiCd Battery In M.S.W (mg kg <sup>-1</sup> <sub>wet wt.</sub> )	Quantity of M.S.W. studied In tonnes	Source
The Netherlands	1998	170	8	10,000(continuous)	STIBAT
The Netherlands	2000	160	9	10,000 (continuous)	STIBAT
Austria	2000	230	11	377 (sampling methodology)	U.B.F.
Belgium	1998 and 1999	100	5 <sup>a</sup>	4.5 (sampling methodology)	I.B.G.E
Germany	2000	370	23 <sup>b</sup>	400 (sampling methodology)	GRS
Sweden	1996	100-200	6-6-13.2 <sup>c</sup>	(sampling methodology)	RVF

Table 3.16 continued overleaf

<sup>27</sup> More information on the applied methodology is given in Annex III (as submitted by CollectNiCad, 2002)

Table 3.16 continued Fraction of Batteries found in MSW: Primary and sealed portable NiCd batteries in various European countries

Country	Year	Primary Battery Weight Ratio In M.S.W.(ppm)	NiCd Battery In M.S.W (mg kg <sup>-1</sup> wet wt.)	Quantity of M.S.W. studied in tonnes	Source
France	1999	150	4	8,900 (one month campaign)	SCRELEC & ADEME

- a) Calculated on the basis of the estimate that the amount of NiCd is 5% of total consumer/sealed portable batteries;  
 b) Based on 82 millions inhabitants and 25.5 millions of tonnes MSW per year (1999);  
 c) Data supplied by Renova (2000).

Similar campaigns have been conducted in Austria, Belgium and Germany but on a much smaller scale (4.5-400 tonnes of MSW). These studies report values between 5 and 23 mg kg<sup>-1</sup> wet wt. resulting in a maximum NiCd battery contribution of 3.01 g Cd/tonne wet wt. ( $23 \cdot 0.138 \cdot 0.95$ ) or 4.3 g Cd/tonne dry wt.

As a reasonable worst case it is assumed in this report that the total cadmium content of MSW equals 10 g Cd/tonne dry wt. The influence of this parameter to the overall assessment is explored in the sensitivity analysis (see subsection “Sensitivity analysis” under Section 3.1.2.2.5). Most of the prevailing evidence coming from MSW sorting studies supports a contribution of NiCd batteries to the overall cadmium load between 0.7 and 1.7 g tonne<sup>-1</sup> dry wt., i.e. a NiCd contribution of 10-20%. Based on the maximum obtained NiCd contribution of 4.3 g Cd/tonne dry wt. an allocation of 43% can be calculated. Taken into account the uncertainty surrounding the proposition of one figure, an allocation range of 10-50% is maintained in this report for the assessment of the current emissions due to NiCd batteries. For the current scenarios the 10% is representative of the typical situation. The 50% is representative of the worst case contribution. However, in modelling towards the future, the assumption of 10% will result in a worst case estimate.

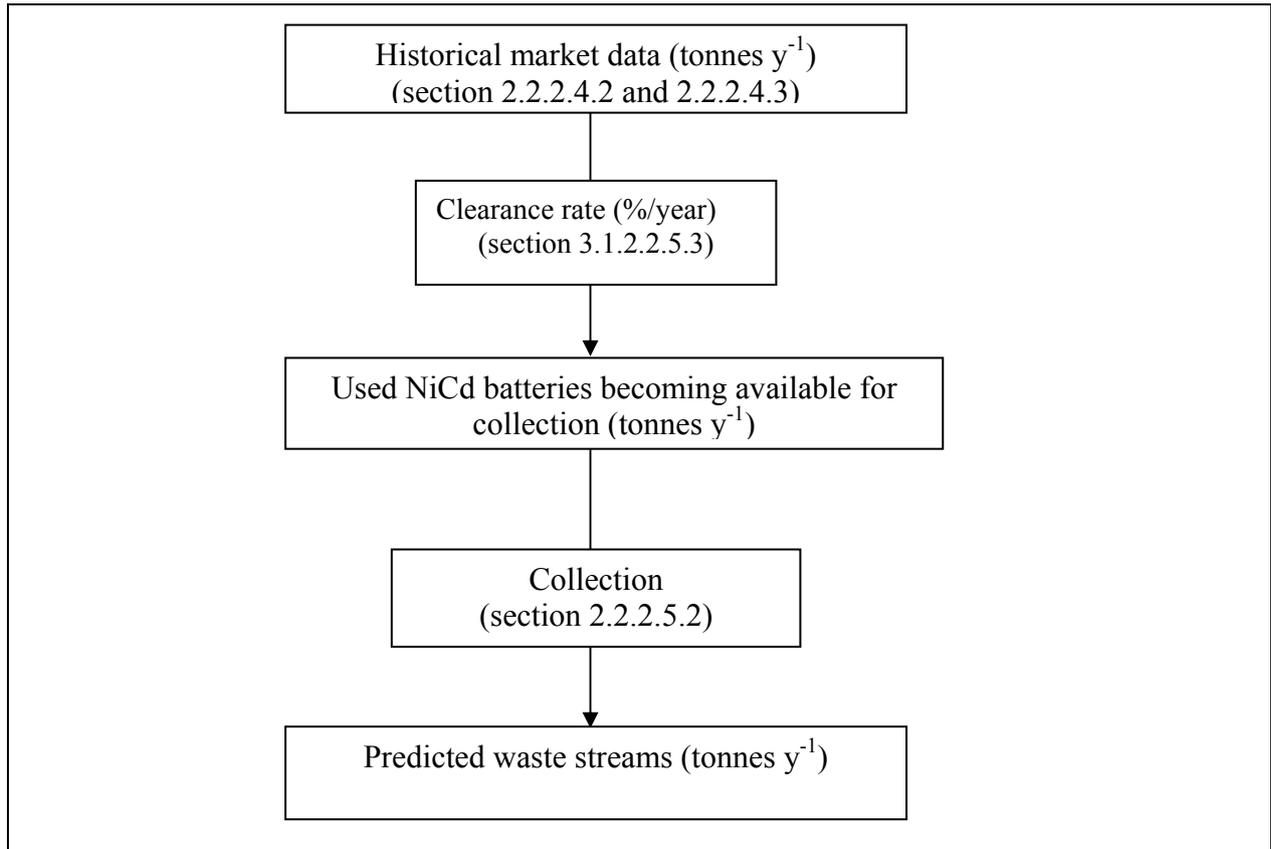
### Forecasts of future battery waste streams

In order to calculate future emissions due to the presence of NiCd batteries in waste it is imperative that realistic forecasts of battery waste streams can be made. For the Municipal Solid Waste stream only the contribution of sealed portable NiCd batteries have been considered<sup>28</sup>.

The predictions of future battery waste streams are hampered by the fact that the length of time between sale/first use and disposal of a battery by the user varies largely according to the type of the battery and its application. The amount of NiCd batteries ending up for the majority of cases in the MSW waste stream is function of the efficiency of collection and the amounts available for collection. The latter is again subject to the battery lifetime and the “hoarding” process. A schematic overview of the different phases in the calculation of the future waste streams is given in **Figure 3.3**.

<sup>28</sup> Industrial NiCd batteries, representing 20% of the cadmium used in NiCd batteries, are recycled at a high rate. In 1999 2,677 tonnes of industrial NiCd batteries were recycled (see Section 2.2.2.5.1). This represents 72% of the total sales for the same year. If it is assumed that there is no time delay between the sales and the occurrence in the waste stream, 82 tonnes  $((3,700 - 2,677) \cdot 0.08)$  of cadmium is disposed in industrial landfills each year. The emissions of industrial landfills are not addressed here.

Figure 3.3 Rationale used for calculating waste arising from NiCd batteries



The different steps are explained more in detail hereafter.

#### *Calculation of the amount of used NiCd batteries coming available for collection*

Future battery waste streams are calculated based on the amount of batteries coming available for collection in a certain year.

The amount of used NiCd batteries available for collection varies with the lifetime of the batteries and the hoarding behaviour of the end user. Since both battery lifetime and hoarding behaviour are difficult to assess, calculating the amount available for collection will thus be subject to an error proportional to the uncertainty over these parameters.

An alternative method, not sensitive to the above uncertainties, is the use of a battery half-life instead of a battery lifetime. The battery half-life is defined as the time needed to collect 50% of the quantity introduced to the market in a given year. This battery half-life can be derived from measurements of the quantity of batteries present in MSW wastes, mixed wastes and industrial wastes in conjunction with battery Date Coding campaigns.

In absence of more data on the subject the amount available for collection will be calculated based on the historical market base line (see Section 2.2.2.4.2 for consumer/sealed portable NiCd batteries) following two models. The first model is a simplified worst case model just taking into account that the batteries will come available for collection/disposal within the average battery lifetime and ignoring the effect of hoarding. In the second model hoarding (especially important for portable sealed NiCd batteries) is incorporated. Inclusion of a hoarding period will have the effect of delaying the reporting of a battery to the waste stream over the assumed hoarding period.

The actual lifetime of a NiCd battery may be five years to twenty-five years depending upon the specific battery design and its application. Reported values for consumer/sealed portable batteries typically range between 3-10 years (Cloke, 1999, Fujimoto, 1999). Similar values (4-8 years) are reported in a Danish study on the mass balance on cadmium (Miljostyrelsen, 2000). In this report the concept of an average battery lifetime for batteries will be used and is defined as the average lifetime until the battery is being collected. For portable batteries an average battery lifetime of 5 years will be used. Industrial batteries are assumed to have an average battery lifetime of 10 years. Results of hoarding studies indicate that the overall hoarded supply on consumer/sealed portable NiCd batteries 15 years after the useful lifetime is 65% (Fujimoto, 1999). Recent information obtained from a similar hoarding study in Europe revealed an average hoarding rate for replacement batteries of 62%. For batteries in large appliances that are disposed of without prior removal of the batteries the hoarding rate can be as high as 95% (TMO-CSA, 2001).

#### *Projections of future battery waste streams*

The amount of NiCd batteries that will end up in the waste stream in a certain reference year is calculated by summing up the respective fractions coming available for collection in that reference year and correcting this amount with the collection ratio. Since some countries have not yet started with collecting NiCd batteries a range of collection ratios covering both the lower as upper ranges is recommended (see Section 2.2.2.5.2) as input in the model to predict future battery waste streams.

#### *Future battery waste streams for (sealed) portable NiCd batteries*

An overview of the models for the (sealed) portable NiCd batteries is given in **Table 3.17**. Further details related to the models' calculations are available in Annex III.

Table 3.17 Overview of the clearance rates (% initial market volume/year) used in the models for predicting waste arising due to (sealed) portable NiCd batteries

MODEL 1: Based on average lifetime of 5 year			
Period (year)	Description	Clearance rate (%/year)	% marketed volume left at the end of the period concerned
1-5	No hoarding (worst case)	20	0
MODEL 2 : Gradual			
Period (year)	Description	Clearance rate (%/year)	% marketed volume left at the end of the period concerned
1 – 5	Useful life-time	1	95
6 – 20	Home storage/hoarding	2.2	62
21 – 30	Destock	6.2	0

In Model 1 no hoarding is considered. It is assumed that the purchased (sealed) portable NiCd batteries will come available for collection/disposal over a period of 5 years. In Model 2 a more gradual approach is being assumed taking into account the hoarding behaviour of the end user. Within the presumed maximum technical lifetime of 30 years the following clearance rates can be distinguished. Five years after market introduction, due to defects or malfunctions, 5% will be available for collection or disposal. Another 33% will be disposed of over the next 15 years. Finally the remaining volume (62% of the initial market volume) will be destocked within 10 years.

It should be clear that neither the choice of the model nor the battery lifetime will alter the predictions of the future risks associated with landfills due to the fact that the gradual model will only result in a time shift when compared to the model without hoarding. The model without hoarding is not realistic but is given in this report to illustrate the statement above.

For each model only those scenarios were considered which are most likely to occur:

- Scenario 1: Production of portable NiCd batteries will continue at a rate of 13,500 tonnes per year until the hypothetical cadmium ban in 2008 is imposed.
- Scenario 2: Production of portable NiCd batteries will continue at a rate of 13,500 tonnes per year.

For both scenarios collection/recycling was taken into account. Until 2001 the reported collection/recycling weights were used. Before 1994 no collection/recycling was assumed. After the year 2001 the scenarios have been run for the assumption of respectively 10 and 75% collection of NiCd batteries.

The evolution of the cadmium content of MSW solely due to NiCd batteries is summarised in the **Tables 3.18** and **Table 3.19**. These figures were obtained by dividing the weight of the disposed NiCd batteries with the average yearly amount of MSW (expressed as dry weight). Between 1995 and 2001 160,058 ktonnes (wet weight.) of MSW was generated. With a content of 70% dry matter this can be converted to 112,041 ktonnes (dry weight). Probably the amount of MSW will increase in the future (EEA, 2000) but this has not been taken into account.

Table 3.18 Cadmium content (g Cd/tonne waste<sub>dry wt.</sub>) in MSW due to sealed portable NiCd batteries.  
Scenario 1: ban imposed

Year	Cd due to other sources <sup>29</sup>	Contribution (sealed) portable NiCd batteries			
		MODEL 1: ACCELERATED		MODEL 2: GRADUAL	
		10% collection	75% collection	10% collection	75% collection
1981	9	0.4	0.4	0.01	0.01
1985	9	2.4	2.4	0.1	0.1
1990	9	6.5	6.5	0.6	0.6
1995	9	12.9	12.9	1.0	1.0
2000	9	14.1	14.1	1.0	1.0
2005	9	15	4.2	4.9	1.4
2010	9	9	2.5	7.5	2.1
2015	9	0	0	9.8	2.7
2020	9	0	0	11.0	3.0
2025	9	0	0	10.2	2.8
2030	9	0	0	7.4	2.1
2035	9	0	0	2.8	0.8
2040	9	0	0		

<sup>29</sup> The current overall cadmium content of MSW is estimated to be 10 g tonne<sup>-1</sup><sub>dry wt.</sub>. If it is assumed that at present only 10% of this content can be allocated to the presence of NiCd batteries, resulting in a worst case assumption for the future Cd content in MSW (see Table 3.20). A current contribution of all other cadmium sources of 9 g tonne<sup>-1</sup><sub>dry wt.</sub> can be calculated.

If a ban is imposed the maximum cadmium content in the MSW due to NiCd batteries is 10.8 g Cd/tonne<sub>dry wt.</sub> for the gradual model and 15 g Cd/tonne<sub>dry wt.</sub> for the accelerated model. In both cases no more NiCd batteries are expected to occur in the waste by the year 2040<sup>30</sup>.

Table 3.19 Cadmium content (g tonne<sup>-1</sup><sub>dry wt. waste</sub>) in MSW due to portable sealed NiCd batteries. Scenario 2: no ban

Year	Cd due to other sources	Contribution (sealed) portable NiCd batteries			
		MODEL 1: ACCELERATED		MODEL 2: GRADUAL	
		10% collection	75% collection	10% collection	75% collection
1981	9	0.4	0.4	0.0	0.0
1985	9	2.4	2.4	0.1	0.1
1990	9	6.5	6.5	0.6	0.6
1995	9	12.9	12.9	1.0	1.0
2000	9	14.1	14.1	1.0	1.0
2005	9	15.0	4.2	4.9	1.4
2010	9	15.0	4.2	7.8	2.2
2015	9	15.0	4.2	11.2	3.1
2020	9	15.0	4.2	14.0	3.9
2025	9	15.0	4.2	14.9	4.1
2030	9	15.0	4.2	15.0	4.2
2035	9	15.0	4.2	15.0	4.2
2040	9	15.0	4.2	15.0	4.2

If no ban is imposed the cadmium concentration in the MSW due to NiCd batteries will increase until a steady state is reached. The steady state cadmium concentration in the MSW obtained is ranging between 4.2 and 15.0 g Cd/tonne<sub>dry wt.</sub> irrespective of the model used. The NiCd contribution for the year 2000 is estimated with the gradual model to be 1.0 g Cd/tonne<sub>dry wt.</sub> Note that the lower range of the currently presumed NiCd contribution is 0.7 g Cd/tonne<sub>dry wt.</sub> (upper range = 1.71. g Cd/tonne<sub>dry wt.</sub>).

#### *Future cadmium content in MSW*

From the previous paragraph a steady state cadmium concentration solely due to the presence of NiCd batteries in MSW is estimated between 4.2 and 15 g tonne<sup>-1</sup><sub>dry wt.</sub>).

The current overall cadmium content of MSW is estimated to be 10 g tonne<sup>-1</sup><sub>dry wt.</sub> If it is assumed that at present only 10% of this content can be allocated to the presence of NiCd batteries a current contribution of all other cadmium sources of 9 g tonne<sup>-1</sup><sub>dry wt.</sub> can be calculated (resulting in a worst case assumption for the future Cd content in MSW). If it is further assumed that this contribution will not change in the future this figure can be taken as the starting figure for the calculation of the future cadmium content in the MSW (see **Table 3.20**).

<sup>30</sup>However, it is clear that even when the production of NiCd batteries has ceased the non-refined cadmium cements obtained as a by-product of zinc refining will obviously still have to be landfilled. This TRAR will not address this issue as it is out of the scope of the study. Moreover, it is obvious that after the year 2040, Cd from other sources will still be present (if no legislative action is taken to prevent these).

Table 3.20 Future cadmium content of MSW

Collection (%)	Cd contribution due to NiCd batteries (g Cd/tonne dry wt.)	Cd contribution due to other sources (g Cd/tonne dry wt.)	Total future Cd content in MSW (g Cd/tonne dry wt.)
10	15	9	24
75	4.2	9	13.2

In the worst case scenario, where the collection rate is only 10%, the cadmium contribution from NiCd batteries may rise to 15 ppm with a batteries' contribution of 63% of the total cadmium content in MSW. When collection is at a 75% rate, the cadmium contribution from NiCd batteries may rise to 13.2 ppm with a batteries contribution of 32% of the total cadmium content in MSW.

### Waste management Strategies in Europe

Waste management practices<sup>31</sup> vary considerably among different countries and regions in the EU. The current status of waste management strategies for the different EU countries is presented in **Table 3.21** and **Table 3.22**. Most data were extracted from the databank provided by ETWC (ETWC, 2002) which on its turn is a compilation of the results of a joint Eurostat/OECD Questionnaire (2000) or based on national reports (France, Norway, Belgium, Sweden, Finland, Austria, Luxembourg and the Netherlands) and OECD statistics (Greece, Italy, Ireland, Spain and Portugal). The data for Germany (landfill and incineration), Spain (incineration) and Portugal (incineration and landfill) were updated with the latest information made available by the Member State.

Table 3.21 Land-filling and incineration of MSW (in ktonnes WW) in Europe for the period 1995-2001

Country	Year	MSW land-filled (ktonnes wet wt.)	MSW incinerated (ktonnes wet wt.)
Austria <sup>a</sup>	1999	1,099	479
Belgium <sup>a</sup>	1998	1,473	1,369
Denmark <sup>c</sup>	1999	361	1,730
Finland <sup>a</sup>	1997	1,610	80
France <sup>a</sup>	1998	23,352	10,781
Germany <sup>b</sup>	2001	16,000	12,000
Greece <sup>d</sup>	1997	3,561	0
Ireland <sup>d</sup>	1995	1,432	0
Italy <sup>a</sup>	1998	20,768	1,949
Luxembourg <sup>a</sup>	1998	62	123
The Netherlands <sup>a</sup>	1999	1,136	3,859

Table 3.21 continued overleaf

<sup>31</sup> Only incineration and landfill practices are being considered in this TRAR. Other treatment methods as composting and recycling of MSW are either not applicable for NiCd batteries (presorting) or irrelevant in view of the quantities.

Table 3.21 continued Land-filling and incineration of MSW (in ktonnes WW) in Europe for the period 1995-2001

Country	Year	MSW land-filled (ktonnes wet wt.)	MSW incinerated (ktonnes wet wt.)
Norway <sup>a</sup>	1998	1,843	374
Portugal <sup>a,e</sup>	1999-2002	2,603	1,060
Spain <sup>a</sup>	1999	17,477	1,327
Sweden <sup>a</sup>	1998	1,300	1,400
UK <sup>a</sup>	1999	26,860	2,590
<b>Total EU-16</b>	<b>160,058</b>	<b>120,937</b>	<b>39,121</b>

- a) Wastebase (ETWC, 2002)  
b) Umweltsbundesamt (UBA, 2001)  
c) Waste Statistics, 1999 (Danish EPA, 2001)  
d) OECD compendium 1999  
e) Lipor II, Calheiros JM and Almeida A., pers. com., 2002

The calculation of the share (%) of MSW waste being land-filled or incinerated is calculated using only the ratio between incineration and land-filling in the different Member States.

Table 3.22 Land-filling and incineration practices (in %) in Europe for the period 1995-2001

Country	Year	% of MSW land-filled	% of MSW incinerated
Austria	1999	69.6	30.4
Belgium	1998	51.8	48.2
Denmark	1999	17.3	82.7
Finland	1997	95.3	4.7
France	1998	68.4	31.6
Germany	2001	57.1	42.9
Greece	1997	100	0
Ireland	1995	100	0
Italy	1998	91.4	8.6
Luxembourg	1998	33.5	66.5
The Netherlands	1999	22.7	77.3
Norway	1998	83.1	16.9
Portugal	1999	71.1	28.9
Spain	1999	92.9	7.1
Sweden	1998	48.1	51.9
UK	1999	91.2	8.8
<b>Total EU-16</b>		<b>75.6</b>	<b>24.4</b>

Overall it can be concluded that land-filling remains the predominant disposal route for waste while there is a growing trend towards increased incineration (EEA, 2000). The overall ratio between incineration and land-filling of MSW within the European Union is 24.4 to 75.6 (situation 1995-2001).

Quantifying the cadmium emissions caused by landfills or incineration of NiCd batteries is hampered by the fact that available data on landfill and incineration emissions always represent the total emissions of cadmium containing materials present in the waste stream. Therefore the overall cadmium emissions are calculated first. By using a specific allocation key the specific contribution of NiCd batteries to the overall cadmium emission can be quantified.

The overall cadmium emissions may vary considerably depending on the used Flue Gas Cleaning System or the presence of a leachate treating system/protective lining in the case of landfills.

In this report the scenario based on the European average situation (24.4% incineration and 75.6% landfill) will be completed by two scenarios (100% land-filling and 100% incineration) to perform a rudimentary sensitivity analysis in order to reflect the extremes in waste management option.

### Overall cadmium emissions from incineration MSW

#### *Current emissions*

Cadmium entering into standard MSW incineration will be distributed among various output fractions such as stack emissions (flue gas), wastewater, fly ash, bottom ash and slag. The distribution pattern of cadmium over these incineration residues is depending on the physical-chemical properties, the gas cleaning technology and the operation and maintenance conditions. While the flue gas and wastewater emissions are immediate, emissions of the incineration residues (via disposal and/or re-use) are delayed.

#### *Flue gas emissions*

Approximately 5,000-6,000 Nm<sup>3</sup> flue gas is generated per tonne<sub>wet wt.</sub> waste incinerated (Van De Wijdeven, 1991). Today, almost all incineration plants have some kind of flue gas cleaning system (FGCS) in place. The amounts of household waste incinerated per flue gas cleaning system in use by the different Member States are presented in **Table 3.23** and were extracted from the national data collected by ISWA (2002). It should be noted that not all countries or incinerators present in a country has been covered. The distribution of the FGCS in percent (based on a weight basis) is presented in **Table 3.24**.

Table 3.23 Amounts of household waste (ktonnes<sub>wet wt.</sub>) treated per Flue Gas Cleaning System (reference year 1999) (ISWA, 2002)

Country	Dry	SD	WET	Dry + WET	SD +WET	ESP	FF	O	Total
Austria	0	0	437	0	0	0	0	0	437
Belgium <sup>a</sup>	38	304	208	0	203	0	0	0	753
Denmark	170	367	718	0	0	5	21	0	1,280
France	803	0	6,465	0	0	706	0	351	8,326
Germany	155	1,117	5,024	272	1,656	0	0	0	8,225
UK	150	488	0	0	0	0	0	0	639
The Netherlands	0	20	1,876	0	917	0	0	0	2,813
Norway	0	11	305	0	0	0	0	0	316

Table 3.23 continued overleaf

Table 3.23 continued Amounts of household waste (ktonnes <sub>wet wt.</sub>) treated per Flue Gas Cleaning System (reference year 1999) (ISWA, 2002)

Country	Dry	SD	WET	Dry + WET	SD +WET	ESP	FF	O	Total
Portugal <sup>c</sup>	0	1,060	0	0	0	0	0	0	1,060
Spain <sup>b</sup>	21	991	320	0	0	0	0	0	963
Sweden	322	0	645	283	0	0	53	0	1,303
<b>Total</b>	<b>1,660</b>	<b>4,358</b>	<b>15,997</b>	<b>555</b>	<b>2,776</b>	<b>712</b>	<b>74</b>	<b>351</b>	<b>26,483</b>

Source ISWA, 2002;

Dry Dry scrubbing;

SD Semi dry scrubbing;

WET Wet scrubbing;

FF Fabric Filter;

ESP Electrostatic precipitator;

O Other;

a) Updated figures for Flanders (OVAM, P. Loncke, pers. com., 2002);

b) Updated figures for Spain (MMA, 2002);

c) Updated figures for Portugal (LIPOR II, Calheiros JM and Almeida A., pers. com., 2002).

Table 3.24 Distribution (%) of Flue Gas Cleaning Systems for different Member States

Country	Dry	SD	WET	Dry + WET	SD +WET	ESP	FF	O	Total
Austria	0	0	100	0	0	0	0	0	100
Belgium	5	40.4	27.6	0	27	0	0	0	100
Denmark	13.3	28.6	56.1	0	0	0.4	1.6	0	100
France	9.7	0	77.6	0	0	8.5	0	4.2	100
Germany	1.9	13.6	61.1	3.3	20.1	0	0	0	100
UK	23.5	76.5	0	0	0	0	0	0	100
The Netherlands	0	0.7	66.7	0	32.6	0	0	0	100
Norway	0	3.4	96.6	0	0	0	0	0	100
Portugal	0	100	0	0	0	0	0	0	100
Spain	1.6	74.4	24.0	0	0	0	0	0	100
Sweden	24.7	0	49.5	21.7	0	0	4.1	0	100
<b>Total</b>	<b>6.3</b>	<b>16.5</b>	<b>60.4</b>	<b>2.1</b>	<b>10.5</b>	<b>2.7</b>	<b>0.3</b>	<b>1.3</b>	<b>100</b>

Source ISWA, 2002;

Dry Dry scrubbing;

SD Semi dry scrubbing;

WET Wet scrubbing;

FF Fabric Filter;

ESP Electrostatic precipitator;

O Other.

From **Table 3.24** it can be concluded that approximately 22% of all the household waste incinerated in Europe is followed by dry and semi-dry flue gas cleaning. Wet flue gas cleaning accounts for 63%. Three percent of the household waste incinerated is followed by ESP or FF only.

Actual measured air emissions of cadmium by Municipal Solid Waste incinerators were available for a number of Member States and when available preference was given to these measured data (indicated in bold/italic). For some Member States (UK, France and Portugal)

actual measured emission data (figures in bold/italic) were available. For other Member States a mix of measured and calculated data were available as best estimates. For example in Germany the cadmium emissions due to MSW incineration is estimated to be 0.3 tonnes in the year 1995 (Rentz et al., 1997; Jockel and Hartje, 1995) and was calculated by multiplying the average cadmium concentration measured in the flue gas of 20 incinerators with the amount of gas formed by the total amount of municipal waste incinerated in Germany. A similar approach has been followed for Spain and Belgium.

In the case no measured data were available the emission to air was estimated by applying the highest emission factor (based on measured data) to the amount of MSW incinerated (see **Table 3.21**).

The modelled/measured annual releases of cadmium to air for the different countries through the incineration of MSW are presented in **Table 3.25** for the scenario: 24.4% incineration.

Table 3.25 Overall cadmium emissions to air (in kg year<sup>-1</sup>) in Europe due to incineration of MSW. Scenario current incineration 24.4%

Country	MSW incinerated (ktonnes wet wt.)	Measured/modelled emissions (kg year <sup>-1</sup> ) <sup>a,b</sup>	Emission factor (g tonne <sup>-1</sup> wet wt.) <sup>c</sup>
Austria	479	86 <sup>d</sup>	0.18
Belgium	1,369	63	0.046
Denmark	1,730	300	0.17
Finland	80	14	0.18
France	10,781	1,922	0.18
Germany	12,000	300	0.025
Greece	0	0	0
Ireland	0	0	0
Italy	1,949	351	0.18
Luxembourg	123	22	0.18
The Netherlands	3,859	53	0.014
Norway	374	41	0.110
Portugal	1,060	3.2	0.003
Spain	1,327	54	0.041
Sweden	1,400	5	0.004
UK	2,590	17	0.007
<b>Total EU-16</b>	<b>39,121</b>	<b>3,231</b>	

- a) Measured data Belgium (FEA, OVAM 2001, MMUM, 2001); Measured data France: ADEME, 1999; Measured data Norway and the Netherlands HARP-HAZ 2002, Measured data Spain: MMA 2002, Measured data Portugal: Lipor, 2002, Measured data Denmark (Miljøstyrelsen, 2000), Measured data Sweden, (RVF's Faktarapport 2001 om Avfallsförbränning, cited in 'com\_302+303\_env\_S9\_annex\_I provided by KEMI). Measured data UK: Environment Agency inventory 2001;
- b) Measured data indicated in bold/italic are most of the time best estimates based on a combination of modelled and measured data;
- c) In case no measured data were available the highest measured emission factor (i.e. France: 0.18 g tonne<sup>-1</sup>) has been applied. This was the case for Austria, Finland, Italy and Luxembourg;
- d) Please note that recently measured data came available for Austrian incinerators which show emissions that are much lower, i.e. 4.2 kg year<sup>-1</sup> (Stubenvoll et al., 2002). Since the current air emissions for the EU 16 already have a negligible contribution to the overall cadmium air emission from all sources (see Table 3.61) in the EU, the regional calculations were not recalculated (the modelled data were kept as such). Only the local emissions were changed.

The total amount of MSW being incinerated in 1995-2001 for the EU-16 was 39,121 ktonnes corresponding with an overall EU incineration share of 24.4%. Based on the calculations above the cadmium emission to the air compartment due to this incineration activity is 3.2 tonnes Cd on a yearly basis.

The observed differences reflect the current technological improvements that have been made in the abatement of air emissions. For example Spain reported that in 2000 almost all incinerators included an active carbon step (Lipor II, personal communication, 2002). The large difference between the UK and France could also be explained by less stringent maximum emission levels in France. The figure of 3,231 kg Cd/year is taken forward for the calculations.

Based on the emission factor ( $\text{g tonne}^{-1}$ ) calculated for each country, the cadmium emission to air has been calculated for the 100% scenario (see **Table 3.26**).

Table 3.26 Cadmium emissions to air (in  $\text{kg year}^{-1}$ ) in Europe due to incineration of MSW. Scenario 100% incineration

Country	MSW incinerated (ktonnes wet wt.)	Emissions ( $\text{kg year}^{-1}$ ) Scenario 100%
Austria	1,578	283
Belgium	2,842	131
Denmark	2,091	363
Finland	1,690	296
France	34,133	6,085
Germany	28,000	525
Greece	3,561	641
Ireland	1,432	258
Italy	22,717	4,091
Luxembourg	185	33
The Netherlands	4,995	69
Norway	2,217	243
Portugal	3,663	11
Spain	18,804	764
Sweden	2,700	10
UK	29,450	216
Total EU-16	160,058	14,018

Based on the calculations above the cadmium emission to air in a 100% incineration scenario would result in an emission of 14 tonnes Cd/year.

#### *Emissions from wastewater*

Emissions to water results essentially from the discharge of wastewater from incineration plants with wet flue gas cleaning systems. The wastewater has been shown to be contaminated with metals and inorganic salts and have high acidity's or alkalinity's (Reimann, 1987). The main sources of wastewater from incinerators are from flue gas treatment as flue gas scrubber water, e.g. alkaline scrubbing of the gases to remove acid gases, and the quenching of incinerator ash. Water pollution from incinerators is generally not regarded as an important problem, because the

limited amount of wastewater generated is of the order of 0.5-2.5 m<sup>3</sup> per tonne of municipal waste incinerated (Williams, 1998). Reimann (2002) reported a water consumption of 1.1 m<sup>3</sup>/tonnes for the FGCS and 0.25 m<sup>3</sup>/tonne as boiler water. Stubenvoll et al. (2002) reported amounts of waste water between 0.3-0.4 m<sup>3</sup>/tonne. In the BREF document on waste incineration (BREF, 2005) volumes between 0.15-0.3 m<sup>3</sup> has been reported. As a worst case assumption the highest volume of wastewater generated (i.e. 2.5 m<sup>3</sup>) is used to calculate the regional contributions. For the local assessment both a lower limit (i.e. ± 0.5 m<sup>3</sup>) as the higher limit is used to calculate the dilution factors (see **Table 3.93**).

Reported wastewater cadmium concentrations (before treatment) are given in **Table 3.27**.

Table 3.27 Average cadmium concentrations in incinerator wastewater (mg L<sup>-1</sup>) (influent) before treatment

	Cd concentration (mg L <sup>-1</sup> )	Reference
Flue gas scrubber water	0.46	Ozvacic et al. (1985)
	0.5	Reiman (1989)
	0.17	Novem/RIVM (1992) cited in Anthonissen and Meyer (1993)
	0.303 (incinerator 1) (average concentration 3 samples)	Aminal (1994)
	0.117 (incinerator 2) (average concentration 3 samples)	Aminal (1994)
	0.45 (stage 1 acid scrubber phase) (average concentration 104 measurements) min-max = < 0.01-0.76 0.37 (stage 2 alkaline scrubber phase) (average concentration 104 measurements) min-max = 0.1-0.62	Reimann (2002)
P50 (of average values)	0.3	Selected for regional calculations
P90 (of average values)	0.47	Selected for local calculations

Reduction of metal concentrations and mercury/cadmium concentration is usually through neutralisation via precipitation with calcium hydroxide in the presence of organic sulphides (e.g. the additive TMT<sub>15</sub> (trimercaptotriazine) (Reimann, 1987, BREF, 2005). Treatment of an effluent with an average cadmium concentration (104 measurements) of 0.45 mg L<sup>-1</sup> with TMT resulted in a cadmium concentration of < 0.01 mg L<sup>-1</sup> indicating a removal efficiency of at least 98.8%<sup>32</sup> (Reimann, 2002). For the calculations in this report it will be assumed that 98.8% of the cadmium is removed to sludge going to a hazardous landfill and that 1.2% remains in the wastewater. This results in effluent concentration of approximately 0.004 mg L<sup>-1</sup> (for the median value) and 0.0056 mg L<sup>-1</sup> (for the P90 value)<sup>33</sup>. Reported Cd concentrations in the effluents of three Austrian MSW incinerator plants (reference year 2000) are 4 to 5.6 times lower and were respectively < 0.001 mg L<sup>-1</sup>, 0.001 mg L<sup>-1</sup> and < 0.05 mg L<sup>-1</sup> (Stubenvoll et al., 2002). Measured effluent concentrations for two incinerators in Norway (Brobekk and Klemterud) in the Oslo region are a factor 2.5 lower and were 0.00159 mg L<sup>-1</sup> and 0.00158 mg L<sup>-1</sup>, respectively (Personal communication Jon-Ivar Andersen, Email 03-03-2003).

<sup>32</sup> For the calculation the detection limit value was divided by two.

<sup>33</sup> This value is also well below the emission limit of 0.05 mg L<sup>-1</sup> (EC, 2000).

The annual releases of cadmium to water for the different countries through the incineration of MSW are presented in **Table 3.28** and **Table 3.29** for two scenarios: 24.4% incineration and 100% incineration. Since 89% of the incinerated MSW is followed by some kind of semi dry or wet FGCS it was assumed that for all countries the total incinerator process produced wastewater.

As indicated above for the regional emissions it has been assumed as a worst case estimate that 2.5 m<sup>3</sup> waste water per tonne<sub>wet wt.</sub> of MSW is generated. For the regional calculations the median influent concentration of 0.3 mg L<sup>-1</sup> has been used (i.e. effluent concentration of 0.004 mg L<sup>-1</sup>). For the local calculations (see Section 3.1.3.2) the 90<sup>th</sup> percentile influent concentration of 0.47 mg L<sup>-1</sup> has been used (i.e. 0.0056 mg L<sup>-1</sup> effluent concentration). However, since information on measured effluent concentration are limited an additional scenario have been developed as sensitivity analysis with the maximum measured influent concentration of 0.76 mg L<sup>-1</sup> (i.e. 0.009 mg L<sup>-1</sup> in the effluent)

Table 3.28 Overall cadmium emissions to water and sludge (in kg year<sup>-1</sup>) in Europe due to incineration of MSW. Scenario current incineration 24.4%

Country	MSW incinerated ((ktonnes <sub>wet wt.</sub> )	Influent WWTP (kg year <sup>-1</sup> )	Emissions to water (kg year <sup>-1</sup> ) Scenario 24.4%	Emissions to sludge (kg year <sup>-1</sup> ) Scenario 24.4%
			1.2 %	98.8%
Austria	479	359	4	355
Belgium	1,369	1,027	12	1,014
Denmark	1,730	1,298	16	1,282
Finland	80	60	1	59
France	10,781	8,086	97	7,989
Germany	12,000	9,000	108	8,892
Greece	0	0	0	0
Ireland	0	0	0	0
Italy	1,949	1,462	18	1,444
Luxembourg	123	92	1	91
The Netherlands	3,859	2,894	35	2,860
Norway	374	281	3	277
Portugal	1,060	795	10	785
Spain	1,327	995	12	983
Sweden	1,400	1,050	13	1,037
UK	2,590	1,943	23	1,919
Total EU-16	39,121	29,341	352	28,989

Based on the calculations above the cadmium emission due to this incineration of MSW is approximately 0.35 tonnes Cd/year to water and 28.9 tonnes Cd/year to sludge.

Table 3.29 Overall cadmium emissions to water and sludge (in kg year<sup>-1</sup>) in Europe due to incineration of MSW. Scenario 100% incineration

Country	MSW incinerated (ktonnes <sub>wet wt.</sub> )	Influent WWTP (kg year <sup>-1</sup> )	Emissions to water (kg year <sup>-1</sup> ) Scenario 100%	Emissions to sludge (kg year <sup>-1</sup> ) Scenario 100%
			1.2 %	98.8%
Austria	1,578	1,184	14	1,169
Belgium	2,842	2,132	26	2,106
Denmark	2,091	1,568	19	1,549
Finland	1,690	1,268	15	1,252
France	34,133	25,600	307	25,293
Germany	28,000	21,000	252	20,748
Greece	3,561	2,671	32	2,639
Ireland	1,432	1,074	13	1,061
Italy	22,717	17,038	204	16,833
Luxembourg	185	139	2	137
The Netherlands	4,995	3,746	45	3,701
Norway	2,217	1,663	20	1,643
Portugal	3,663	2,747	33	2,714
Spain	18,804	14,103	169	13,934
Sweden	2,700	2,025	24	2,001
UK	29,450	22,088	265	21,822
Total EU-16	160,058	120,044	1,441	118,603

Based on the calculations above the cadmium emission to water in a 100% incineration scenario would result in an emission of approximately 1.4 tonnes Cd/year to water and 118.6 tonnes Cd/year to sludge.

#### *Delayed emissions from incinerator residues*

While the emissions with flue gas are immediate, emissions from the residual fractions will be delayed and may result in a diffuse emission of cadmium to the environment. In this study a distinction is only made between bottom ash and fly ash. Other flue gas cleaning products generated in the process of removing acid gases are not specifically addressed.

A number of studies have been carried out concerning the fate and distribution of cadmium in municipal solid waste incineration plants. The distribution of cadmium as a mass balance for incinerators equipped with different FGCs is given in **Table 3.30**.

Table 3.30 Partitioning of cadmium (%) in the various output fractions of a MSW incinerator

Flue gas (%)	Bottom- and boiler ash (%)	Fly ash (%)	Waste water (%)	Sludge and salt (%)	FGCS	Reference
12.1	10.8	77.1	/	/	ESP	Zimmerman (1996)
12	12	76	/	/	ESP	Brunner and Monch (1986)
< 2.5	15	80	N.A.	3	/	IAWG (1995)
0.1	21.5	78.5	< 0.1	N.A.	ESP/WET /AC	Morf et al. (2000)
0.02	15	72	< 0.001	13	ESP/WET	VROM (1997)
2.6	5.5	69.9	0	21.4	ESP/WET	Wiaux (1997)
0	7	89	0	4	ESP/WET	Lemann et al. (1995)

/ Not applicable;  
 N.A. Not available;  
 ESP Electrostatic precipitator;  
 WET Wet scrubbing;  
 AC Active carbon.

In general the largest fraction of cadmium can be found in FGCS residues such as fly ash (77-89%), i.e. the particulate material collected by electrostatic precipitators also called ESP dust. On average 78% of the cadmium can be found in the fly ash and 12% in the bottom ash. If only the solid residues are considered this ratio becomes 87% fly ash and 13% bottom ash.

Data on amounts of bottom ash and fly ash generated in the different Member States (ISWA, 2002) are presented in **Table 3.31**.

Table 3.31 Distribution of bottom ash and fly ash for different Member States (reference year 1999) based on ISWA (2002)

Country	Total waste incinerated (ktonnes wet wt.) <sup>a</sup>	Bottom ash (ktonnes dry wt.)	Fly ash (ktonnes dry wt.)	Bottom ash (%)	Fly ash (%)
Austria	450	107	8	23.9	1.8
Belgium	191	25	5	13.1	2.6
Denmark	2,359	473	63	20.1	2.7
France	10,852	1,840	210	17.0	1.9
Germany	12,853	3,200	366	24.9	2.8
UK	1,074	289	31	26.9	2.9
The Netherlands	2,379	590	84	24.8	3.5
Norway	144	25	4	17.0	2.6
Portugal	322	59	27	18.4	8.5
Spain	996	188	59	18.8	5.9
Sweden	1,968	371	87	18.9	4.4
Total	33,589	7,167	944	21.3	2.8

a) Household waste and industrial waste

In general it can be concluded from **Table 3.31** that on average bottom ash constitutes 21.3% by weight of the waste input and fly ash 2.8% by weight of the waste input. Van der Poel (1999) reports similar figures.

These figures were used to calculate the amount of bottom- and fly ash produced by incineration MSW (see **Table 3.32**).

Table 3.32 Distribution of bottom ash and fly ash for different Member States Scenario under current incineration scenario of 24.4%

Country	MSW incinerated (ktonnes <sub>wet wt.</sub> )	Bottom ash (ktonnes <sub>dry wt.</sub> )	Fly ash (ktonnes <sub>dry wt.</sub> )
Austria	479	102	13
Belgium	1,369	292	38
Denmark	1,730	368	48
Finland	80	17	2
France	10,781	2,296	302
Germany	12,000	2,556	336
Greece	0	0	0
Ireland	0	0	0
Italy	1,949	415	55
Luxembourg	123	26	3
The Netherlands	3,859	822	108
Norway	374	80	10
Portugal	1,060	226	30
Spain	1,327	283	37
Sweden	1,400	298	39
UK	2,590	552	73
Total EU-16	39,121	8,333	1,095

From **Table 3.32** it can be concluded that at present 8,333 ktonnes of bottom ash and 1,095 ktonnes of fly ash have to be disposed of on a yearly basis. The cadmium concentrations in the fly ash and bottom ash are calculated based on the cadmium balances for scenario 1 (24.4% incineration) presented in **Figure 3.3**. For bottom ash a concentration of 3.8 mg Cd/kg<sub>dry wt.</sub> can be calculated (31,366 kg Cd/8,333 ktonnes bottom ash). For fly ash a concentration of 192 mg Cd/kg<sub>dry wt.</sub> is obtained (209,908 kg Cd/1,095 ktonnes).

These figures are in concordance with data reported in the literature. Reported cadmium concentrations in fly ash range from 50 to 1,000 mg kg<sup>-1</sup><sub>dry wt.</sub> (EEA, 2000) but can be substantially higher (EPA, 1991). Cadmium concentrations in bottom ash are in general lower. Ranges reported in the Netherlands are 0.1-25 mg kg<sup>-1</sup><sub>dry wt.</sub> for bottom ash and 8-337 mg kg<sup>-1</sup><sub>dry wt.</sub> for fly ashes (Anthonissen and Meijer, 1993; Verhagen and Meijer, 2000). Typical cadmium concentrations in bottom ash and fly ash as reported by the International Ash Working Group are 0.3-70.5 mg kg<sup>-1</sup><sub>dry wt.</sub> for bottom ash and 50-450 mg kg<sup>-1</sup><sub>dry wt.</sub> for fly ash (IAWG, 1997). The calculated concentrations (3.8 mg kg<sup>-1</sup><sub>dry wt.</sub> for bottom ash and 192 mg kg<sup>-1</sup><sub>dry wt.</sub> for fly ash) are well in the range of these literature values.

Most of the fly ash generated by incinerators in the EC is land-filled with or without prior treatment. For fly ash it is general practice that they are placed in hazardous waste landfills or used for reclamation of old mine shafts or quarries. If treated the most common treatment form in the EC Member States is probably solidification/stabilisation with hydraulic binders (cement or cement-like substances) often supplemented with the mixing of various additives (Argus,

2000). However, in some countries fly ash are (still) re-used. The Netherlands produced in 1999 90 ktonnes of fly-ash from which 41 ktonnes (= 45%) was re-used with the largest application being as fill material in asphalt (25-30%) (VVAV, 2000, Anthonissen and Meijer, 1993). Belgium and the UK also indicate a re-use of fly ash (Jacobs et al., 2001; EA 2002). In the framework of the upcoming legislation it is, however, unlikely that the use of fly ashes in asphalt will be a viable option for the future.

The use of processed bottom ash in engineering applications just started in some countries like the UK whereas its use in the Netherlands in civil engineering started since the 1980's. The ashes are used unbounded as a bulk fill, for example, to construct embankments, as a substitute aggregate or for bound uses through incorporation into road paving (tarmac, asphalt) or construction blocs.

In the UK bottom ash processing in the year 2000 reached 270 ktonnes or 42% of the bottom ash production for that year (EA 2002). The percentage of bottom ash recycled in other countries such as the Netherlands, Denmark and France is respectively 100%, 70% and 50% (EA, 2002). In Germany approximately 80% of bottom ash is being re-used mainly in road and street construction and 20% of the bottom ash is presently deposited into landfills (personal communication with Bernt Johnke, Umweltbundesamt, Germany, July 31, 2002).

The re-use and/or land-filling of incineration residues may result in a long-term diffuse emission potentially contaminating groundwater, surface water and soil. A field study examining the leaching from two road construction sites showed that substantial leaching of metals from the road construction occurred but, transport through the underlying soil layer was limited due to soil-metal binding processes (Wesselink, 1995). In general two approaches can be used to determine the composition – and thus the potential future emissions -of residual leachates: (1) the generation of simulated leachates, and (2) the study of field-generated leachates. Most often laboratory leachability simulation studies are being used to understand the potential leachability of cadmium in MSW ash. But because a number of such leaching procedures exist, the data generated from these leachate tests have been criticised for the variability in experimental conditions, and for their inability to predict long-term leaching behaviour for all type of disposal options (EPA, 1991). Whether or not the results of these laboratory tests underestimate or overestimate the potential release of contaminants is still under discussion. But most often, the re-use of incineration residues is dependent on the outcome of these leaching tests. If the results of the leaching test are exceeding an imposed limit the bottom- or fly ash is classified as hazardous waste and should be land-filled in a hazardous landfill. For example some countries such as Belgium and the Netherlands provide guidance on acceptable contaminant levels in construction materials in terms of potential impacts on health and the environment. Both the Netherlands and Belgium rely for their conclusion, on whether the material can be used as construction material or not, on the outcome of the column test NEN 7343 (VLAREA, 1998, Aalbers et al., 1996). For non-prefabricated construction materials (unbounded use) maximal allowable cadmium emissions of 0.03 -0.07 mg kg<sup>-1</sup> have been reported. For prefabricated construction materials 1.1 mg/m<sup>2</sup> is reported. Furthermore the total cadmium concentration should preferentially below the target value of 10 mg kg<sup>-1</sup> dry wt. In Germany similar legislation is in place. For cadmium the target value for re-use is 20 mg kg<sup>-1</sup> dry wt. and the cadmium concentration in the eluate should not exceed 5 µg L<sup>-1</sup> (LAGA 1994 cited in Förstner and Hirschmann, 1997).

It can be concluded that at present 8,333 ktonnes of bottom ash and 1,095 ktonnes of fly ash have to be disposed of on a yearly basis. The cadmium concentrations in the bottom ash and fly ash are respectively 3.8 mg Cd/kg dry wt and 192 mg Cd/kg dry wt. The re-use and/or land-filling

of incineration residues may result in a long-term diffuse emission potentially contaminating groundwater, surface water and soil.

The use of incineration residues is only allowed if the results of leaching tests are favourable. How limit values can be established in relation to the results of leaching tests have also not been addressed. The impact of the expected increase in cadmium content of bottom ash and fly ash (see subsection “Future emissions” under Section 3.1.2.2.5) on the re-usability of these incineration residues has also not been quantified because it is believed that this issue represents a general waste management problem rather than belonging to a substance specific risk assessment. For example most often the classification as hazardous waste or the re-use of incinerator residues is governed by the leachability of other metals as well such as copper, lead or zinc (OVAM, 2001; RIVM/LAE, 1998). The emissions associated with land-filling of incineration products have not been assessed.

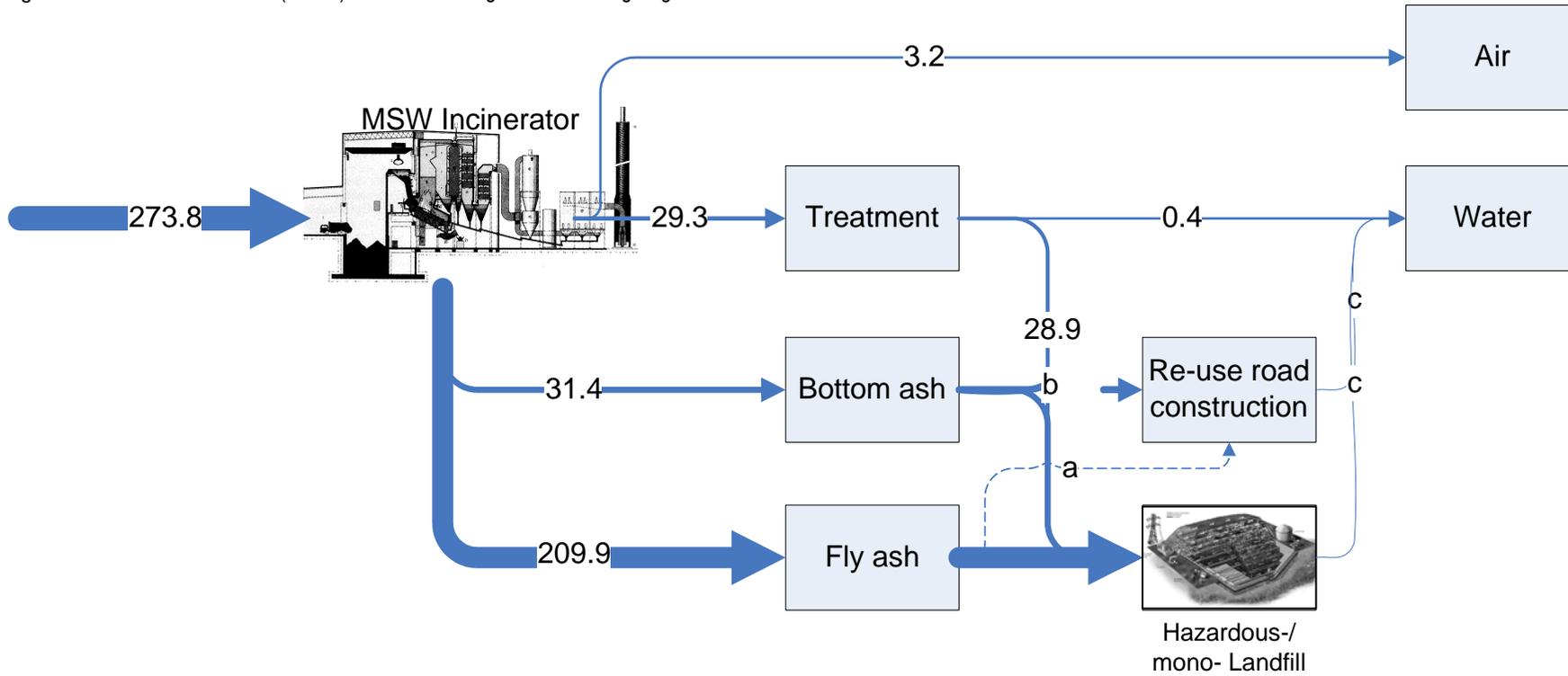
#### *Summary of overall cadmium emissions due to incineration of MSW*

An overview of the overall cadmium releases to the different compartments due to incineration of MSW containing 10g/Cd tonne<sub>dry wt</sub> is summarised for the different scenarios in **Figures 3.4-3.5**.

An example calculation is given hereunder for the current incineration practice (24.4%):

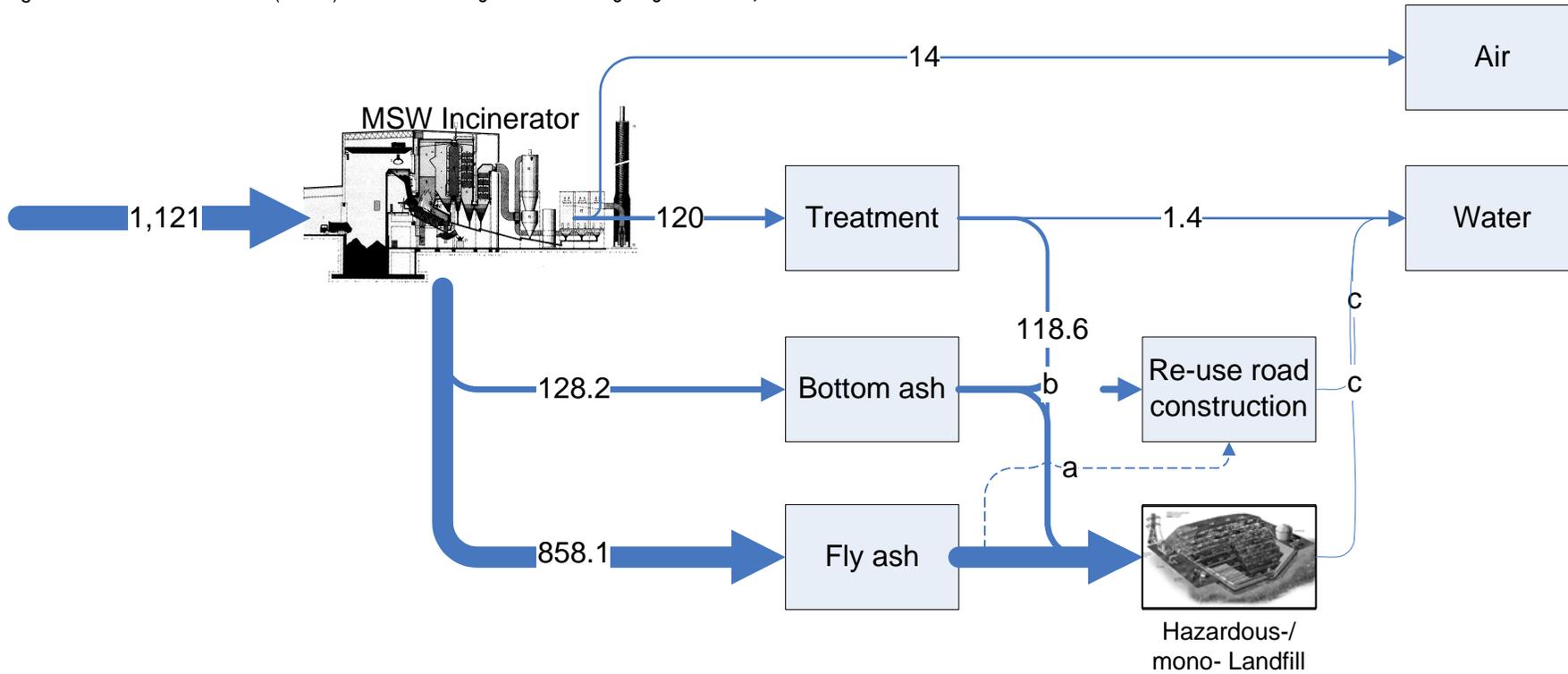
- Cd-content MSW = 10 g tonne<sup>-1</sup><sub>dry wt</sub>;
- Total volume of waste incinerated = 39,121,000 tonnes wet weight = 27,384,700 tonnes<sub>dry wt</sub>;
- Cadmium load present in MSW: 10 g tonne<sup>-1</sup><sub>dry wt</sub> · 27,384,700 tonnes<sub>dry wt</sub> = 273.8 tonnes Cd;
- Direct cadmium emissions to air = 3,231 kg (see **Table 3.25**) = 3.2 tonnes;
- Direct cadmium emissions to water = 352 kg (see **Table 3.28**) = 0.4 tonnes;
- Cadmium load to hazardous sludge = 28,989 kg (see **Table 3.28**) = 28.9 tonnes;
- Cadmium flow to incinerator residues = 273.8 tonnes Cd – 3.2 tonnes – 0.4 tonnes – 28.9 tonnes = 241.3 tonnes;
- Cadmium load to bottom ash = 241.3 tonnes · 0.13 = 31.4 tonnes;
- Cadmium load to fly ash = 241.3 · 0.87 = 209.9 tonnes.

Figure 3.4 Overall cadmium flow (tonnes) due to incinerating MSW containing 10 g Cd/tonne - Scenario 24.4 % incineration.



- a) Most often fly ash is land-filled but some countries (The Netherlands, UK, and Belgium) still re-use a part of their fly ash;
- b) Depending on the leaching results bottom ash can either be land-filled or re-used in road construction;
- c) The delayed water emissions of re-use in road constructions and hazardous landfills have not been quantified.

Figure 3.5 Overall cadmium flow (tonnes) due to incinerating MSW containing 10 g Cd/tonne<sub>dry wt</sub> -100% incineration.



- a) Most often fly ash is land-filled but some countries (The Netherlands, UK and Belgium) still re-use a part of their fly ash;
- b) Depending on the leaching results bottom ash can either be land-filled or re-used in road construction;
- c) The delayed water emissions of re-use in road constructions and hazardous landfills have not been quantified (c).

*Allocation of current air emissions to a regional/local scale*

The allocation of the total EU air emission amount to the regional and the local scale has been performed by dividing the regional emissions with the number of incinerators per country (see **Table 3.33**). Measured data are indicated in bold/italic. For those countries where no measured data were available an emission factor of 0.18 g Cd/tonne MSW<sub>wet wt.</sub> has been used.

Table 3.33 Allocation of air emissions to regional/local scale. Scenario current incineration 24.4%

Country	No. incineration plants <sup>a</sup>	Air emissions/country (kg year <sup>-1</sup> ) scenario 24.4% (see Table 3.22)	Air emissions/ plant (kg year <sup>-1</sup> .plant)
Austria <sup>b</sup>	3	86 h	28.6 h
Belgium	18	63	3.5
Denmark <sup>f</sup>	31	300	9.7
Finland <sup>c</sup>	1	14	14
France	117	1,922	16.4
Germany	60	300	5
Italy	62	351	5.7
Luxembourg <sup>c</sup>	1	22	22
The Netherlands	11	53	4.8
Norway <sup>d</sup>	8	41	5.1
Portugal	2	3.2	1.6
Spain	8	54	6.8
Sweden <sup>e</sup>	22	5	0.2
UK <sup>g</sup>	11	17	1.5
<b>Total</b>	<b>355</b>	<b>3,231</b>	
<b>Average</b>	<b>25 plants/country (=355/14)</b>	<b>231 kg year<sup>-1</sup>/country (= 3,231/14) 10% rule = 323</b>	<b>9.1 kg year<sup>-1</sup>/plant = (3,231/355)</b>

a) Based on ISWA 2002;

b) Schuster, 1999;

c) Juniper 1997;

d) SFT, 2002;

e) RVF, 2002;

f) Waste Statistics 1999, Danish EPA (2001);

g) Environment Agency 2002;

h) Actual measured data have come available recently (Stubenvoll et al., 2002). These values indicate a cadmium emission of 4.2 kg year<sup>-1</sup> or, on average, 1.4 kg year<sup>-1</sup> plant.

Since emissions incineration plants are not (yet) considered in the TGD emission tables, the following approach is proposed to allocate incineration plant emissions to the regional/local scale. On the basis of country specific information, for 14 EU countries, a country average number of incineration plants of 25 can be calculated. In these 25 plants a hypothetical amount of 2,794 ktonnes of MSW (see **Table 3.25**: "MSW incinerated" divided by 14 countries = 39,121/14) can be incinerated, thereby emitting a Cd amount to air of 231 kg year<sup>-1</sup> (Scenario 24.4%). Comparing these data to the emitted Cd amounts for individual countries, it seems that 9 out of 14 countries are covered, except for Denmark, France, Italy and Germany. Measured/estimated data in Belgium are between 1-12 kg/plant. For the UK typically concentration between 0.5 and 5 kg/plant are reported. Although France is accounting for 59% of

the total EU air emission it is proposed to use the 10% rule to derive a reasonable worst case emission estimate of the regional emission since incineration activities (large number of site) are reasonably spread over the EU territory. Applying the TGD 10% rule to the total EU air emission amount gives a regional air emission amount of 323 kg year<sup>-1</sup> which is comparable with the calculated 231 kg year<sup>-1</sup> per region. On the basis of country specific information for incineration plants (air emission and number of incineration plants) an EU weighted average emitted Cd amount per plant of 9.1 kg year<sup>-1</sup> can be calculated. In comparison with the average emission per plant in each country it seems that Luxembourg, France, Denmark and Finland are the countries not completely covered. Individual measured data were available for France. The 90<sup>th</sup> percentile of these measurements is 36.7 kg year<sup>-1</sup>/plant. Measured data in Austria (Stubenvoll et al., 2002) indicate an emission of 1.4 kg year<sup>-1</sup>. This value has been used for the local PEC calculations for Austrian incinerators.

The country specific local air emission estimates ranging between 0.2-16.4 kg year<sup>-1</sup>/plant have been used in the local PEC calculations (see Section 3.1.3.2.3). These values have been taken forward in the risk characterisation together with the generic scenario based on the 10% rule and average emission of 9.1 kg Cd/year.plant. Since France contributes for 59% of the total emission to air and individual measured data were available an additional scenario for France based on these measured data was also taken forward into the risk characterisation (i.e. 36.7 kg)

In the 100% incineration scenario the allocation from the EU scale to the regional scale is performed applying the 10% rule to the EU emission amount. A regional emission amount of 1,402 kg year<sup>-1</sup> is calculated. Comparing this value to the country specific emission amounts shows that 14 out of 16 countries are covered. Larger air emissions have been obtained for France and Italy. In the 100% incineration scenario it is assumed that the number of incineration plants is proportionally increased to the amount of MSW to incinerate. Hence, on a local scale the exposure scenario will be similar to that from the 24.4% incineration scenario.

Measured cadmium loads to the surface water was lacking for most incinerators. Therefore the calculated water emissions (see **Table 3.28**) based on a generic median effluent concentration of 0.004 mg L<sup>-1</sup>. have been used to calculate the EU emissions to surface water using the 10% rule in analogy to the air emission estimate. For the local scenario (PEC calculation and risk characterisation) the 90<sup>th</sup> percentile Cd effluent concentration (0.005 mg L<sup>-1</sup>= (1.2 · 0.42)/100) has been used.

A summary of all continental and regional emissions to air and surface water is given in **Table 3.34**.

Table 3.34 Total annual amount of Cd emissions to air and water within the EU from incineration plants

Scenario	Released amount Cadmium (kg/y)	Continental (90%) (kg/y)	Regional (10%) (kg/y)
Air			
24.4% incineration	3,231	2,908	323
100% incineration	14,018	12,616	1,402
Water			
24.4% incineration	352	317	35
100% incineration	1,441	1,297	144

Table 3.34 continued overleaf

Table 3.34 continued Total annual amount of Cd emissions to air and water within the EU from incineration plants

Scenario	Released amount Cadmium (kg/y)	Continental (90%) (kg/y)	Regional (10%) (kg/y)
	Landfill		
24.4% incineration	240,465	216,419	24,047
100% incineration	1,104,947	994,452	110,495

### Contribution of NiCd batteries to the overall cadmium emissions

With the assumption that NiCd batteries account for 10-50% of the total MSW cadmium content, the contribution of NiCd batteries can be calculated by multiplying the overall cadmium emissions as presented in **Figures 3.3 to 3.6** by 0.1 and 0.5 (**Tables 3.35** and **Table 3.36**).

Table 3.35 Contribution of NiCd batteries to the overall cadmium emissions due to incineration- Scenario 10 mg kg<sup>-1</sup> dry wt. total cadmium in MSW

Scenario	24.4% incineration		100% incineration	
	10%	50%	10%	50%
Allocation key				
Compartment	Direct emissions (kg year <sup>-1</sup> )			
Air	323	1,617	1,402	7,009
Water	35	176	144	721
Compartment	(kg)			
Cadmium going to landfill	24,047	120,233	110,495	552,473

Table 3.36 Contribution of NiCd batteries to the continental and regional cadmium emissions due to incineration. Scenario 10 mg kg<sup>-1</sup> dry wt. total cadmium in MSW

Scenario		Released amount Cadmium (kg/y)	Continental (90%) (kg/y)	Regional (10%) (kg/y)
		Air		
24.4% incineration	0.1	323	291	32
	0.5	1,617	1,455	162
100% incineration	0.1	1,402	1,262	140
	0.5	7,009	6,308	701
		Water		
24.4% incineration	0.1	35	31.5	4
	0.5	176	158	18
100% incineration	0.1	144	130	14
	0.5	721	649	72
		Landfill		
24.4% incineration	0.1	24,047	21,642	2,405
	0.5	149,113	134,202	14,911
100% incineration	0.1	110,495	99,456	11,050
	0.5	552,473	497,226	55,247

### Future emissions

The future total cadmium concentration in MSW is expected to range between 13.2 and 24 g tonne<sup>-1</sup> dry wt (see **Table 3.20**) with an estimated specific contribution of NiCd batteries of respectively 4.2 g tonne<sup>-1</sup> dry wt. (= 4.2/13.2 = 32%) and 15 g tonne<sup>-1</sup> DW (= 15/24 = 63%).

As a worst case exercise the future emissions due to the expected increase of cadmium in the MSW for a 100% incineration scenario are presented.

#### *Future cadmium emissions to air*

There is no evidence for increased cadmium air emission due to an increase in cadmium load in the MSW unless the gas cleaning system fails (van der Poel, 1999). Therefore these emissions can be dealt with irrespective of the cadmium concentration in the MSW (an increase in cadmium concentration will of course be translated into higher cadmium concentrations in the solid residues). Higher overall cadmium air emissions are expected to occur related to an increase in the incineration practice and the higher amount of MSW that is likely to be generated in the future (EEA, 2000). However, the latter has not been taken into account. It is assumed that each year the same amount of MSW is being incinerated (i.e. 160,058 ktonnes<sub>wet wt.</sub>) resulting in an overall emission of 14 tonnes Cd/year (see **Table 3.26**).

#### *Future cadmium emissions from wastewater*

Due to an increased cadmium load it can be expected that the washing water from the scrubber system will contain a higher cadmium concentration. If a linear relationship between the effluent concentration and the cadmium content in the MSW is assumed the cadmium concentration in the untreated effluent can then be adjusted for an altered waste composition, based on the ratio of the cadmium concentration in the influent for the current reference situation (10 g tonne<sup>-1</sup> dry wt. cadmium). The equation hereunder demonstrates how future changes in cadmium wastewater concentration (before treatment) due to changing cadmium content of the MSW can be calculated with the assumption of a linear relationship (see **Table 3.37**).

$$CdConc_{Future,wastewater} = \frac{CdConc_{Present,wastewater}}{CdConc_{Present,MSW}} \times CdConc_{Future,MSW}$$

CdConc <sub>Future, Wastewater</sub> :	Future cadmium concentration in the wastewater (mg L <sup>-1</sup> )
CdConc <sub>Present, wastewater</sub> :	Present cadmium concentration in the wastewater (mg L <sup>-1</sup> ) = 0.3 mg L <sup>-1</sup> (see Table 3.24)
CdConc <sub>Future, MSW</sub> :	Future cadmium concentration in MSW (g) <sup>34</sup>
CdConc <sub>Present, MSW</sub> :	Present cadmium concentration in MSW (g) = 10 g tonne <sup>-1</sup>

Table 3.37 Future cadmium content of wastewater produced by the incineration process (influent of on-site treatment plant)

Collection (%)	Total future Cd content in MSW (g tonne <sup>-1</sup> )	Cd concentration in wastewater <sup>a</sup> (mg L <sup>-1</sup> )
10	24	0.72
75	13.2	0.4

a) Before treatment

<sup>34</sup> Obtained via the modelling of future NiCd waste arisings (see subsection "Forecasts of future battery waste analysis" under Section 3.1.2.2.5). Remark: note that the total amount of the MSW will probably also further increase (EEA, 2000) but this has not been taken into account.

After treatment 98.8% of the cadmium will be removed resulting in effluent concentrations of 0.005-0.009 mg L<sup>-1</sup>.<sup>35</sup> These effluent concentrations have been used for the regional scenario. For the local scenarios future effluent concentrations have been calculated based on the current 90<sup>th</sup> percentile influent concentration of 0.47 mg L<sup>-1</sup> resulting in future influent concentrations of 0.62 and 1.13 mg L<sup>-1</sup> (i.e. 0.007- 0.0135 mg L<sup>-1</sup> effluent concentration).

#### *Future cadmium content of residues*

The increase of the cadmium content in the MSW will be translated into an increase in the cadmium concentration of the incineration residues such as bottom ash and fly ash. In **Table 3.38** the expected bottom ash and fly ash concentrations have been calculated based on the assumption that bottom ash constitutes 21.3% by weight of the waste input and fly ash 2.8% by weight of the waste input.

Table 3.38 Future cadmium content (mg kg<sup>-1</sup> dry wt.) of bottom ash and fly ash: current and future scenarios

Total Cd content in MSW (g tonne <sup>-1</sup> )	Scenario	Cd content in bottom ash (mg kg <sup>-1</sup> dry wt.)	Cd content in fly ash (mg kg <sup>-1</sup> dry wt.)
10	24.4% incineration	3.8	192
13.2	100% incineration	5.0	253
24	100% incineration	9.1	463

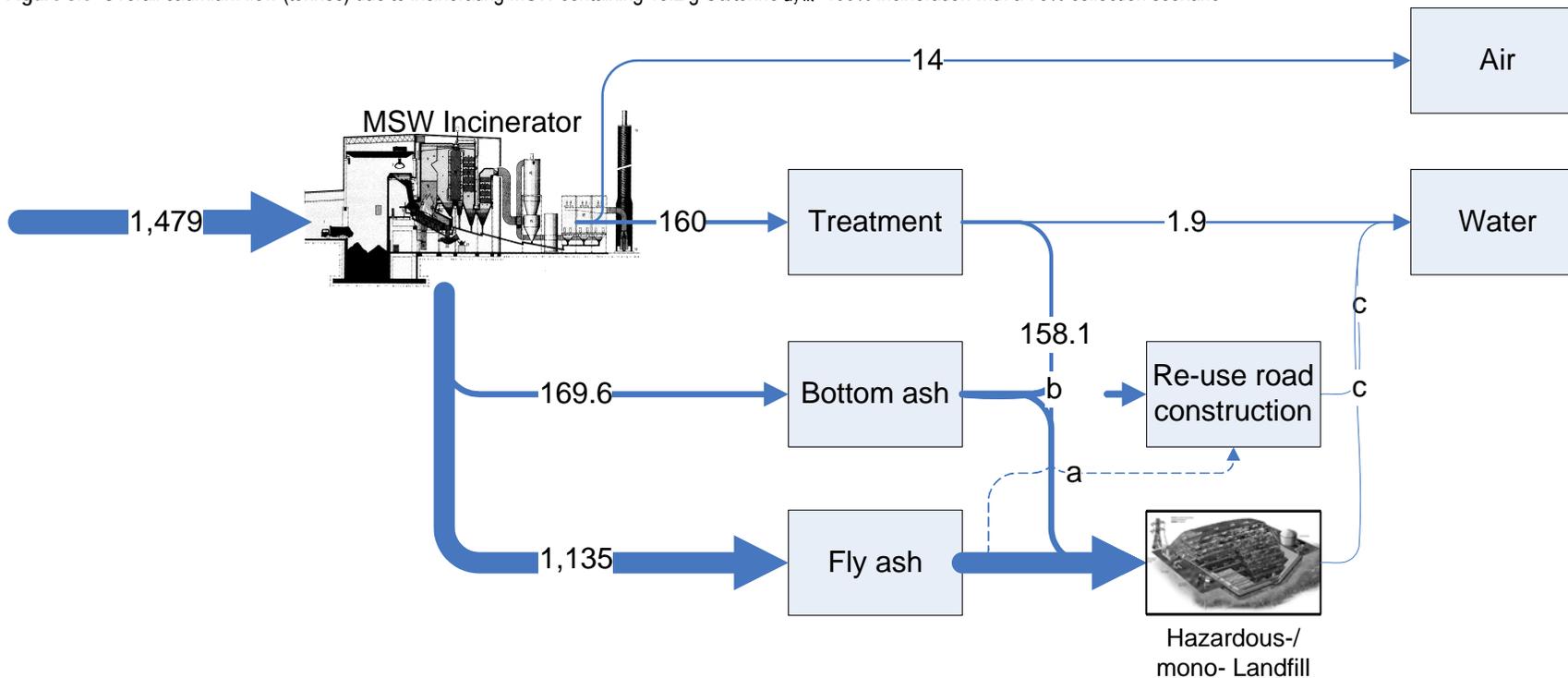
N.B. Shaded cells represent the current scenario.

From these results it can be concluded that the future cadmium content in fly ash and bottom ash is likely to double in the future under the 10% collection scenario (total Cd content in MSW: 24 g tonne<sup>-1</sup>). In case the collection efficiency is 75% (total Cd content in MSW: 13.2 g tonne<sup>-1</sup>) the cadmium content is expected to increase with 25%.

An overview of the future overall cadmium releases for a 100% incineration scenario to the different compartments due to incineration of MSW is summarised for the different scenarios in **Figures 3.6-3.7**.

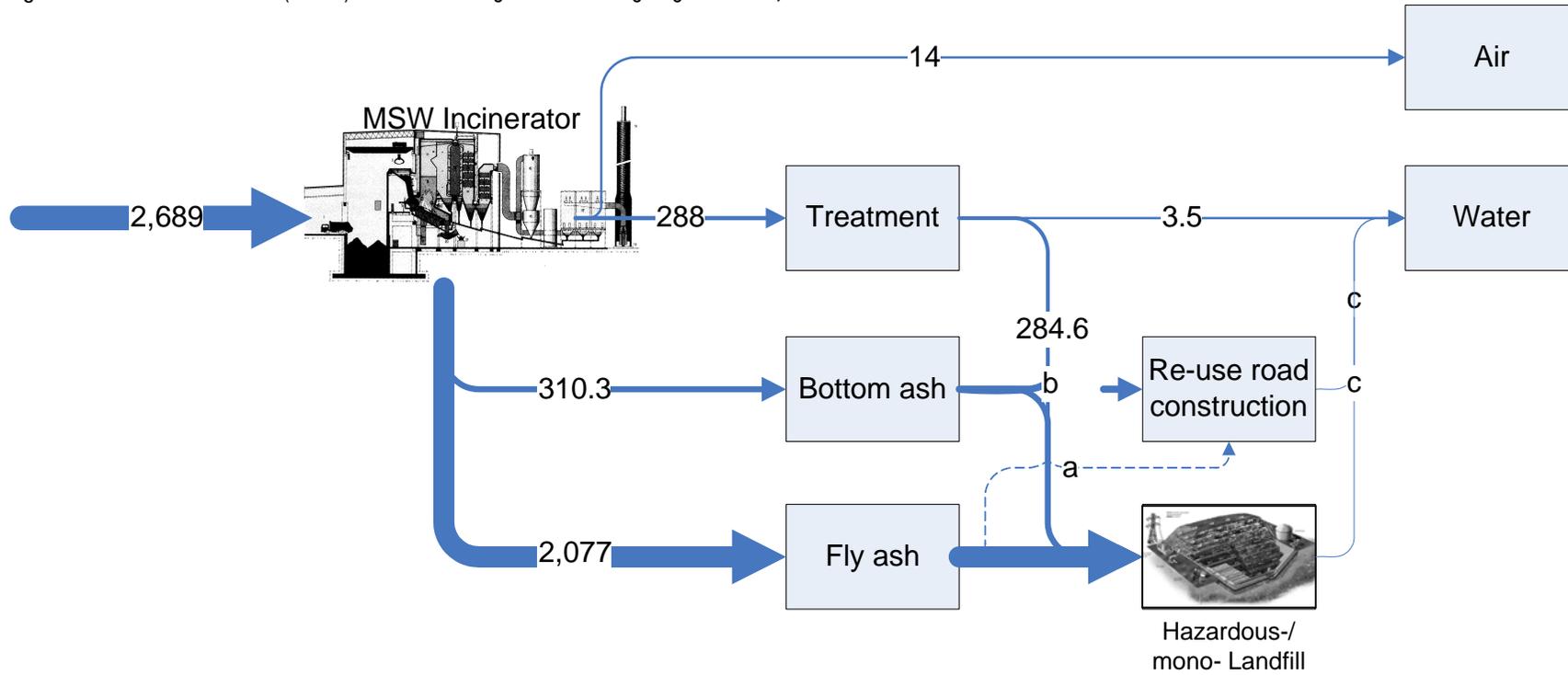
<sup>35</sup> These values are below the current EC limit of 0.05 mg L<sup>-1</sup> (EC, 2000).

Figure 3.6 Overall cadmium flow (tonnes) due to incinerating MSW containing 13.2 g Cd/tonne<sub>dry wt</sub> -100% incineration with a 75% collection scenario



- a) Most often fly ash is land-filled but some countries (The Netherlands, UK and Belgium) still re-use a part of their fly ash;
- b) Depending on the leaching results bottom ash can either be land-filled or re-used in road construction;
- c) The delayed water emissions of re-use in road constructions and hazardous landfills have not been quantified (c).

Figure 3.7 Overall cadmium flow (tonnes) due to incinerating MSW containing 24 g Cd/tonne<sub>dry wt</sub> -100% incineration with a 75% collection scenario



- a) Most often fly ash is land-filled but some countries (The Netherlands, UK and Belgium) still re-use a part of their fly ash;  
 b) Depending on the leaching results bottom ash can either be land-filled or re-used in road construction;  
 c) The delayed water emissions of re-use in road constructions and hazardous landfills have not been quantified (c).

*Allocation of future EU air and water emissions to the continental and regional scale*

For the 100% incineration scenario the allocation from the EU scale to the regional scale is performed applying the 10% rule to the EU emission amount. A regional emission amount of 4,199 kg year<sup>-1</sup> is calculated. Analogous to the air emission estimation, the EU emissions to surface water are allocated to the region using the 10% rule.

Table 3.39 Total annual amount of overall Cd emissions to air and surface water within the EU from incineration plants- Future scenarios

Scenario	Cd content MSW (g tonne <sup>-1</sup> )	Released amount Cadmium (kg year <sup>-1</sup> )	Continental (90%) (kg year <sup>-1</sup> )	Regional (10%)(kg year <sup>-1</sup> )
Air				
100% inc. 75% coll.	13.2	14,018	12,616	1,402
100% inc. 10% coll.	24	14,018	12,616	1,402
Surface water				
100% inc. 75% coll.	13.2	1,921	1,729	192
100% inc. 10% coll.	24	3,457	3,111	346
Landfill				
100% inc. 75% coll.	13.2	1,462,997	1,316,697	146,300
100% inc. 10% coll.	24	2,671,499	2,404,349	240,435

The specific contribution of NiCd batteries for all waste streams of MSW incineration is given in **Table 3.40** and **Table 3.41**.

Table 3.40 Future contribution of NiCd batteries to the overall cadmium emissions due to incineration

Scenario	100% inc. (75% collection, 13.2 g cadmium/tonne MSW dry wt)	100% inc. (10% collection, 24 g Cd/tonne MSW dry wt.)
Allocation key (%)	32	63
Compartment	Direct emissions (kg year <sup>-1</sup> )	
Air	4,486	8,831
Water	615	2,178
Compartment	(kg)	
Cadmium going to landfill	468,159	1,683,044

Table 3.41 Contribution of NiCd batteries to the continental and regional cadmium emissions due to incineration

Scenario	Allocation key (%)	Released amount Cadmium (kg year <sup>-1</sup> )	Continental (90%) (kg year <sup>-1</sup> )	Regional (10%) (kg year <sup>-1</sup> )
Air				
100% inc. 75% coll.	32	4,486	4,037	449
100% inc. 10% coll.	63	8,831	7,948	883
Surface water				
100% inc. 75% coll.	32	615	554	62
100% inc. 10% coll.	63	2,178	1,960	218
Landfill				
100% inc. 75% coll.	32	468,159	421,343	46,816
100% inc. 10% coll.	63	1,683,044	1,514,734	168,304

#### *Overall cadmium emissions from land-filling MSW*

Release of pollutants from a landfill can occur over an indefinite period. Hence, the daily or annual release may result in a very small PEC and does not reflect the long-term emissions of a landfill. For the moment no specific guidance is provided by the TGD on how to quantify the current and future landfill emissions. Due to the large uncertainties associated with this subject, the analysis that is performed in this report should merely be considered as a semi-quantitative approach.

Both regional and local emissions of land-filling have been addressed. Only for the local scenario the issue of dilution in time (long term emissions) has been analysed. The local emissions associated with land-filling MSW are given in this report for three separate time horizons beginning from waste placement:

- Short term time frame (20 years) corresponding roughly to the landfill's period of active decomposition.
- Intermediate term time frame (100 years) corresponding roughly to the life span of a given generation.
- Long term time frame (500 years) corresponding to an indefinite time reference where emissions of any given environmental flow have reached or nearly reached their theoretical yield.

#### *Leachate generation*

Emissions of landfills can occur primarily by generation of landfill gasses and leaching of contaminants. In the case of metals, emissions by generation of landfill gas are negligible in all cases except for Hg and possibly Cd (Baccini et al., 1987, Finnveden, 1996). However, in this

document the pollution via leachate release is being considered as the most important long term flux impacting the environment since production of landfill gas lasts about one to two decades.

Leachate is generated as a result of the expulsion of liquid from the waste due to its own weight or compaction loading (termed primary leachate) and the percolation of water through a landfill (termed secondary leachate). The source of percolating water could be precipitation, irrigation, groundwater or leachate recirculated through the landfill.

### *Leachate quality*

#### Current situation

In general, metals (specifically chromium, nickel, copper, zinc, cadmium, lead and mercury) are currently not present in high amounts in leachates from municipal landfills. Typical contaminant concentrations ( $\mu\text{g L}^{-1}$ ) found in the interstitial water (leachate) of municipal solid waste landfills as collected by Assmuth (1992) are given in **Table 3.42**.

Table 3.42 Typical contaminant concentrations ( $\mu\text{g L}^{-1}$ ) of municipal solid waste leachates

Substance	Mean	Maximum
Cd	< 0.5-3.4	5
Cr	4.9-14	39
Cu	1.5-30	90
Pb	4.9-19	800
Zn	23-60	90
Toluene	< 0.1-200	200
Dichloromethane	1.1-55	84
PCB compounds	< 0.05-0.71	0.71
Pentachlorophenol	0.05-5.3	13

An overview of reported cadmium concentrations in MSW leachates is given in **Table 3.43**.

Table 3.43 Overview of total cadmium concentrations ( $\mu\text{g L}^{-1}$ ) in leachates of MSW landfills

N° of landfills	Type/origin	Min	Max	Mean	Percentiles	Reference
180	Germany: mainly old landfills with unknown solid content closed 15-20 years ago		1,330/173/136		P90 < 5	Eggenberger and Waber (2000)
71	Switzerland: closed within 10 years are still in use France, Italy and Japan		100 $\mu\text{g L}^{-1}$ (1 site)		P80 < 5 P75 < 3	
13	Finland: MSW and industrial landfills		5	0.5-3.4		Assmuth (1992)
21	UK: landfills with primarily domestic waste inputs	< 10	20	< 10		Robinson (1995)
Not reported	Sweden: active municipal landfills	< 0.5	2,700		P50 = 5	Seman (1986) cited in Flyhammer (1995)

Table 3.43 continued overleaf

Table 3.43 continued Overview of total cadmium concentrations ( $\mu\text{g L}^{-1}$ ) in leachates of MSW landfills

N° of landfills	Type/origin	Min	Max	Mean	Percentiles	Reference
Not reported	Sweden: active municipal landfills	< 3	14		P50 < 3	Björklund (1989) cited in Flyhammer (1995)
Not reported	MSW and co-disposal landfills: France Germany The Netherlands UK			< 10 6 4 up to 30 with co-disposal < 10		Hjelmar et al. (1994)
Not reported	MSW landfills	0.5  0.7	1,400  525	6  37.5		Ehrig (1990) cited in Dahm et al. (1994)  Kruse et al. (1993) cited in Dahm et al. (1994)
1	Sweden: 95 % MSW, 5 % sewage sludge 1 years 2 years 20-22 years			40 15 6		Flyhammar et al. (1998)
71	Landfills (USA/France) with more than 75 % MSW. Recent sites (< 1 year) and older sites more than 20 years.				P50: 2.5-7	EREF (1999)
51 landfill total 10 landf/30 measurement points 16/55 19/110 6/21	Germany 1-5 years 6-10 years 11-20 years 21-30 years	0.2 0.2 0.1 0.2	50 192 70 18	11 5.8 3.9 2.8		Krümpelbeck (1999)

The data compiled by Eggenberger and Waber (2000) from 71 investigated landfills in Switzerland, Italy, Japan and France indicate that about 80% of the leachates have Cd concentrations below  $5 \mu\text{g L}^{-1}$  and 75% below  $3 \mu\text{g L}^{-1}$ . A similar distribution of Cd-concentrations in landfill leachates and contaminated ground water is obtained for old landfills (closed 15-25 years ago) in Germany. The results of 1,422 analyses from leachates of mainly old landfills (180) in Germany and more recent landfills (closed 10 years or still in use) in Switzerland and some data from France, Italy and Japan, revealed that roughly 90% of the investigated leachates Cd-concentrations is below  $5 \mu\text{g L}^{-1}$ . It has to be mentioned that the Cd background concentrations as measured in uncontaminated shallow groundwater are very low, being generally below  $1 \mu\text{g L}^{-1}$ . Flyhammer (1995) reported different cadmium concentrations in leachates from landfills in different countries and suggested to use  $5 \mu\text{g Cd/L}$  as an average concentration in leachate from landfills (active and closed landfills) in Nordic countries. Similar

values were reported in the Netherlands, Finland, US and France (see **Table 3.40**). Overall there seems to be a decreasing trend of the cadmium concentration in the leachate with the age of the landfill (Krümpelbeck, 1999, Flyhammar et al., 1998).

The measured concentration value represents the cadmium leached out from all cadmium sources present in the MSW. Since data on leachability of cadmium in MSW compounds is limited it is very difficult to assess the contribution of the NiCd batteries to this value. Only a few leaching tests have been conducted with NiCd batteries. These tests conducted under both aerobic and anaerobic conditions at a temperature of 50°C for 100 days showed corrosion around the positive terminal. Analysis of the leachate revealed total concentrations less than 0.01 mg L<sup>-1</sup>. Field studies where NiCd batteries were deposited in a municipal landfill for seven months showed similar signs of corrosion at the positive terminal but less than had been produced in the anaerobic leachate test (Bromley et al., 1983). Similar observations were obtained in another study on the degradation of NiCd batteries under domestic waste landfill conditions (Jones et al., 1977). Long-term burial tests (not under landfill simulating conditions) with NiCd batteries have shown that after 13 years no exposure of the battery interior components had yet occurred. Only the exterior of the battery did show signs of corrosion (Oda, 1993). From the studies indicated above it is not possible to draw a general conclusion on when the interior of a NiCd battery will be exposed. According to Bromley et al. (1983) this is not expected to occur between 1 and 5 years after deposition. Data on the leaching after exposure of the interior have not been found.

In this report the current overall cadmium concentration, most representatives for the average situation, in an MSW landfill leachate is considered to be 5 µg L<sup>-1</sup> and this value was used to perform the regional calculation. In the risk characterisation next to a local scenario with a leachate concentration of 5 µg L<sup>-1</sup> an additional scenario have been developed based on an assumed cadmium leachate concentration of 50 µg L<sup>-1</sup> (see future changes in leachate quality).

Furthermore it is assumed in this report that each waste component has the same likelihood of leaching out one gram of cadmium (e.g. one gram of cadmium in a certain amount of paper was assumed to have the same likelihood of leaching out as one gram of cadmium in NiCd batteries).

As a result the emissions due to NiCd batteries can be estimated to be 0.5-2.5 µg L<sup>-1</sup> (based on the finding that 10-50% of the overall cadmium content in MSW is due to NiCd batteries).

#### *Future changes in leachate quality*

The impact of increasing cadmium content in the MSW on the composition of the leachate cannot be predicted on the basis of current knowledge since there is no direct relationship between the total content of Cd and the leachability of Cd. A 10% increase in total content of Cd in the MSW land-filled will not necessarily lead to a 10% increase in the leached amount of Cd. The leachability will depend on the chemical nature of the cadmium and the leaching conditions.

In this report the cadmium concentration in the leachate originating from a fixed amount of cadmium being land-filled is assumed to be constant over time. The question arises whether or not it is reasonable to assume one constant leachate concentration since the conditions in landfills are changing during the different degradation phases in a landfill. For metals the critical phase in the short term of a landfill is the acid anaerobic phase where the pH will drop due to the decomposition of the easily degradable material. Few studies have attempted to characterise leachates as being acetogenic or methanogenic (Ehrig, 1983 and Robinson and Gronnow, 1993 in Finnveden 1996). From these studies it can be concluded that the constant concentration assumption for the time period surveyed is reasonable for the metal cadmium. However, it is acknowledged that landfills have not yet reached their final development stage and as a result it

is unclear what may happen after 100 year. Considering the geochemical evolution of waste deposits towards more oxidising and more acidic conditions with time, at first higher emissions could be expected in the future (Eggenberger and Waber, 2000). However, according to simulation work by Belevi and Baccini (1989), it is more plausible that alkaline conditions will be maintained for 2,000 years and that hence higher remobilisation rate of some metals due to lower pH is not expected at least for many centuries (Bozkurt et al., 2000). The effect of varying redox potentials and the effect of acid rain on the chemical equilibrium of a waste body were investigated by Gade et al. (1998). The results showed that severe mobilisation is not expected and a long term entrance of acid rain is not expected to exhaust the carbonate buffer before 400,000 years. And even if the carbonate buffer would be exhausted there will be still another buffer (silicates) effective.

Overall the cadmium concentration in the leachate seems to decrease with the age of the landfill (Krümpelbeck, 1999, Flyhammar et al., 1998). According to Gade et al. (1997, 1998, 1999, 2000), who investigated the behaviour of two Bavarian hazardous waste landfills with regard to their mineralogy, secondarily newly formed minerals (carbonates, phosphates, sulfates) reduced the mobility of the metals present in the waste. Under anaerobic conditions metals that form sulfides (e.g. cadmium, copper, zinc, nickel and lead) will tend to be immobilised as sulfides. In the long run when landfills develop aerobic conditions additional solubility limiting phases including carbonates and hydroxides will retard metal mobility in the future.

Johnson et al. (1999) suggested that  $\text{CdCO}_3$  (otavite) precipitation is important for cadmium. Recent modelling work (Ross et al., 2000) on the retention and speciation of heavy metals (cadmium, chromium and zinc) in both immature and mature post methanogenic leachates indeed indicated that carbonate precipitation is likely the solubility limiting phase for cadmium. According to the performed geochemical modelling on mature waste, carbonate precipitation is likely to prevent cadmium concentrations rising from 60 to 90  $\mu\text{g L}^{-1}$ . The laboratory results indicated, however, that for the aerobic columns, cadmium concentrations generally remained below 10  $\mu\text{g L}^{-1}$  suggesting that the retention mechanism is probably not precipitation alone. Similar observations were observed by Gade et al. (1999) who predict a maximum cadmium concentration of 81  $\mu\text{g L}^{-1}$  but observed a measured concentration of one order of magnitude lower i.e. 7.8  $\mu\text{g L}^{-1}$  suggesting that other mechanisms such as adsorption phenomena are also limiting cadmium release.

In order to assess possible impact on the environment from possible higher cadmium concentrations in the future the risks will be quantified in the sensitivity analysis (see subsection “Sensitivity analysis” under Section 3.1.2.2.5) for an arbitrary chosen leachate concentration (i.e. 50  $\mu\text{g L}^{-1}$  which is close to the solubility limit for cadmium carbonate). The leachate concentration of 50  $\mu\text{g L}^{-1}$  can be considered as a conservative/worst case leachate concentration because in this case we are assuming that aerobic precipitation is the only metal retention mechanisms.

#### *Leachate quantity*

Leachate production is highly dependent on the landfill design and local climatic conditions. Precipitation represents the largest single contribution to the production of leachate. There is some variation in the potential generation of leachate within the EU because precipitation and evapotranspiration depends on geographical location. In Mediterranean areas (Greece, Spain and Italy) leachate generation is the smallest during summer season and leachate generation occurs principally during the colder, wet season (i.e. from October to April). For example an annual leachate production, expressed as height of water of 40-80 mm/year has been calculated for a landfill site near Athens (Greece, rainfall: 387 mm/y, Kouzeli-Katsiri et al., 1993). In a landfill

site near Madrid (Gössele, 1993) the leachate production was calculated to be 7 mm/year and in a landfill near Pavia (Italy, Baldi et al., 1993) it was 82 mm/year. Leachate quantities tend to be higher in the North of the EU than the South. In Sweden an average leachate volume of 250-300 mm/year is reported during operation (Nilsson, 1993). In Denmark similar figures have been reported: 320-400 mm during operation and 56-89 mm/year (Hjelmar, 1988-1989). But equally large variations can be found from East to West and over relatively short distances within Member States (Hjelmar et al., 1994). Reported leachate volumes vary from 25 m<sup>3</sup> to 3,000 m<sup>3</sup> per hectare (Flyhammer, 1995, Qiang et al., 2002).

The results of various empirical studies are indicating that the average percentage of precipitation that results in leachate production depends on the age of the landfill and is largely controlled by the presence and type of cover. In general it has been noted that the amount of leachate produced is between 15 and 50% of the respective rainfall, depending mainly on the final landfill cover type and the manner of waste compaction (Canziani and Cossu, 1989). As an average to realistic worst-case scenario in this report the water balances has been calculated for a relatively high precipitation rate (800 mm/year) for different scenarios representative for common nowadays (or modern) landfill practices.

#### Scenario development

The EU directive on the landfill of waste (1999/31/EC) indicates that appropriate measures shall be taken, with respect to the characteristics of the landfill and the meteorological condition in order to:

- control water from precipitation to enter the landfill;
- to collect contaminated water and leachate
- and to treat contaminated water and leachate collected from the landfill to the appropriate standard required for their discharge.

It is further stated that protection of groundwater has to be achieved by the combination of a geological barrier and a bottom liner during the operational/active phase and by the combination of a geological barrier and a top liner during the passive post closure phase. For non hazardous landfills it is therefore required to have a leachate collection and bottom sealing (consisting of an artificial sealing liner and drainage liner > 0.5 m in addition to a geological barrier (> 0.5 m). If the prevention of leachate formation is necessary a surface sealing can be applied. The requirements for a top cover are at least a topsoil cover (> 1m) and a drainage layer (> 0.5m).

Although in the future all landfills will have to meet the requirements of the new EU landfill directive it is acknowledged that at the moment different landfill practices exist. Therefore the leachate generation simulations have been conducted in this report for 4 different sets of conditions representative for different landfill practices and the consecutive life stages of a landfill.

Set 1: corresponds with a landfill with no top cover

Set 2: corresponds with a landfill with daily top cover

Set 3: corresponds with a landfill with an intermediate top cover

Set 4: corresponds with a landfill with a final top cover

In addition two sub-scenarios have been added in which the composition of the bottom liner or top liner has been changed:

- In this report both a single compacted clay liner as a single composite liner system are considered as a bottom liner. Proper functioning of a bottom liner system is critical to the containment effectiveness of a landfill. During the past few decades the trend has been to use composite liner systems comprising both clay and synthetic geomembranes together with interspersed drainage layers.
- For a final cap or cover system the following systems are considered in this report: 1) a cover system consisting of a top soil, drainage layer and a single compacted clay liner, 2) a cover system consisting of a top soil, drainage layer and a single composite clay line. The main purpose of a landfill final cover is to minimise water infiltration into the landfill to reduce the amount of leachate generated after closure.

An overview of the different landfill profiles considered in this report is given in **Figure 3.8**. The thickness of the layers and final cover materials are in agreement with the new landfill directive and are representative for common landfill practice.

Figure 3.8 Landfill profile structure for different landfill designs

	Set 1: No cover		Set 2: Daily cover		Set 3: Intermediate cover		Set 4: Final cover	
Top cover							Soil (1.5 m)	
							Soil (1.5 m)	
							Sand (0.5m)	
					Soil (1.5 m)		Sand (0.5m)	HDPE
			Soil (0.3 m)				Clay (1m)	Clay (1m)
Waste	Waste (20 m)		Waste (20 m)		Waste (20 m)		Waste (20 m)	
Bottom	Sand (0.5m)	Sand (0.5m)	Sand (0.5m)	Sand (0.5m)	Sand (0.5m)	Sand (0.5m)	Sand (0.5m)	Sand (0.5m)
	Clay (1m)	HDPE	Clay (1m)	HDPE	Clay (1m)	HDPE	Clay (1m)	HDPE
		Clay (1m)		Clay (1m)		Clay (1m)		Clay (1m)

### Water balance

The most common way to calculate the amount of leachate is a simple water balance. In a water balance the amount of leachate is calculated as being the amount of precipitation minus the surface run-off, evapotranspiration, change in soil cover and waste moisture content.

$$L = P - R/O - ET - \Delta ST - \Delta SWST$$

L = Leachate quantity

P = Precipitation

R/O = run off

$\Delta ST$  = change in soil moisture content

ET = Evapotranspiration

$\Delta SWST$  = change in solid waste moisture content

In this report the leachate production has been addressed with the theoretical landfill leachate model HELP (Hydrologic Evaluation of Landfill Production, US-EPA, Schroeder et al., 1994a and b). The HELP model is a sophisticated version of the water balance method and is used all over the world to predict leachate generation. The configuration of the model allows handling any type of cover, liner and can even address leakage.

In order to perform the model calculations a generic landfill has been defined. At the moment an average representative European standard landfill is hard to define. Since future landfills are assumed to be reasonably large a landfill of 20 hectares have been chosen for the generic reasonable worst case (large surface area hence more leachate production) local scenario. An overview of the main input data used in the modelling is given in **Table 3.44**. Default values chosen were based on values most commonly cited in literature (Kjeldsen and Christensen, 2001; Nielsen and Hausschild, 1998; Nielsen et al., 1998; EREF, 1999; Schroeder et al., 1994; Hjelmar et al., 1994; etc.).

Table 3.44 Default values used for the generic landfill

Parameter	Unit	Value
Surface of the landfill	m <sup>2</sup>	200,000
Total depth of MSW land-filled	m	10-20
Bulk density of MSW		0.6
Volumetric water content in MSW		0.3
Field capacity MSW	%	29.2
Wilting point MSW	%	7.7
Duration of operation phase	Year	15
Duration of post closure phase	Year	30
Moderately compacted clay cover	m	1
Drainage layer (sand)	m	0.5
Slope drainage layer	%	1
Top cover (sandy loam)	m	0.3 (daily cover) 1.5 (final cover)
Slope top cover	%	1 <sup>a</sup>

Table 3.44 continued overleaf

Table 3.44 continued Default values used for the generic landfill

Parameter	Unit	Value
HDPE liner	m	0.01
Precipitation	m/year	0.8 (i.e. 0.799) <sup>b</sup>

- a) The choice was made to represent a reasonable worst case situation (OVAM, pers. com., 2002);  
b) Calculated default value.

The HELP model was run for the 4 different sets of data and for one landfill location. As location for the landfill the Netherlands was chosen. The HELP model generated the weather and climatic data over a simulation period of 100 years. This resulted in an average annual precipitation of 0.799 m/year for the Netherlands and is used as a default average to realistic worst case scenario with regard to the amount of leachate generated for the different landfill scenarios. Mediterranean countries will have lower leachate volumes. Scandinavian countries will have similar leachate volumes as in the Netherlands.

During the operation phase the landfill cells are relatively flat. Therefore the area subjected to runoff was set to zero. Runoff was only taken into account when the final top cover was in place. In the cases where runoff is ignored any precipitation will result in more leachate resulting in a maximum leachate generation during landfill operations.

**Tables 3.45-48** show the average annual results of the HELP model for a generic landfill taking into account the different landfill stages.

Table 3.45 Annual leachate generation for a landfill with no top cover and a bottom liner consisting of a single compacted clay liner or a single composite liner

Parameter	Scenario 1 : No top cover			
	Bottom liner: single compacted clay		Bottom liner: composite liner	
	m <sup>3</sup> /ha/year	%	m <sup>3</sup> /ha/year	%
Precipitation	7,999	100	7,999	100
Run-off	0	0	0	0
Evapotranspiration	5,645	70.6	5,645	70.6
Change in water storage	- 3.9	0.05	262	3.3
Leachate collected from drainage layer	119	1,5	2,024	25
Fugitive leachate	2,239	28	68	0.8

Table 3.46 Annual leachate generation for a landfill with a daily cover and a bottom liner consisting of a single compacted clay liner or a single composite liner

Parameter	Scenario 2: Daily cover			
	Bottom liner: single compacted clay		Bottom liner: composite liner	
	m <sup>3</sup> /ha/year	%	m <sup>3</sup> /ha/year	%
Precipitation	7,999	100	7,999	100
Run-off	0	0	0	0
Evapotranspiration	5,454	68.2	5,454	68.2
Change in water storage	- 3	0.03	300	3.5
Leachate collected from drainage layer	143	1.8	2,193	27.4
Fugitive leachate	2,406	30.1	73	0.9

Table 3.47 Annual leachate generation for a landfill with an intermediate cover and a bottom liner consisting of a single compacted clay liner or a single composite liner

Parameter	Scenario 3: Intermediate cover			
	Bottom liner: single compacted clay		Bottom liner: composite liner	
	m <sup>3</sup> /ha/year	%	m <sup>3</sup> /ha/year	%
Precipitation	7,999	100	7,999	100
Run-off	0	0	0	0
Evapotranspiration	5,454	68.2	5,454	68.2
Change in water storage	2	0.03	284	3.5
Leachate collected from drainage layer	136	1.7	2,189	27.4
Fugitive leachate	2,412	30.1	73	0.9

Table 3.48 Annual leachate generation for a landfill with a final cover (with or without a composite liner) and a bottom liner consisting of a single compacted clay liner or a single composite liner

Parameter	Scenario 4: Final cover			
	Final top cover: top soil , sand, composite liner			
	Bottom liner: single compacted clay		Bottom liner: composite liner	
	m <sup>3</sup> /ha.y	%	m <sup>3</sup> /ha.y	%
Precipitation	7,999	100	7,999	100
Run-off	1,850	23.1	1,850	23.1
Evapotranspiration	6,101	76.3	6,101	76.3
Change in water storage	31	0.4	32	0.4
Leachate collected from drainage layer	0.4	0.005	15.3	0.2
Fugitive leachate	16	0.2	0.25	0.003

Table 3.48 continued overleaf

Table 3.48 continued Annual leachate generation for a landfill with a final cover (with or without a composite liner) and a bottom liner consisting of a single compacted clay liner or a single composite liner

Parameter	Scenario 4: Final cover			
	Final top cover: top soil, sand, single compacted clay liner			
	Bottom liner: single compacted clay		Bottom liner: composite liner	
	m <sup>3</sup> /ha.y	%	m <sup>3</sup> /ha.y	%
Precipitation	7,999	100	7,999	100
Run-off	39	0.5	39	0.5
Evapotranspiration	5,454	68.2	5,454	68.2
Change in water storage	3.5	0.04	288	3.6
Leachate collected from drainage layer	105	1,3	2,148	26.8
Fugitive leachate	2,398	30	71	0.9

The amount of leachate generated is the highest during the filling/operational phase (no cover, daily cover and intermediate cover) of the landfill and mounts up to 31.8% (= 2,545 m<sup>3</sup>/ha/year = precipitation - evapotranspiration - run-off from **Table 3.46** and **Table 3.47**) of the initial precipitation (7,999 m<sup>3</sup>/ha/year). The use of a final cover with composite liner reduces the total amount of leachate significantly to 0.2% (= 16 m<sup>3</sup>/ha/year). In the absence of a composite liner in either the top or bottom barrier the amount of leachate produced is still substantial (2,506 m<sup>3</sup>/ha/year see **Table 3.48** = 7,999 - 39 - 5,454). From the results presented above it is clear that the net release of leachate into the environment (i.e. fugitive leachate) is dependent on the presence and efficiency of a leachate collection system and subsequent treatment. In case the final cover and the bottom layer only consists of a single compacted clay liner 2,398 m<sup>3</sup>/ha/year of fugitive leachate is produced (96% of the total volume leachate = 2,506 m<sup>3</sup> produced). In case only the final top cover consists of a composite liner only approximately 0.6% (16 m<sup>3</sup>/ha) of the total volume leachate generated results in fugitive leachate. In the ideal case where both the bottom barrier and the top cover are comprised of a composite liner only 0.25 m<sup>3</sup>/ha/year of fugitive leachate is produced which is negligible.

In order to cover all landfill types two landfill profiles are further considered in the local assessment:

- Landfill profile 1: landfill with bottom liner and final top layer consisting of a single compacted clay liner;
- Landfill profile 2: landfill with bottom liner and final top liner consisting of a single composite liner.

For the latter Scenario, the ageing of the geomembrane have been taken into account. It is assumed that the geomembrane will remain effective during the operational and post closure phase (= 45 years in total). While the top cover can be renewed, the renewal of the bottom liner is less feasible. Therefore it is assumed that after 45 years the bottom liner will only consist of a single compacted clay liner.

Taking into account the leachate volumes of the consecutive life stages of a landfill (see Section on leachate generation), the cumulated leachate volume expressed as m<sup>3</sup> per ha for the different time horizons (20, 100 and 500 years) can be calculated (see **Table 3.49**). For the time period of 0-2 years after waste placement, the landfill cells are assumed to have no cover or to be covered

with a daily top cover. From years 2-5 years after waste placement cells are covered with an intermediate top cover. From years 5-15 after waste placement the cells are for 40% covered with a final top cover. After year 15 the landfill is assumed to be completely covered with a final top cover.

Table 3.49 Amount of leachate generated per ha of landfill over time

Time since waste placement (years)	Cumulative leachate generation (m <sup>3</sup> /ha)			
	Landfill profile 1		Landfill profile 2	
	Collected	Fugitive	Collected	Fugitive
20	2,426	47,747	23,900	791
100	4,001	239,607	24,129	1,697
500	/	1,198,907	/	8,263

The collection of the landfill leachate is assumed to proceed throughout the active period of the landfill's operating life and is extended after the closure of a landfill for another 30 years (if a significant quantity of leachate is still being produced that contains high concentrations of contaminants).

The highest volume of leachate collected is in the operational phases of the landfill and decreases with time. For a generic landfill of 20 ha with a composite bottom liner and no top cover (see **Table 3.45**) 111 m<sup>3</sup>/day (= (2,024 m<sup>3</sup>/ha/year · 20 ha)/365 day.) is collected and has to be treated. If the leachate collection volume is averaged over 20 year and taking into account the different life stages of a landfill approximately 65 m<sup>3</sup>/day is collected.

For this report the value of 100 m<sup>3</sup>/day is taken forward in the local exposure calculations (see Section 3.1.3.2) as being representative for the amount of leachate collected per day for a generic landfill of 20 hectare. This figure is in the min-max range from the figures in literature: 5-650 m<sup>3</sup>/day (Robinson et al., 1995) for landfills of different landfill surface areas.

The cadmium emissions (see **Table 3.50**), before treatment, were then calculated for the generic local landfill with a surface area of 20 hectares and assuming a current leachate concentration of 5 µg L<sup>-1</sup>.

Table 3.50 Local cadmium emissions to water (in kg) for the generic local landfill (surface area of 20 ha)

Time since waste placement (years)	Leachate concentration = 5 µg L <sup>-1</sup>			
	Cumulative cadmium emission (kg)			
	Landfill profile 1		Landfill profile 2	
Leachate	Collected <sup>a</sup>	Fugitive	Collected <sup>a</sup>	Fugitive
20	0.2	4.8	2.4	0.1
100	0.4	24.0	2.4	0.2
500	/	120	/	0.8

a) Before treatment.

From **Table 3.50** it is clear that the amount of cadmium released in the future<sup>36</sup> from a landfill is limited. The current generic landfill will contain at the end 1,200-2,400 ktonnes (wet wt.) of MSW

<sup>36</sup> up to 500 year and under the assumption that the leachate concentration keeps constant during this time frame

(= 840-1,680 ktonnes<sub>dry wt.</sub>) over and if we assume a 15 year filling period (80-160 ktonnes MSW/year). With a total cadmium content of  $10 \text{ g tonne}^{-1}$ <sub>dry wt.</sub> and emission factors (kg Cd emitted/kg Cd land-filled) between  $1.5 \cdot 10^{-3}$  (24.4 kg/16,800 kg) and  $1.5 \cdot 10^{-4}$  (2.6 kg/16,800 kg) can be calculated in case the landfill contains 2,400 ktonnes MSW. In comparison Finnveden (1996) reported an emission factor of  $5.0 \cdot 10^{-4}$  for a time survey period of 100 years. This indicates that the largest part of the land-filled cadmium (99.85-99.98%) remains in the landfill. If 24.4 kg Cd is released over a period of 100 year this means that on average 0.24 kg is released yearly which is a release rate of 0.001% per year. If only a landfill height of 10 m. is assumed (1,200 ktonnes MSW) the release factor is 0.0028%. Ehrig (1989) suggested a similar release rate of 0.002% per year.

Baccini et al. (1987) reported that more than 99.9% of the metals are still found in the residual solids at the end of the intensive reactor phase. It has, however, been suggested that metal concentrations in landfill leachate may rise again (Eggenberger and Waber, 2000). The environmental impact after a hypothetical infinite time period has not been addressed in this report since our knowledge on this issue is insufficient.

#### *Regional emissions of land-filling MSW*

The regional emissions of cadmium per year from MSW landfills in the EU can be calculated with the following formula.

Cadmium flux ( $\text{kg year}^{-1}$ ) = Landfill surface (ha) · leachate generation ( $\text{m}^3/\text{ha}/\text{year}$ ) · cadmium concentration in the leachate ( $5 \cdot 10^{-6} \text{ kg/L}$ )

In this report a concentration of  $5 \mu\text{g Cd/L}$  is taken as a representative value for the average situation in MSW landfill leachate. In the previous section (local emissions landfill) a maximum leachate volume of  $2,500 \text{ m}^3/\text{ha}/\text{year}$  was calculated for an average rainfall of  $7,999 \text{ m}^3/\text{ha}/\text{year}$ . The only unknown in the equation is the total surface area of the landfills. Reported landfill areas range between  $< 1 \text{ ha}$  to  $> 10 \text{ ha}$  while new established landfills are assumed to be reasonably large (average 20 ha, Hjelmar et al., 1994). However, almost no reliable data on the total number of MSW landfills or their landfill surface were found for most of the Member States. The values that have been reported for operational landfills for some countries are listed in **Table 3.51**. The cadmium flux has been calculated with the equation described above.

Table 3.51 Cadmium fluxes ( $\text{kg year}^{-1}$ ) of operational MSW landfills for some countries

Country <sup>a</sup>	MSW land-filled (ktonnes)	Number of land-fills	ktonne MSW.y per landfill	Average surface area /landfill (ha)	Total surface area (ha)	Calculated cadmium flux (kg/y)	Reference
Finland	1,610	/	/	9.3	/	/	Assmuth (1992)
Sweden	1,300	270-280	4.8	10	2,800	42	Flyhammar (1995) and RVF (2002)
UK	26,860	764	17.2	18.9	14,482	181	Mc. Mellin (2002)
		+		+	+		
		796		9.1	7,300	91	
Germany	16,000	376	42.5	10 <sup>a</sup>	3,760	235	UBA (2001)
The Netherlands	1,136	39	29	30.7	1,198	14.9	VVAV (2000)
Average			23.4	14.7			

a) Very rough approximation on the average landfill area.

The calculated cadmium fluxes range between 14.9 (The Netherlands) and 272 kg year<sup>-1</sup> (UK sum). As stated in the previous sections these fluxes are directly related to the landfill surface area and the yearly precipitation. Since the total landfill surface area for most of the Member States is unknown an indirect approach had to be developed in order to assess the overall cadmium emissions for these countries. Based on the information in **Table 3.51** an average landfill surface of 14.7 ha can be calculated. Furthermore approximately 23.4 ktonnes MSW (wet wt.) is land-filled per landfill each year<sup>37</sup> based on an average of the data from Sweden, UK, Germany and the Netherlands. The latter information can be used to translate the amount of MSW land-filled (ktonnes) in each year per country (presented in **Table 3.21**) into a number of landfills. Assuming that each landfill has a surface area of 14.7 ha the total landfill surface can be calculated. Finally the cadmium flux is calculated with the equation mentioned above.

As an example the emission for France is calculated as follows:

Amount land-filled each year = 23,352 ktonnes<sub>wet wt.</sub>

Number of landfills = 23,352/23.4 = 998

Total landfill surface = 998 · 14.7 ha = 14,671 ha

Total cadmium flux (kg year<sup>-1</sup>) = 14,671 ha · 2,500 m<sup>3</sup>/ha.y · 5.10<sup>-6</sup>.kg/L = 183 kg year<sup>-1</sup>

The generated flux (leachate) may either be discharged to an off-site municipal sewage plant, discharged directly to surface water or enter into the groundwater compartment. Collection and discharge to a Sewage Treatment Plant (STP) is by far the most common discharge route for leachates from municipal waste landfills. A smaller proportion of leachate is discharged directly to surface waters. The latter is only allowed if the leachate quality fulfils certain requirements (sometimes pre-treatment, e.g. aerated lagoons, is needed). Most often this quality is governed by the presence of increased levels of BOD, COD and ammonium (see **Table 3.52**).

Table 3.52 Detailed analysis of leachate sample taken at Chapel Farm landfill, Swindon, Wiltshire, 1990-1991 (Robinson, 1995)

Parameter	Concentration (mg L <sup>-1</sup> )
COD	850-10,600
BOD <sub>5</sub>	239-4,100
Ammoniacal-N	283-531
Chloride	834-4,670
Cd	< 0.01-0.02

Metals have been regarded only as a minor problem in the waste management of leachates and only rarely posed a significant problem in leachates from domestic waste landfills (Robinson, 1995). Discharge criteria to surface water vary from one Member State to another. Landfill effluent requirements for cadmium as prescribed in the legislation of different European countries and reported by Doedens and Theilen (1992) vary between 2-5 µg L<sup>-1</sup> (The Netherlands) to 100 µg L<sup>-1</sup> (Germany, Austria, Switzerland). The highest proportion of

<sup>37</sup> This value is much smaller than the calculated amount of MSW landfilled each year for the local generic landfill scenario, i.e. 80-160 ktonne<sub>wet wt.</sub> MSW/year). However, the driving parameter is the surface area. For the generic local landfill a surface area of 20 ha has been assumed which is within the same order of magnitude as the average landfill surface area of 14.7 hectare based on reported values.

landfills discharging directly to surface water is 23% (Germany) with less than 10% in other Member States (Hjelmar et al., 1994).

Permitted discharge to groundwater is uncommon for modern MSW landfills but may occur by old landfills or in the framework of an engineered leachate attenuation-site (Robinson, 1995).

Since the number of sites designed with bottom liners and on-site leachate treatment plants is currently increasing it is proposed to use the following regional allocation key for assessing the current emissions of landfills operational to date:

- 10% direct discharge to groundwater (attenuation/dilution-sites)
- 10% direct discharge to surface water (sometimes an on-site pre-treatment step is included)
- 80% collected and discharged via public sewer systems or transported via tankers to a STP. In a STP an overall cadmium removal efficiency of 60% is assumed (CBS, 2002)<sup>38</sup>.

It should be clear that a direct discharge to groundwater or surface water is only possible when the leachate quality is considered suitable. Since for our regional assessment we are working with a cadmium leachate concentration of  $5 \mu\text{g L}^{-1}$  this is of suitable quality since according to some legislation we can discharge from 2-5 up to  $100 \mu\text{g L}^{-1}$ . Therefore the scenario of direct discharge to surface water is included. If the quality is insufficient a form of pre-treatment is needed

The above regional scenario was validated with the data presented in the extensive report of Robinson (1995). The semi-quantitative and qualitative information on leachate management in the EU reported on a country by country basis also gives support to the aforementioned allocation key (EC Report, 1994). Some further more recent information was received from MSs during the risk assessment process (UBA, 2002; UK, 2002).

An overview of the overall cadmium emissions to groundwater/surface water and sludge (in  $\text{kg year}^{-1}$ ) in Europe due to land-filling of MSW is presented in **Table 3.53** and **Table 3.54**. The overall cadmium flux was calculated with the methodology described in previous paragraphs.

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<sup>38</sup> Although it could be questioned that the removal rate of 60% is also applicable to effluents with low cadmium concentrations ( $\mu\text{g L}^{-1}$  range) the removal percentage of 60% is deemed appropriate since the landfill leachate is not the only cadmium source in the STP resulting in overall higher cadmium concentrations in the final STP influent. At local scale, the landfill on-site STP needs in general further tertiary 'polishing' water treatment techniques to reduce cadmium concentrations below  $5 \mu\text{g L}^{-1}$  (see Baeyens, pers. com., 2003; Verstraete, pers. com., 2003) and this does not seem (yet) a standard practice in landfill management to date (EC Report, 1994; UK, com. 2002; RDCHW, 2002).

Table 3.53 Overall cadmium emissions to groundwater/surface water and sludge (in kg year<sup>-1</sup>) in Europe due to land-filling of MSW (operational landfills only). Current scenario: 75.6% land-filling

Country	MSW land-filled (ktonnes <sub>wet wt.</sub> )	Total cadmium flux (kg/y)	Fugitive emissions to surface water (kg year <sup>-1</sup> )	Fugitive emissions to groundwater (kg year <sup>-1</sup> )	Collected leachate	
Allocation key			10%	10%	80%	
					Emissions to surface water (kg year <sup>-1</sup> ) after treatment	Sludge (kg/y)
					40%	60%
Austria	1,099	9	1	1	3	4
Belgium	1,473	12	1	1	4	6
Denmark	361	3	0.3	0.3	1	1
Finland	1,610	13	1	1	4	6
France	23,352	183	18	18	59	88
Germany	16,000	235	24	24	75	113
Greece	3,561	28	3	3	9	13
Ireland	1,432	11	1	1	4	5
Italy	20,768	163	16	16	52	78
Luxembourg	62	0.5	0.05	0.05	0.2	0.2
The Netherlands	1,136	75	1	1	5	7
Norway	1,843	14	1	1	5	7
Portugal	2,603	20	2	2	7	10
Spain	17,477	137	14	14	44	66
Sweden	1,300	42	4	4	13	20
UK	26,860	272	27	27	87	131
<b>Total EU-16</b>	<b>120,937</b>	<b>1,158</b>	<b>116</b>	<b>116</b>	<b>371</b>	<b>556</b>

The total amount of MSW being land-filled in 1995-2001 for the EU-16 was 120,937 ktonnes<sub>wet wt.</sub> (84,656 ktonnes<sub>dry wt.</sub>) on yearly basis corresponding with an overall EU land-filling share of 75.6% (see subsection “Waste management strategies in Europe” under Section 3.1.2.2.5). A total yearly cadmium flux of 1,158 kg has been calculated. Based on the calculations above the cadmium emission to the groundwater compartment due to land-filling MSW is 116 kg Cd/year. An additional 487 kg is emitted to surface water and 556 kg of cadmium can be found in the sludge.

Similar to the section on local emissions of land-filling the release rate (%) per year can be calculated. If it is assumed that the landfills have a 15-year filling period then 1,269,838 ktonnes MSW (dry wt.) have been land-filled. With a total cadmium content of 10 g tonne<sup>-1</sup><sub>dry wt.</sub> a total of 12,698,380 kg of cadmium is present. If 1,158 kg Cd is released per year a release rate of approximately 0.01% per year is calculated.

Table 3.54 Overall cadmium emissions to groundwater/surface water and sludge (in kg year<sup>-1</sup>) in Europe due to land-filling of MSW (operational landfills only). Scenario: 100% land-filling

Country	MSW land-filled (ktonnes <sub>wet wt.</sub> )	Total cadmium flux (kg/y)	Fugitive emissions to surface water (kg year <sup>-1</sup> )	Fugitive emissions to groundwater (kg year <sup>-1</sup> )	Collected leachate	
Allocation key			10%	10%	80%	
					Emissions to surface water (kg year <sup>-1</sup> ) after treatment	Sludge (kg/y)
					40%	60%
Austria	1,578	12	1	1	4	6
Belgium	2,842	22	2	2	7	11
Denmark	2,091	16	2	2	5	8
Finland	1,690	13	1	1	4	6
France	34,133	268	27	27	86	129
Germany	28,000	220	22	22	70	106
Greece	3,561	28	3	3	9	13
Ireland	1,432	11	1	1	4	5
Italy	22,717	178	18	18	57	86
Luxembourg	185	1	0.1	0.1	0.5	1
The Netherlands	4,995	39	4	4	13	19
Norway	2,217	17	2	2	6	8
Portugal	3,663	29	3	3	9	14
Spain	18,804	148	15	15	47	71
Sweden	2,700	21	2	2	7	10
UK	29,450	231	23	23	74	111
<b>Total EU-16</b>	<b>160,058</b>	<b>1,257</b>	<b>126</b>	<b>126</b>	<b>402</b>	<b>603</b>

Based on the calculations above the cadmium emission in a 100% land-filling scenario would result in an emission to the groundwater compartment of 126 kg Cd/year. An additional 528 kg is emitted to surface water and 603 kg of cadmium can be found in the sludge.

The allocation of the total EU landfill emissions to the regional scale has been performed with the 10% rule (see **Table 3.55**).

Table 3.55 Total annual amount of Cd emissions to groundwater/surface water and sludge within the EU from land-filling MSW

Scenario	Released amount Cadmium (kg year <sup>-1</sup> )	Continental (90%) (kg year <sup>-1</sup> )	Regional (10%) (kg year <sup>-1</sup> )
	Surface water		
75.6% land-filling	487	438	49
100% land-filling	528	475	53

Table 3.55 continued overleaf

Table 3.55 continued Total annual amount of Cd emissions to groundwater/surface water and sludge within the EU from land-filling MSW

Scenario	Released amount Cadmium (kg year <sup>-1</sup> )	Continental (90%) (kg year <sup>-1</sup> )	Regional (10%) (kg year <sup>-1</sup> )
	Surface water		
	Groundwater		
75.6% land-filling	116	104	12
100% land-filling	126	113	13
	Sludge		
75.6% land-filling	556	500	56
100% land-filling	603	543	60

*Contribution of NiCd batteries to the overall cadmium emissions of land-filling MSW*

With the assumption that NiCd batteries account for 10-50% of the total MSW cadmium content, the contribution of NiCd batteries can be calculated by multiplying the overall cadmium emissions as presented in **Table 3.52** by 0.1 and 0.5 (see **Table 3.56** and **Table 3.57**).

Table 3.56 Contribution of NiCd batteries to the overall cadmium emissions due to land-filling of MSW

Scenario	75.6% land-filling		100% land-filling	
	10%	50%	10%	50%
Allocation key				
Compartment	Direct emissions (kg year <sup>-1</sup> )			
Surface water	49	244	56	264
Groundwater	12	58	13	63
Sludge	56	278	60	302

Table 3.57 Contribution of NiCd batteries to the continental and regional cadmium emissions due to land-filling of MSW

Scenario		Released amount Cadmium (kg year <sup>-1</sup> )	Continental (90%) (kg year <sup>-1</sup> )	Regional (10%) (kg year <sup>-1</sup> )
		Surface water		
75.6% land-filling	0.1	49	44	5
	0.5	244	220	24
100% land-filling	0.1	56	50	7
	0.5	264	238	26

Table 3.57 continued overleaf

Table 3.57 continued Contribution of NiCd batteries to the continental and regional cadmium emissions due to land-filling of MSW

Scenario		Released amount Cadmium (kg year <sup>-1</sup> )	Continental (90%) (kg year <sup>-1</sup> )	Regional (10%) (kg year <sup>-1</sup> )
Groundwater				
75.6% land-filling	0.1	12	11	1
	0.5	58	52	6
100% land-filling	0.1	13	12	1
	0.5	63	57	6
Sludge				
75.6% land-filling	0.1	56	50	6
	0.5	278	250	28
100% land-filling	0.1	60	54	6
	0.5	302	272	30

### Sensitivity analysis

The values used in the previous sections to produce the emissions of MSW incinerators and MSW landfills represent average or estimated values. Therefore, a large amount of uncertainty is associated with these numbers. This uncertainty is difficult to take into account explicitly. However, a sensitivity analysis was performed on some of the input parameters used to determine the effect that varying the parameters had on the overall results. The following parameters and ranges were used:

Table 3.58 Variation of model parameters used in the sensitivity analysis

Incinerator					
Model parameter	Unit	Minimum value	Default value	Maximum value	Affected parameter
Total Cd content in MSW	g tonne <sup>-1</sup> dry wt.	5	10	15	bottom ash and fly ash concentrations Cadmium land-filled
Amount of wastewater	m <sup>3</sup> /tonne	0.6	2.5	5	Emissions to water
Effluent concentration	mg L <sup>-1</sup>	0.1	0.3	1	Emissions to water
Treatment efficiency	%	90	98.8	99.9	Emissions to water
Landfill					
Leachate concentration landfill	µg L <sup>-1</sup>	0.5	5	50	Emissions to water
Percolation flux	%	1	10	20	Emissions to water
Treatment efficiency STP	%	40	60	80	Emissions to water
Allocation key					
Contribution NiCd batteries	%	10	50		Emissions to water

Ranges were chosen in such a way that they covered at least the figures reported in literature. The upper limit for the leachate concentration (50 µg L<sup>-1</sup> that is close to the solubility limit for cadmium carbonate, Ross et al. (2000)<sup>39</sup>) in landfill leachates is added to represent a worst case

<sup>39</sup> Via laboratory experiments and modelling techniques it was concluded that levels close to 5 µg L<sup>-1</sup> and an order of magnitude higher could be expected from moderately mature and mature wastes.

future leachate concentration as a result of an increasing cadmium content in the MSW. It should be stressed that this seems indeed a worst case since under aerobic conditions predicted solubility limits are around an order higher than measured leachate concentrations suggesting that other mechanisms such as adsorption phenomena are limiting cadmium release.

However, as it has already been indicated in subsection “Overall cadmium emissions from landfilling MSW” under Section 3.1.2.2.5 the composition of the future leachate cannot be predicted based on current knowledge since there is no direct relationship between the total content of Cd and the leachability of Cd. If the simplified assumption is taken that there would exist a simple direct linear relationship between the cadmium leachate concentration and the cadmium content in the solid mass as has been assumed in other studies (e.g. Leenaars and Steketeer, 1997 (in: van der Poel, 1999) and Camobreco et al. (1999)) this could be calculated as followed:

$$CdConc_{Future,leachate} = \frac{CdConc_{present,leachate}}{CdConc_{present,MSW}} \times CdConc_{Future,MSW}$$

$CdConc_{Future,leachate}$  = future cadmium concentration in the leachate ( $\mu\text{g L}^{-1}$ )

$CdConc_{Present,leachate}$  = present cadmium concentration in the leachate ( $\mu\text{g L}^{-1}$ ) =  $5 \mu\text{g L}^{-1}$

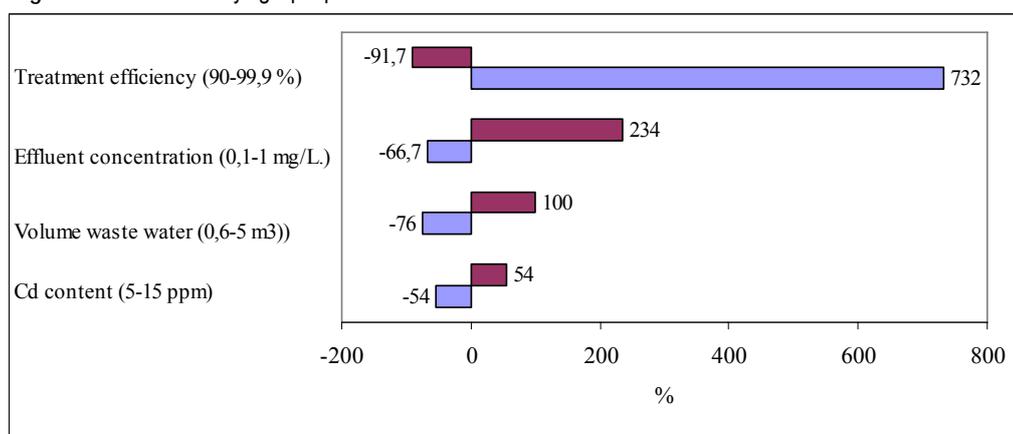
$CdConc_{Future,MSW}$  = future cadmium concentration MSW (g)<sup>40</sup> = 24 g

$CdConc_{Present,MSW}$  = present cadmium concentration in MSW (g) = 10 g

The maximum leachate concentration is calculated based on the ratio of the current cadmium concentration in the leachate for one average tonne of waste to the total cadmium present in the average tonne of waste. The future cadmium concentration in the MSW has been calculated in Section 3.1.3.2.1. The results showed that a maximum steady state concentration in the MSW corresponds to  $24 \text{ g tonne}^{-1}$  dry wt. From these assumptions and using the formula above a worst-case future leachate concentration of  $12 \mu\text{g L}^{-1}$  can be calculated which is well within the range ( $0.5\text{-}50 \mu\text{g L}^{-1}$ ) used in the sensitivity analysis.

The effects of varying the different input parameters (by the values shown in **Table 3.58**) on the overall results are shown in **Figures 3.9-3.10**. On the figures, the dark bar shows the effect of the maximum value and the grey bar shows the effects of the minimum values.

Figure 3.9 Effects of varying input parameters on MSW incinerator emissions

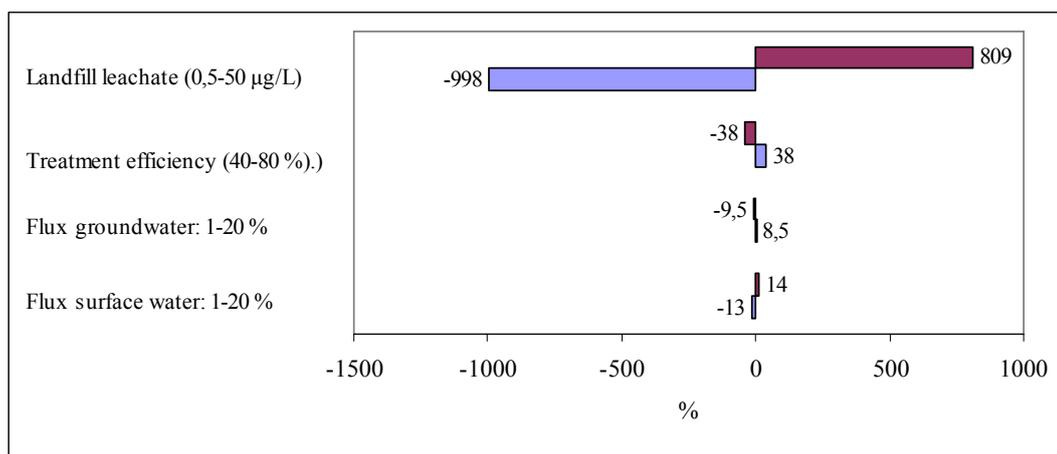


<sup>40</sup> Obtained via the modelling of future NiCd waste arisings (see subsection “Forecasts of future battery waste arisings” under Section 3.1.2.2.5). Remark: note that the total amount of the MSW will probably also further increase (EEA, 2000) but this has not been taken into account in this TRAR.

From **Figure 3.9**, varying the different parameters has a significant effect on the overall results:

- Cadmium concentrations in bottom ash and fly ash vary with 50%: 1.6-25.9 g tonne<sup>-1</sup> dry wt. (bottom ash); 82.9-300 g tonne<sup>-1</sup> dry wt. (fly ash);
- Emissions to surface water and sludge are the most influenced by the choice of treatment efficiency. A lower treatment efficiency (90%) will result in a higher emission to water (+ 732%).

Figure 3.10 Effects of varying input parameters on MSW landfill water emissions



From **Figure 3.10**, varying the different parameters has a significant effect on the overall results:

- The choice of the flux to groundwater or surface water has only a minor influence ( $\pm 8.5$ -14%);
- The choice of the treatment efficiency in the STP has a moderate influence ( $\pm 38$ %);
- The choice of leachate concentration has the highest impact and varies between – 998% to 809%.

Based on the results above it can be concluded that modifying certain default parameters can have a large effect on the overall emissions of the disposal phase. Where possible the effect of changing these parameters has been taken into account in this report. First of all the emissions to the different compartments have been quantified based on the European average situation (24.4% incineration and 75.6% landfill) and completed by two scenarios (100% land-filling and 100% incineration). The effect of increased total cadmium content in MSW is covered in the future scenarios (10 and 75% collection) for MSW incinerators with a cadmium content of respectively 13.2 and 24 g tonne<sup>-1</sup> dry wt. The effect of a hypothetical higher landfill leachate concentration of 50 µg L<sup>-1</sup> has also been taken forward as a scenario. Furthermore for landfills the assessment was performed with and without the presence of a STP.

### 3.1.2.2.6 Summary: releases to the environment due to battery related life cycle steps

The overall cadmium emission of the disposal phase originating from all products containing cadmium in MSW can be found in **Table 3.35** (incineration current situation), **Table 3.39** (incineration future situation) and **Table 3.55** (landfills). In **Tables 3.59-63** only a summary of the cadmium EU emissions from different parts of the life cycle of NiCd batteries taken forward

in the analysis is given. It is important to note that a large uncertainty surrounds the figures of the disposal phase (see subsection “Sensitivity analysis” under Section 3.1.2.2.5).

Table 3.59 Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of NiCd batteries (realistic scenario: 24.4% incineration and 75.6% land-filling). Scenario 10 mg kg<sup>-1</sup> dry wt. cadmium

Life cycle stages	Emission distribution in kg year <sup>-1</sup>				
	Air	Water	Urban/ind. soil/agr. soil	Ground-water	Total release
1 Manufacturing of NiCd batteries and/or battery packs	51	65	0	0	116
2 Incorporation into battery powered devices and applications	0	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>• Collection</li> <li>• Processing</li> <li>• Recovery</li> </ul>	1.8	0.1	0	0	1.9
5 Disposal (10-50% NiCd batteries contribution) <ul style="list-style-type: none"> <li>• Incineration (24.4%)</li> <li>• Land-filling (75.6%)</li> </ul>	323-1,617 N/A	35-176 49-244	N/A 56-278	N/A 12-58	358-1,793 117-580
<b>Total</b>	<b>376-1,670</b>	<b>149-485</b>	<b>56-278</b>	<b>12-58</b>	<b>593-2,491</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.60 Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of NiCd batteries (worst case scenario: 100% incineration). Scenario 10 mg kg<sup>-1</sup> dry wt. cadmium

Life cycle stages	Emission distribution in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	51	65	0	116
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>• Collection</li> <li>• Processing</li> <li>• Recovery</li> </ul>	1.8	0.1	0	1.9

Table 3.60 continued overleaf

Table 3.60 continued Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of NiCd batteries (worst case scenario: 100% incineration). Scenario 10 mg kg<sup>-1</sup> dry wt. cadmium

Life cycle stages	Emission distribution in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
5 Disposal (10-50% NiCd contribution)				
• Incineration (100%)	1,402-7,009	144-721	N/A	1,546-7,730
• Land-filling (0%)	N/A	N/A	N/A	N/A
<b>Total</b>	<b>1,455-7,062</b>	<b>209-786</b>	<b>0</b>	<b>1,664-7,848</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.61 Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of NiCd batteries (worst case scenario: 100% land-filling). Scenario 10 mg kg<sup>-1</sup> dry wt. cadmium

Life cycle stages	Emission distribution in kg year <sup>-1</sup>				
	Air	Water	Urban/ind. soil/agr. soil	Ground-water	Total release
1 Manufacturing of NiCd batteries and/or battery packs	51	65	0	0	116
2 Incorporation into battery powered devices and applications	0	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/	/
4 Recycling					
• Collection					
• Processing	1.8	0.1	0	0	1.9
• Recovery					
5 Disposal (10-50% NiCd contribution)					
• Incineration (0%)	0	0	N/A	0	0
• Land-filling (100%)	N/A	56-264	60-302	13-63	129-629
<b>Total</b>	<b>53</b>	<b>121-329</b>	<b>60-302</b>	<b>13-63</b>	<b>247-747</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.62 Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 13.2 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Emission distribution in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	51	65	0	116
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>• Collection</li> <li>• Processing</li> <li>• Recovery</li> </ul>	1.8	0.1	0	1.9
5. Disposal (32% NiCd batteries contribution) <ul style="list-style-type: none"> <li>• Incineration (100%)</li> <li>• Land-filling (0%)</li> </ul>	4,486 N/A	615 N/A	N/A N/A	5,101 N/A
<b>Total</b>	<b>4,539</b>	<b>680</b>	<b>0</b>	<b>5,219</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.63 Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 24 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	51	65	0	116
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>• Collection</li> <li>• Processing</li> <li>• Recovery</li> </ul>	1.8	0.1	0	1.9

Table 3.63 continued overleaf

Table 3.63 continued Summary of the distributions in kg (total in EU) of Cd emissions to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 24 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
5. Disposal (63% NiCd batteries contribution)				
• Incineration (100%)	8,831	2,178	N/A	11,009
• Land-filling (0%)	N/A	N/A	N/A	N/A
<b>Total</b>	<b>8,882</b>	<b>2,243</b>	<b>0</b>	<b>11,125</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

### 3.1.2.3 Releases based on update site-specific exposure data (reference year 2002)

#### 3.1.2.3.1 Cadmium metal and cadmium oxide production

As described in Section 2.1.2, the number of companies still manufacturing cadmium metal is reduced to three. Only one plant is still producing cadmium oxide.

An overview of Cd emissions to water and air from Cd metal and CdO production is presented in **Table 3.64**, **Table 3.65**, **Table 3.66** and **Table 3.67** (reference year 2002). Information on waste for these sectors is presented in **Table 3.68** and **Table 3.69**. These data are extracted from plant information recently submitted by the remaining Cd metal/CdO producing plants in the EU-16 (Industry Questionnaire 2004).

#### *Cadmium metal production*

- The three remaining cadmium metal producing plants all reported information on emissions to water (emission factors varying between 1.10 and 277 g tonne<sup>-1</sup>). The total Cd emission to the aquatic environment from the three existing Cd metal producing plants (plant 1, 6, 7) in 2002 is 70.5 kg year<sup>-1</sup>. Water emission data for the year 2004 are reported for Cd metal production plant 7. The total yearly Cd emission to water is reduced by a factor of 1.6; the emission factor is reduced with 16% (i.e. 232 g tonne<sup>-1</sup> versus 277 g tonne<sup>-1</sup>). As mentioned in the section below, on changes in emission reduction measures, substantial changes have taken place at this site in the collection and treatment of waste water in the period 2002-2004, resulting in a reduction of water emissions.
- All companies presented information on air emissions (stack emissions) (emission factors varying between 23.8 and 259 g tonne<sup>-1</sup>). The total EU emission to the air compartment from cadmium metal producers is 94.6 kg Cd/year.
- For all sites fugitive emissions are included in the reported stack emissions. One site reports that fugitive emissions amount to 60-70% of total air emissions.
- Number of emission days to water and air is 365 days for all sites.

- Measured effluent concentrations (annual mean), effluent discharge rates and type of receiving surface water (ditch, tide influenced river, sea) are reported for all companies.
- For two out of three companies, detailed information with respect to on-site treatment of waste water in a WWTP is submitted. There are two physico-chemical treatment plants in use on-site 7; one central water treatment plant and one weak acid treatment plant. In the central water treatment plant; lime (CaO) and sodium sulphide (Na<sub>2</sub>S) are used as the main precipitation agents. The main reaction is precipitation of the metals as hydroxides in the pH range of 8.3-8.5. In order to control the Cd concentration in the effluent, some sodium sulphide is added before the water enters a thickener in which the hydroxides/sulfides are settled. The effluent/overflow from the thickener is polished in sand filters. The water treatment plant is continuously controlled (24 hours a day: pH, flow and other parameters). The waste water from Cd metal production-site 1 is purified in an on-site waste water treatment plant using a bacteriological process in which metal sulphates are converted into metal sulphides. In the first step of this process –Biological DeSulfurisation (BDS) stage-process water containing a high sulphate concentration is treated. The BDS-process consists of an initial chemical pre-purification step (separation of metals (solids) and fluoride from the waste water) followed by a bacteriological purification stage (conversion of sulphate to sulphides). The sludges (metal-sulphates, solids) arising from previous treatment steps are recycled to the main production process. The effluent from the BDS water purification step is further purified in the next step, the SRB (Sulphate Reducing Bacteria) water purification process (capacity of 400 m<sup>3</sup>/hour). The SRB water purification plant is fed with waste water containing low concentrations of metals and sulphate, i.e. the effluent from the BDS process and water from the geohydrological control system. In an UASB (‘upflow anaerobic sludge blanket’) reactor bacteria –fed by ethanol- convert sulphates to sulphides. The excess of formed sulphide is converted by bacteria to sulphur in a fixed film reactor. The sludge of metal sulphides is recycled to the main zinc production process. This technique is known as BAT. The purified water is discharged to a ditch. The effluent from the water purification plant of site 1 is controlled 52 times a year by taking flow proportional samples; the analytical method is according to national standard 6426; the detection limit is 0.3 µg L<sup>-1</sup>. Site 6 mentions that the waste water is treated in an on-site water treatment plant; the effluents from this site are treated together with discharges from another metal producing site (distribution 50:50). There are no details on the treatment steps available.
- Waste is not generated during Cd metal production (dross, sludge, solid waste is recycled in the production).
- The flow of the receiving surface water –necessary to calculate a site specific dilution factor- is available for 2 companies (site 1, 6). Site 7 discharges its waste water to a sea environment for which a default dilution factor of 100 is applied.

Significant changes in production/emission reduction measures since 1996 are reported as follows:

- Site 1: in 2000, change of raw material (Century concentrate). Due to new national regulation entering into force, and the fact that Century concentrate was dustier than the concentrates worked up before, a lot of actions were taken: closed conveyor system, closed storage bins with under pressure and baghouse, house keeping etc. Cadmium concentration in Century concentrate is lower as in the concentrates used till 2000. So several Cd emissions (related to diffuse concentrate/calcline emissions) are proportional lower. Former concentrate until 2000: 0.19% Cd, after 2001: 0.12% Cd. Cd production in 1997: 745 tonnes, 2004: 549 tonnes. Cd emission is only for a small part related to the Cd plant, most of the Cd emissions are related to the zinc production. Since 2002 further remediation

actions took place: formerly untreated historically contaminated water from the plant area is now also treated in the WWTP (see also the footnote of **Table 3.64**).

- Site 6: none reported.
- Site 7: 2001-2003. Collecting and treating/reuse of approximately 90% diffuse emissions and storm/runoff waters from the industrial site. A containment basin was built under the industrial site to collect surface and storm water. 2003. Modernising the central water treatment plant. 2003-2004. Construction of a new quay to reduce pollution/runoff due to spill during unloading of raw materials. 1995-to date: installation of abatement systems in stacks in the leaching plant.

### *Cadmium oxide production*

- The only remaining Cd oxide production plant reports that no waste water discharges from the site occur since the production of cadmium oxide is a totally dry process.
- Very recently an update of the air emission data is provided. Total Cd emission to the atmosphere amounts to 6.6 kg year<sup>-1</sup> (in-house methods; predicted; year 2005 stack measurements: 53-55 µg Cd/m<sup>3</sup>, average flow rate: 10,000 m<sup>3</sup>/hour; number of emission hours: 6,000 hours/year, 2 stacks). Please note that for the year 2004 the total Cd emission to the air is reported as 11.7 kg year<sup>-1</sup> (independent laboratory) (based on an average Cd concentration of 97 µg/m<sup>3</sup> (two stacks), average flow rate: 10,000 m<sup>3</sup>/hour; number of emission hours: 6,000 hours/year). Both emission values will be taken forward to the exposure assessment and risk characterisation.
- Number of emission days to air is 256 days.
- Information on waste is not available.

### Release to water

Table 3.64 Aquatic emissions from Cd metal producing plants in the EU-16

Plant N°	Production volume	Production emission <sup>¶</sup>	Emission factor	Conc.l effluent <sup>(c)</sup>	Number of emission days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Low flow receiving water <sup>(b)</sup>	Year
	tonne y <sup>-1</sup>	kg y <sup>-1</sup>	g tonne <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	
1	485	12.0 <sup>(d) (f)</sup>	25	M (T)	365	0.004 <sup>(g)</sup>	9,060	12,000	2002
6	420	0.50 <sup>(d)</sup>	1.10	M (T)	365	0.0007 <sup>(h)</sup>	1,169	13 10 <sup>6</sup>	2002
7*	209	58 <sup>(e)</sup>	277	M (T)	365	0.05	3,200	-*	2002
7*	155	36 <sup>(e)</sup>	232	M (T)	365	0.030	3,200	-*	2004

a) Mean annual;

b) 10<sup>th</sup> percentile of flow rate or 1/3 of annual mean flow rate (TGD - EC, 2003);

c) M: measured value, E: estimated value, D: dissolved concentration, T: total concentration;

d) Emission of Cd from Zn or Zn and Pb production;

e) Only process discharges, no diffuse discharges (surface/storm water etc) included;

f) The total emission in 2002 consists of discharge of effluent from water purification plant and discharge of other water from the plant area (historic contaminated). Since 2005, the discharge from water from the plant area has been stopped; since then all waste water is treated in the purification plant;

g) The effluent concentration of 4 µg L<sup>-1</sup> is a weighted average Cd concentration for both types of water discharges (effluent: avg conc. 1.5 µg L<sup>-1</sup>, P90: 2.3 µg L<sup>-1</sup>; discharge: 2,736,115 m<sup>3</sup>/year; other plant area water: avg concentration: 13.6 µg L<sup>-1</sup>; total discharge: 571,334 m<sup>3</sup>/year);

¶ Annual averages;

\* Emission to the sea;

h) Measured by supervision authority.

Table 3.65 Aquatic emissions from Cd oxide producing plants in the EU-16

Plant N°	Production volume	Production emission <sup>¶</sup>	Emission factor	Conc. In effluent <sup>®</sup>	Number of emission days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Low flow receiving water <sup>(b)</sup>	Year
	tonnes y <sup>-1</sup>	kg y <sup>-1</sup>	g tonne <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	
12	4,498	0 <sup>(d)</sup>	0		0	20	0	0	2002

a) Mean annual;

b) 10<sup>th</sup> percentile of flow rate or 1/3 of annual mean flow rate (EC, 2003);

c) M: measured value, E: estimated value, D: dissolved concentration, T: total concentration;

d) No emissions to water; thermal/dry process;

¶ Annual averages.

### Release to air

Table 3.66 Atmospheric emissions from Cd metal producing plants in the EU-16

Plant N°	Production volume	Production emission amount <sup>¶</sup>	Emission factor	Year
	tonnes y <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
1	485	30.4 <sup>(a)(b)</sup>	62.7	2002
6	420	10.0 <sup>(a)(c)</sup>	23.8	2002
7	209	54.2 <sup>(a)(d)</sup>	259	2002

¶ Annual averages;

a) Cd emission from whole plant (including Zn and/or Pb production);

b) Total emissions: stack and diffuse emissions; diffuse emissions: 60-70% of total; stack emissions: 30-40% of total emissions;

c) All emissions from point sources and fugitive emissions from roof openings for the whole zinc production process (extensive monitoring programme 2001/2002). Emissions from cadmium production are difficult to separate;

d) Total emissions from the zinc smelter; approx. 90 emission points to air. Approximately 90% of the emission comes from 20% of the emission points which all are equipped with abatement systems (demisters or scrubbers).

Table 3.67 Atmospheric emissions from Cd oxide producing plants in the EU-16

Plant N°	Production volume	Production emission amount <sup>¶</sup>	Emission factor	Year
	tonnes year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
12 <sup>(a)</sup>	n.d.	6.6 <sup>(a)</sup>	n.d.	2005
12	n.d.	11.7 <sup>(b)</sup>	n.d.	2004

¶ Annual averages;

a) Cd in stack emissions is recently measured (year 2005): average Cd concentration: 55 µg/m<sup>3</sup> (punctual measurement, in-house methods; no further information available);

b) Cd in stack emissions measured by external laboratory (year 2004; no further information available); average Cd concentration : 97 µg/m<sup>3</sup>;

n.d. No data available.

Waste

Table 3.68 Waste information for Cd metal producing plants in the EU-16

Plant N°	Type of waste produced	Quantity of waste (tonnes y <sup>-1</sup> )	Cd content %	Waste disposal type	Year
1	No waste produced  Recycling of liquids directly into the leaching process. Recycling of solid wastes (scalings) by the residue recycling.  Sludge out off the water purification is used as secondary raw material.	Not applicable  n.d.	Not applicable  n.d.	Internal recycling  Internal recycling	2002  2002
6	No waste related to cadmium production	Not applicable	Not applicable	Not applicable	2002
7	Normally no waste is produced during production of Cd metal. The Cd is a by product from the hydrometallurgical Zn metal production from Zn concentrates. In the Cd foundry some dross is produced but the material is recycled to the production.  Sludges from the water treatment plants are deposited in mountain cavern deposits together with the other process wastes, however, the metal containing hydroxide cake from the weak acid treatment plant is recycled to the zinc process.	Not applicable	Not applicable	Internal recycling	2002

n.d. No data available.

Table 3.69 Waste information for Cd oxide producing plants in the EU-16

Plant N°	Type of waste produced	Quantity of waste (tonnes y <sup>-1</sup> )	Cd content %	Waste disposal type	Year
12	n.d.	n.d.	n.d.	n.d.	2002

n.d. No data available.

### 3.1.2.3.2 Release during processing and use

#### NiCd batteries' production and recycling

As described in Section 2.2.1 the number of companies producing NiCd batteries has further decreased in recent years. Five NiCd battery producers and three NiCd battery recyclers are still in operation. At present, updates on environmental emissions to water and air have been submitted by 3 NiCd battery producers and 3 recyclers (year 2002). Please note that the previous update of exposure information for these sectors was 1999/2000. The data are summarised in **Table 3.70**, **Table 3.71**, **Table 3.72** and **Table 3.73**. Waste information was collected from battery manufacturing and recycling plants. The data are presented in **Table 3.74** and **Table 3.75**.

#### *Production of NiCd batteries*

- Three out of five remaining NiCd battery producing plants submitted information on emissions to water (site 2, 3, 4). It should be noted however that emissions from site 2 include emissions from battery manufacturing as well as Cd recycling. The site is involved in both activities and wastewater emissions cannot be split between two factories. The total Cd emission to the aquatic environment from NiCd battery producing plants is 49.1 kg year<sup>-1</sup>. It should be noted as well that the updated emissions are derived on the basis of annual average effluent concentrations, as opposed to the emissions given in the original TRAR document (see Section 3.1.2.2.1) in which P90's values were calculated on monthly average effluent concentrations.
- Two companies (site 2, 4) provided information on air emissions (stack emissions). The total Cd emission to the air compartment from this sector is 8.5 kg year<sup>-1</sup>. As mentioned before, site 2 is both a NiCd battery producing and Cd recycling site. The reported emission figure of 5 kg year<sup>-1</sup> is originating from battery manufacturing only. For site 3 no information is provided since air emissions are not monitored. According to the company, there are no requirements for air monitoring in the permit since the plant runs a wet process (most emissions are to water).
- Fugitive emissions are not monitored.
- Number of emission days to water and air varies between 330 and 344 days.
- Measured effluent concentrations (annual mean), effluent discharge rates and type of receiving surface water (tide influenced river, sea, river) are reported for all companies.
- New information with respect to on-site treatment of waste water in a WWTP is not submitted. It is assumed that all waste waters are treated in an on-site WWTP/municipal STP before being discharged into surface waters.
- The following Cd containing waste arises from battery production: old batteries, powders, sludge, plates, other. In general all materials are recycled (external recycling in Cd recycling plants). In some cases sludge can also be land-filled.
- The flow of the receiving surface water –necessary to calculate a site specific dilution factor- is available for 3 companies (site 2, 3, 4).

#### *Recycling of NiCd batteries*

- Three NiCd battery recycling plants (site 1, 2, 2bis) reported information on emissions to water. Site 1 reports very low emissions to water for the year 2002 i.e. 0.13 kg year<sup>-1</sup>.

Moreover, wastewater emissions -and emission factors- from this site are further reduced in 2003/2004 ( $0.06 \text{ kg year}^{-1}$ ) due to efforts to conform to ISO 14000, for which the site has been certified in February 2005 (details are included in the section below: 'significant changes in emission reduction measures'). The information for site 2bis is already included in the NiCd battery producing section, since waste water emissions could not be split between NiCd-battery manufacturing and recycling plant. Site 2 states that no site emissions are discharged to surface water. All waste waters are collected and treated off-site in an external waste water treatment plant (total volume of waste water:  $100 \text{ m}^3/\text{year}$ , no further update data available) (1996 data: 35 tonnes fluid waste per year; Cd content: 20 ppm (total Cd); effluent concentration of off-site STP:  $0.2 \text{ mg L}^{-1}$ ).

- Three Cd recycling plants (site 1, 2, 2bis) provided information on air emissions (stack emissions). Site 1 reports air emissions of  $3.97 \text{ kg Cd/year}$  for the year 2002. In analogy with water emissions, air emissions –and emission factors- are further reduced in 2003/2004 i.e. to  $0.91 \text{ kg year}^{-1}$  as a result of measures taken to obtain an ISO 14000 certificate (building coverage, aspiration devices) (details are included in the section below: 'significant changes in emission reduction measures'). The total Cd emission to the air compartment from the site 2bis is  $0.85 \text{ kg year}^{-1}$ . Please note that the reported figure for this site –NiCd battery manufacturing and Cd recycling plant- is related to recycling only. The very low emission of  $0.002 \text{ kg Cd/year}$  for site 2 is validated on the basis of the submitted air measurements' report (IUTA-Prüfbericht, 2004). The low emission figure is a result of very low Cd concentrations detected in the stack emissions (Cd conc.  $2.5 \text{ } \mu\text{g}/\text{m}^3$ ) combined with a low gas flow rate ( $78 \text{ m}^3/\text{hour}$  maximum).
- Fugitive emissions are not monitored.
- Number of emission days to water and air is 330-360 days.
- Since for site 2 wastewater is not discharged locally (near the site), but collected and treated off-site, other water related emission information for this site (effluent discharge rate, type of receiving water and flow rate of surface water) is not relevant. The information relevant for site 2bis is reported in the section on NiCd battery manufacturing. Measured effluent concentrations (90P value/annual mean), effluent discharge rate and type and flow (low flow rate) of receiving surface water (river) are reported for site 1.
- Waste arising from the recycling of NiCd batteries e.g. batteries plastic boxes, metallic boxes, concentrated electrolytes, Fe/Cd electrodes is recycled or land-filled. Waste arising from the treatment of stack (air) emissions and waste water (dust filters, sludges) is recycled.

Significant changes in production/emission reduction measures since 1999/2000 are reported as follows:

- NiCd battery manufacturing plants: not available
- Cd recycling site 1: Invested improvements in building coverage and investment of aspiration device with a capacity of  $60,000 \text{ m}^3/\text{hour}$  to prevent diffuse emissions to air (since 2002). Improvements are ongoing in 2005. Wastewater and air emissions: efforts to conform to ISO 14000, for which the site has been certified in February 2005. The main changes that took place at the level of waste water emissions are the following: a) Because of the negative impact of the presence of cooling liquid -originating from electric vehicles batteries- and hydrocarbons -sometimes present in the electrolyte from batteries- on the WWTP efficiency, it was decided to collect the cooling liquid –during the batteries dismantlement- separately and send it for recycling. The electrolyte collecting system was modified by adding a hydrocarbon separator. The following actions were undertaken to

reduce air emissions: a) high efficiency systems were modified: i.e. two rows of filters were installed instead of one; in this manner maintenance operations are secured, peaks are avoided and Cd emissions are reduced. b) Furthermore, work was done on the empowerment of the operators using these air treatment systems by setting up luminous devices, which indicate the state of sealing. The use of these ‘warnings’ improved the follow up of the installations as well as immediately reduced the delays due to maintenance intervention.

- Cd recycling site 2: Installation of active carbon filter between furnaces and chimney (installed between 2002 and today).

### Release to water

Table 3.70 Aquatic emissions from NiCd batteries producing plants in the EU-16

plant N°	Consumption volume (expressed as Cd)		Emission <sup>¶</sup>	Emission factor	Col in effluent <sup>(c)</sup>	Number of emission days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Low flow receiving water <sup>(b)</sup>	Year
	tonne year <sup>-1</sup>	kg year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	
2*/2bis	453		11.5 <sup>(d)*</sup>	25.4	M (T)	330	0.11	326	432,000*	2002
3	454		13.7	30.2	M (T)	330	0.06	655	17 10 <sup>6</sup>	2002
4	771		23.9	31.0	M (T)	344	0.10	673	1,244,160	2002
6	No update data		No update data							
7	No update data		No up data							

a) Mean annual;

b) 10<sup>th</sup> percentile of flow rate or 1/3 of annual mean flow rate (EC, 2003);

c) M: measured value, E: estimated value, D: dissolved concentration, T: total concentration;

d) Emissions from battery manufacturing plant and Cd recycling plant combined, emissions cannot be split between two factories;

¶ Annual averages;

\* Emission to the sea.

Table 3.71 Aquatic emissions from NiCd batteries recycling plants in the EU-16

Plant N°	Production volume (expressed as Cd)		Emission <sup>¶</sup>	Emission factor Inc. in effluent <sup>(c)</sup>	Number of emission days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Low flow receiving water <sup>(b)</sup>	Year
	Tonne year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	
1	853	0.13	0.15	M (T)	191	0.37 (90P) 0.16 (avg)	4.2	11,232	2002
1	816	0.06	0.07	M (T)	177	0.24 (90P) 0.1 (avg)	3.3	11,232	2004
2	62	0 <sup>(d)</sup>	0	0	360	0	0	0	2002
2bis	See data on-site is in Table 3.7								

a) Mean annual effluent flow for the year 2002 is 4.2 m<sup>3</sup> d<sup>-1</sup> and for 2004 is 3.3 m<sup>3</sup> d<sup>-1</sup>;

b) 10<sup>th</sup> percentile of flow rate or 1/3 of annual mean flow rate (EC, 2003);

c) M: measured value, E: estimated value, D: dissolved concentration, T: total concentration; ¶annual averages;

d) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant.

Release to air

Table 3.72 Atmospheric emissions from NiCd batteries producing plants in the EU-16

Plant N°	Consumption volume (expressed as Cd)	Production emission amount <sup>¶</sup>	Emission factor	Year
	tonne year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
2	453	5.0 <sup>(a)</sup>	11.04	2002
3	454	n.d. <sup>(b)</sup>	n.d.	2002
4	771	3.5	4.54	2002
6	No update data	No update data		
7	No update data	No update data		

<sup>¶</sup> Annual averages; n.d.: no data available;

- a) Emission from battery manufacturing only; air emissions are broken down between two plants; battery manufacturing and Cd recycling;
- b) Air emissions are not monitored. No requirement in the permit since the plant runs a wet process, therefore most emissions are releases in the water.

Table 3.73 Atmospheric emissions from NiCd batteries recycling plants in the EU-16

Plant N°	Production volume (expressed as Cd)	Production emission amount <sup>¶</sup>	Emission factor	Year
	tonne year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
1	853	3.97	4.55	2002
1	816	0.91	1.10	2004
2	771	0.0019 <sup>(a)</sup>	0.00002	2002
2bis	453	0.85 <sup>(b)</sup>	8.30	2002

<sup>¶</sup> Annual averages;

- a) Submitted air emissions are checked versus the analysis report and proved to be correct. Air emissions are that low due to the fact that in air emission no considerable amount of Cd can be found (conc. 2.5 µg/m<sup>3</sup>) and the fact that the gas stream is very low due to technical reasons (78 m<sup>3</sup>/hour maximum); analysis performed by external laboratory;
- b) Emissions from Cd recycling unit on the site of battery manufacturing plant 2.

Waste

Table 3.74 Waste information for NiCd batteries producing plants in the EU-16

Plant N°	Type of waste produced	Quantity of waste	Cd content	Waste disposal type	Year
		(tonnes y <sup>-1</sup> )	%		
2	Old batteries	20.6	7%	Recycling plant	2002
	Powders (from sludge recycling)	25	95%	Recycling plant	
	Plates	38	27%	Recycling plant	
	Other (filters etc)	6	5%	Incineration	

Table 3.74 continued overleaf

Table 3.74 continued Waste information for NiCd batteries producing plants in the EU-16

Plant N°	Type of waste produced	Quantity of waste	Cd content	Waste disposal type	Year
		(tonnes y <sup>-1</sup> )	%		
3	Old batteries	72	7-10%	External recycling plant	2002
	Sludge (filtercakes)	218	57% water, 4% Cd on dry weight	Special (CET1) landfill	
	Plates	51	48%	External recycling plant	
	Others (filters etc.)	17	20%		
4	Old batteries	185	13%	External recycling plant	2002
	Sludge (filtercakes)	187	50% water, 9.7% Cd on dry weight	External recycling plant	
	Plates	117	18%	External recycling plant	
	Others (filters etc.)	1	5%		
6	No update data	No update data			
7	No update data	No update data			

Table 3.75 Waste information for NiCd batteries recycling plants in the EU-16

Plant N°	Type of waste produced	Quantity of waste	Cd content	Waste disposal type	Year
		(tonnes y <sup>-1</sup> )	%		
1	Batteries plastic boxes	256	0.33 mg kg <sup>-1</sup>	Industrial landfill	2002
	Batteries metallic boxes				
	Fe/Cd electrodes after treatment; Concentrated electrolytes	169.5	0.1 mg kg <sup>-1</sup>	Recycling	
	Process slag, air treatment dust, used filters, rainwater sludges.	262.7	0.5 mg kg <sup>-1</sup>	Industrial landfill	
		186.2	4.2 mg kg <sup>-1</sup> .	Neutralisation	
				Internal treatment.	
2	n.a.	n.a.	n.a.	n.a.	2002
2bis	Old batteries	1,024	9%	Recycling	2002
	Powders	25	95%		
	Plates	38	27%		

### Production of Cd containing pigments

Compiled updated emission information for the three remaining Cd pigments producers was submitted (year 2003). A summary of releases to water and air is given in **Table 3.76** and **Table 3.77**. Waste information is presented in **Table 3.78**.

- The three remaining Cd pigments producing plants (site A, B, C) reported information on emissions to water (emission factors not available). The total Cd emission to the aquatic environment in 2003 is 10.9 kg year<sup>-1</sup>. Please note that year 2004 waste water emission data have been provided by site C; Cd emission from this site amounts to 4.4 kg year<sup>-1</sup> (as opposed to 6.9 kg year<sup>-1</sup> for the year 2003).
- All companies presented information on air emissions (stack emissions) (site-specific emission factors not available). The total EU emission to the air compartment from cadmium pigments producers is 11.0 kg Cd/year.
- Information on fugitive emissions is not provided.
- The number of emission days to water and air varies between 318-365 days.
- Measured effluent concentrations (annual mean), effluent discharge rates and type of receiving surface water (river) are reported for all companies. The effluent from site C is analysed daily (usually a 24 hours composite sample). Effluent samples are analysed by Atomic Absorption using either 'flame' or 'graphite furnace'. The laboratory participates in the Aqua check scheme (Water Proficiency Testing and Laboratory Performance Monitoring) as a means of ensuring accurate results for metals in aqueous effluents.
- New information with respect to the on-site treatment of waste water in a WWTP is submitted for all sites. For Cd pigments producing sites in general, the on-site treatment of aqueous effluent is an integral part of the production process. The treatment of the aqueous effluent is a chemical/physical process involving pH change to precipitate Cd, followed by filtration to remove Cd carbonate. For site C specifically, all aqueous waste is collected and treated by raising the pH to 9 using sodium carbonate solution in a stirred treatment vessel. This precipitates the soluble Cd as carbonate. The resultant suspension is filtered through a filter press to remove suspended solids. The filtrate is tested for suspended solids, re-filtered and then passed to a (settling) 'pool' that allows a continuous discharge of effluent to the receiving river over 365 days/year.
- Sludge from the treatment of waste water and other solid wastes are land-filled.
- The flow of the receiving surface water –necessary to calculate a site specific dilution factor- is available for all companies.

Significant changes in production/emission reduction measures since 1996 are reported as follows:

- The most significant changes are for losses to solid wastes. Figures submitted for the previous draft of the RAR were lower because at that time waste solids from treatment of production waste water were sent to zinc refiners for recovery of zinc and cadmium. Environmental pressures have forced the closure of the relevant zinc refiners, and the waste solids now have to be sent to landfill.

Release to water

Table 3.76 Aquatic emissions from Cd pigments producing Plants in the EU-16

Plant N°	Production/consumption volume	Processing emission <sup>¶</sup>	Emission factor	Conc. in effluent <sup>(c)</sup>	Number of emission days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Low flow receiving water <sup>(b)</sup>	Year
	tonne year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	M <sup>3</sup> d <sup>-1</sup>	
A	n.d.	1.0	n.d.	M(T)	365	0.02	145	3,333	2003
B	n.d.	3.0	n.d.	M(T)	318	0.02 <sup>(f)</sup>	498	1,681,920	2003
C	n.d.	6.9 <sup>(d)</sup>	n.d.	M(T)	365	0.12 <sup>(e)</sup>	156	45,000	2003
C	n.d.	4.4	n.d.	M(T)	365	0.08 (90P) 0.05 (avg)	240	45,000	2004

a) Mean annual;

b) 10<sup>th</sup> percentile of flow rate or 1/3 of annual mean flow rate (EC, 2003);

c) M: measured value, E: estimated value, D: dissolved concentration;

d) Waste water consists of process waste water and rainwater collected from buildings and exterior storage areas;

e) Average Cd concentration in effluent for the year 2004 is 0.05 mg L<sup>-1</sup>; 90P value: 0.08 mg L<sup>-1</sup>. Total discharge: 87480 m<sup>3</sup>/d. T: total concentration;f) P90 in effluent for the year 2004: 0.054 mg L<sup>-1</sup>; <sup>¶</sup>annual averages; n.d.: no data available.Release to air

Table 3.77 Atmospheric emissions from Cd pigments producing plants in the EU-16

Plant N°	Production/consumption volume	Processing emission <sup>¶</sup>	Emission factor	Year
	tonne year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
A	n.d.	2.50	n.d.	2003
B	n.d.	5.60	n.d.	2003
C	n.d.	2.90	n.d.	2003

<sup>¶</sup> Annual averages;

n.d. No data available.

Waste

Table 3.78 Waste information for Cd pigments producing plants in the EU-16

Plant N°	Type of waste produced	Quantity of waste	Cd content	Waste disposal type	Year
		(tonnes y <sup>-1</sup> )	%		
A	Solid waste and sludge	15	n.d.	landfill	2002
B	Solid waste and sludge	6.8	n.d.	landfill	2002
C	Solid waste and sludge	7.3	n.d.	landfill	2002

n.d. No data available.

Production of Cd containing stabilisers

As a result of the Vinyl 2010 commitment the number of producers in the EU-16 dropped to only a few. Only 2 companies currently acknowledged to the Rapporteur that some production still

took place at their sites located in Italy. Emission data are summarised in **Table 3.79** and **Table 3.80**. Waste information is presented in **Table 3.81**.

- The two remaining Cd stabiliser producing plants (site X, Y) reported information on emissions to water (emission factors  $< 9.0$ - $< 41.0$  g tonne<sup>-1</sup>). The total Cd emission to the aquatic environment in 2002 is  $< 1.4$  kg year<sup>-1</sup>.
- All companies presented information on air emissions (stack emissions) (emission factors  $< 1.3$ - $38$  g tonne<sup>-1</sup>). The total EU emission to the air compartment from cadmium stabiliser producers is  $< 0.74$  kg Cd/year. The analytical method used to measure Cd in air emissions from site Y is the following: MIP P-PRO-101 rev 2, 2003.
- Information on fugitive emissions is not provided.
- Depending on the site, the number of emission days to water varies between 220-365 days. The number of emission days to air varies between 50-220 days. The number of production days for site Y is 40-60 days.
- Measured effluent concentrations (annual mean), effluent discharge rates and type of receiving surface water (municipal STP, river, canal) are reported for both companies. For site Y, the analysis of waste water (ICP, dl:  $5$  µg L<sup>-1</sup>) is done every 15 days on an average sample collected during this period with an automatic sampling system (internal laboratory). Two times per year the analysis is performed by a certified external laboratory on punctual sampling (EPA 200.8, 1994; dl:  $1$  µg L<sup>-1</sup>).
- New information with respect to on-site treatment of waste water in a WWTP is submitted by company Y. This site has a physico-chemical treatment plant (comprising the following main units: homogenisation basin ( $600\text{m}^3$ ), complex additivation, flocculation, sedimentation, filter press for sludges and sand filters for treated water) followed by active carbon filters. For site X, wastewaters are treated in an on-site WWTP (type is unknown) before being discharged to a municipal STP.
- Solid waste is land-filled.
- The flow of the receiving surface water –necessary to calculate a site specific dilution factor is available for both companies.

Release to water

Table 3.79 Aquatic emissions from Cd stabiliser producing plants in the EU-16

Plant N°	Production/consumption volume	Production emission amount <sup>¶</sup>	Emission factor	Conc. in effluent <sup>(c)</sup>	Number of emission days	Concentration in effluent <sup>(a)</sup>	Effluent flow <sup>(a)</sup>	Low flow receiving water <sup>(b)</sup>	Year
	tonnes year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>			mg l <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> d <sup>-1</sup>	
X	17	< 0.70 <sup>(d)</sup>	<41	M (T)	220	On-site WWTP : < 0.005  Municipal STP : < 0.00037 <sup>(e)</sup>	370	831,050	2002
Y	77	< 0.69	<9.0	M (T)	365	< 0.005 <sup>(f)</sup>	352	86,400	2002
Y	77	< 0.69	<9.0	M (T)	365	< 0.001 <sup>(g)</sup>	352	86,400	2002

a) Mean annual;

b) 10th percentile of flow rate or 1/3 of annual mean flow rate (EC, 2003);

c) M: measured value, E: estimated value, D: dissolved concentration, T: total concentration;

d) Emission to municipal STP;

e) Cd concentration in effluent from municipal STP; calculated from Cd concentration in effluent from on-site WWTP; taking into account removal at STP: 60%; extra dilution: 2000 m<sup>3</sup>/d/370 m<sup>3</sup>/d = 5.4.; <sup>¶</sup>annual averages;

f) Analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;

g) Analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

Release to air

Table 3.80 Atmospheric emissions from Cd stabiliser producing plants in the EU-16

Plant N°	Production/consumption volume	Production emission amount <sup>¶</sup>	Emission factor	Year
	tonnes year <sup>-1</sup>	kg year <sup>-1</sup>	g tonne <sup>-1</sup>	
X	17	0.64	38.0	2002
Y	77	<0.10 <sup>(a)</sup>	<1.3	2002

<sup>¶</sup> Annual averages;

a) Analysis performed by internal laboratory.

Waste

Table 3.81 Waste information for Cd stabiliser producing plants in the EU-16

Plant N°	Type of waste produced	Quantity of waste	Cd content	Waste disposal type	Year
		(tonnes y <sup>-1</sup> )	%		
X	Solid waste	37 kg Cd	37 kg Cd	offsite inertisation and land-filling	2002
Y	n.d.	n.d.	n.d.	n.d.	2002

n.d. No data available.

Use of Cd/CdO in alloys, plating and other uses

For these uses, no site-specific update information was submitted to the Rapporteur.

### 3.1.2.3.3 Releases during the production of other non-ferrous metals

In this section, the Cd releases from four sites that stopped Cd metal production and that submitted emission information are briefly discussed. An overview of Cd emissions to water and air for each of the four non-ferrous metal producing sites is presented in Annex VI.

From this information, it can be concluded that, although the production of Cd metal stopped, Cd emissions to water and air can still be substantial -up to 427 kg Cd/year to water and 56.6 kg Cd/year to air respectively. The Cd emissions arise from the production of other non-ferrous metals (i.e. Zn and Pb). No production volumes related to other non-ferrous metals were submitted, so no corresponding emission factors could be calculated.

### 3.1.3 Predicted environmental concentrations (PEC)

#### 3.1.3.1 Local exposure assessment: in production, processing and use scenarios excluding those related to batteries

Point sources have a major impact on the environmental concentration on a local scale.

Local exposure concentrations are calculated from emission data submitted by Industry (Industry Questionnaire, 1997) according to the EU-Technical Guidelines Document (TGD, 1996). Calculated values are compared with measured concentrations near Cd emitting plants (Ind. Questionnaire, 1997) and where large differences occur, results are analysed and evaluated.

#### 3.1.3.1.1 Aquatic compartment

##### Calculated local concentrations

Calculation of local PEC-values for the aquatic compartment is performed according to the method described in the TGD (1996). On a local scale it is assumed that wastewater will pass through a STP before being discharged into the environment. Once discharged, complete mixing of the effluent in the surface water is assumed. The calculation involves several sequential steps: it includes the calculation of the discharge concentration (if not available) of a STP to a water body, the dilution effect and the removal from the aqueous medium by adsorption to suspended matter. Volatilisation and degradation are ignored because these processes are not applicable for Cd. Local sedimentation of Cd is ignored. Input data were submitted via the Industrial Questionnaire (1997).

The first step in the assessment of the local PEC values in the aquatic environment is the determination of the site-specific effluent concentration. If not available, it was calculated from reported daily releases to surface water ( $\text{kg d}^{-1}$ ) and the local effluent flow rate ( $\text{m}^3 \text{d}^{-1}$ ).

$$C_{\text{effluent}_{\text{STP}}} = \frac{\text{EMISSION}_{\text{local}}}{\text{EFFLUENT}_{\text{local}_{\text{STP}}}} \cdot 10^3$$

EMISSION<sub>local</sub>: Local emission amount from point source ( $\text{kg d}^{-1}$ )  
 EFFLUENT<sub>local<sub>STP</sub></sub>: effluent discharge rate of STP ( $\text{m}^3 \text{d}^{-1}$ )  
 C<sub>effluent<sub>STP</sub></sub>: Cd concentration in effluent of STP ( $\text{mg L}^{-1}$ ).

If no effluent discharge rate was submitted, a default value of 2,000 m<sup>3</sup> d<sup>-1</sup> (TGD, 1996) was used.

In the second step, the concentration in the receiving surface water is calculated. Complete mixing of the effluent with the receiving water is assumed. The calculation of the dilution factor is based on the given flow rate of the receiving water-body (or default: 18,000 m<sup>3</sup> d<sup>-1</sup>) and on the given discharge rate of the industrial STP (or default: 2,000 m<sup>3</sup> d<sup>-1</sup>). In the absence of both data, a default dilution factor of 10 is used for emissions to freshwater. A default dilution factor of 100 is used for emissions to the sea.

$$D = \frac{\text{EFFLUENT}_{\text{localSTP}} + \text{FLOW}}{\text{EFFLUENT}_{\text{localSTP}}}$$

D: Dilution factor  
 EFFLUENT<sub>localSTP</sub>: Effluent discharge rate of local STP (m<sup>3</sup> d<sup>-1</sup>)  
 FLOW: Flow rate of the receiving water (m<sup>3</sup> d<sup>-1</sup>)

The local available concentration of Cd in water is estimated taking into account the fraction of chemical that is adsorbed to suspended matter (TGD, 1996). The local concentration in the receiving surface water during the emission period is then calculated with the equation:

$$C_{\text{local}_{\text{water}}} = \frac{C_{\text{effluent}_{\text{STP}}} \cdot 1,000}{(1 + K_p \cdot C_{\text{susp}} \cdot 10^{-6}) * D}$$

C<sub>local<sub>water</sub></sub>: Local concentration in surface water during emission period (µg L<sup>-1</sup>)  
 C<sub>effluent<sub>STP</sub></sub>: Cd-concentration in local STP effluent (µg L<sup>-1</sup>)  
 K<sub>p</sub>: Solids-water partition coefficient of suspended matter (130000 L kg<sup>-1</sup>).  
 C<sub>susp</sub>: Concentration of suspended matter in watercourse (default = 15 mg L<sup>-1</sup>)  
 D: Dilution factor (default 10)

The value of K<sub>p</sub> can be derived from the ratio of dissolved to total Cd concentrations in waterbodies. The dissolved fraction is generally the fraction passing a 0.45 µm membrane filter. The K<sub>p</sub>-value varies with environmental conditions. Factors having a large influence on the actual K<sub>p</sub>-value are the pH, the total metal concentration, the water hardness and the nature and concentration of complexing agents. A range of measured K<sub>p</sub> values is presented in **Table 3.82**. In the calculations presented here, a European average value of K<sub>p</sub> = 130 10<sup>3</sup> L kg<sup>-1</sup> is used.

Table 3.82 The solid- water partition coefficient of suspended matter (K<sub>p</sub>) in different freshwaters

Location	K <sub>p</sub> (L kg <sup>-1</sup> ) average	K <sub>p</sub> (L kg <sup>-1</sup> ) minimum	K <sub>p</sub> (L kg <sup>-1</sup> ) maximum	Source
Flanders	17 10 <sup>3</sup>	0.28 10 <sup>3</sup>	280 10 <sup>3</sup>	VMM, 1997
the Rhine, Meuse and Schelde rivers in The Netherlands	n.a.	30 10 <sup>3</sup>	300 10 <sup>3</sup>	Ros and Slooff, 1990
4 locations in the Netherlands 1983-1986	129 10 <sup>3</sup>	n.a.	n.a.	Crommentuijn et al., 1997a
7 locations in the Netherlands 1988-1992	151 10 <sup>3</sup>	n.a.	n.a.	Crommentuijn et al., 1997a
3 locations in the Netherlands 1992-1994	224 10 <sup>3</sup>	n.a.	n.a.	Crommentuijn et al., 1997a
St Lawrence River basin 1991-1992	100 10 <sup>3</sup>	7.9 10 <sup>3</sup>	794 10 <sup>3</sup>	Quemerais and Lum, 1997

n.a. Not available

The calculated surface water concentrations are actual contributions to the receiving water. The local PEC values are obtained by adding the regional PEC value for water to the calculated local concentration in surface water.

$$PEC_{local\_water} = C_{local\_water} + PEC_{regional\_water}$$

$PEC_{local\_water}$ : Predicted environmental concentration during emission episode ( $\mu\text{g L}^{-1}$ )

$C_{local\_water}$ : Local concentration in surface water during emission episode ( $\mu\text{g L}^{-1}$ )

$PEC_{regional\_water}$ : Regional concentration in surface water ( $0.11 \mu\text{g L}^{-1}$  Table 3.157)

The local PEC values of Cd in surface water are presented in **Table 3.83**. The local PEC values range from 0.11 to  $5.54 \mu\text{g L}^{-1}$  for Cd/CdO-producing plants and from 0.11 to  $2.86 \mu\text{g L}^{-1}$  for Cd/CdO-processing plants.

Table 3.83 The local  $PEC_{water}$  (dissolved fraction) for Cd-producing and -processing plants in the EU-16. PEC's include background Cd

use-	N°	Production emission <sup>¶</sup>	Processing emission <sup>¶</sup>	Dilution factor	$C_{local\_water}$	$PEC_{local\_water}$	Year
Category		kg year <sup>-1</sup>	kg year <sup>-1</sup>		$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	
Cd-production	1	23.9		12	1.26	1.37	1996
	2	614		320	0.47	0.58	1996
	3*	15.7		100 <sup>(a)*</sup>	0.03*	0.14*	1996
	4*	21.6		100 <sup>(a)*</sup>	0.41*	0.52*	1996
	5	77.8		10 <sup>(a)</sup>	5.4	5.5	1996
	6	0.18		29,500	$7.8 \cdot 10^{-6}$	0.11	1996
	7*	70		100 <sup>(a)*</sup>	0.20*	0.31*	1996
	8	11		930	0.01	0.12	1996
	9*	17.4		100 <sup>(a)*</sup>	0.02*	0.13*	1999
	10	0 <sup>(1)</sup>		0 <sup>(1)</sup>	0 <sup>(1)</sup>	0.11	1996
	11	0 <sup>(2)</sup>		0 <sup>(2)</sup>	0 <sup>(2)</sup>	0.11	1996
	13*	372		100 <sup>(a)*</sup>	0.58*	0.69*	1996
	CdO-producers	11		0 <sup>(2)</sup>	0 <sup>(2)</sup>	0 <sup>(2)</sup>	0.11
12			0 <sup>(2)</sup>	0 <sup>(2)</sup>	0 <sup>(2)</sup>	0.11	1993
Cd-stabilisers	F		0.03	500	0.0007	0.11	1996
	G		0.5	25	0.18	0.29	1996
	H		0.78	100	0.027	0.14	1996
	I		0.1	10	0.01	0.12	1996
	J		0	0	0	0.11	1996
	K		4.1	10	0.58	0.69	1996
	L		0	0	0	0.11	1996
M		0	0	0	0.11	1996	

Table 3.83 continued overleaf

Table 3.83 continued The local  $PEC_{water}$  (dissolved fraction) for Cd-producing and -processing plants in the EU-16. PEC's include background Cd

use-	N°	Production emission¶	Processing emission¶	Dilution factor	$C_{local,water}$	$PEC_{local,water}$	Year
Category		kg year-1	kg year-1		$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	
	windows manufacturer		0	0	0	0.11	1996
Cd-pigments	A		0.6	50	0.14	0.25	1996
	B		4.02	1,000	0.001	0.11	1996
	C		5.9	700	0.04	0.15	1996
	D		0.9	250	0.03	0.14	1996
	E		13.4	24,800	0.001	0.11	1996
Cd-plating	EU		250	10 <sup>(a)</sup>	2.75	2.9	1996
Cd-alloys	EU		61.3	10 <sup>(a)</sup>	1.7	1.81	1996

\* Emission to the sea; ¶annual averages;

n.a. Not available;

1) No water emissions: waste waters are recycled;

2) No water emissions: dry process;

a) Default value: 10 (freshwater), 100 (sea water).

### Measured local concentrations

Monitoring data from Cd-producing plants were submitted via the Industrial Questionnaire (1997). In general, most of these plants have implemented a monitoring program to control the effluent concentrations and the concentrations in the receiving water flow at and around the point of discharge. In **Table 3.84** measured and calculated data are presented as dissolved concentrations. Submitted measured values are generally total concentrations and are often limited to one value per site rather than ranges. Moreover, measurements do not always refer to the same year as the one for which PEC values are calculated (e.g. site 2). In order to be able to compare measured and calculated values, total measured values are converted to dissolved values assuming a dissolved fraction of 33% of the total measured Cd concentration (dissolved fraction =  $1/((1+K_p \cdot C_{susp}) \cdot 10^{-6})$  with  $K_p = 130 \cdot 10^3 \text{ L kg}^{-1}$ ,  $C_{susp} = 15 \text{ mg L}^{-1}$ ; TGD, 1996). Measured concentrations range from  $< 0.1 \mu\text{g L}^{-1}$  to  $10 \mu\text{g L}^{-1}$ . At some plants measurements were performed at different locations and Cd-concentrations were found to decrease with distance from the point of discharge.

Only few comparisons between predicted and measured concentrations can be made. Model predictions fit observations except for the plants that emit their effluents to the sea. Environmental characteristics of both receiving water and effluent water have a very important influence on the final dissolved Cd concentrations in the receiving waterbody. Dilution factors of 1.0 to 3.4 do not seem realistic when effluents are emitted to the sea. Factors influencing the final dissolved exposure concentration are the amount and composition of suspended matter, water hardness, pH and Cd concentration of the receiving water before the point of discharge. Predictions of local concentrations can only be improved if local conditions are assessed in detail.

Table 3.84 The measured local Cd concentrations in the effluent receiving water and the local  $PEC_{water}$  concentrations for Cd-producing and -processing plants in the EU-16

Use- Category	Plant N°	Production	Processing	$PEC_{local_{water}}$		Year
		emission amount	emission amount	calculated	measured <sup>(2)</sup>	
		kg y <sup>-1</sup>	kg y <sup>-1</sup>	µg L <sup>-1</sup>	µg L <sup>-1</sup>	
Cd-production	1	23.9		1.37	1.0	1996
	2	614		0.59	0.1 (1994)	1996
	3*	15.7		0.15*	1.5-10 (500m-1km)	1996
	4*	21.6		0.52*	1.6 (10m, 1995)	1996
	5	77.8		5.5	5	1996
	6	0.18		0.11	0.15	1996
	7*	70		0.32*	0.03 (1997) <sup>(a)</sup>	1996
	8	11		0.12	n.a.	1996
	9*	17.4		0.13	< 0.05 (2000)	1999
	10	0 <sup>(1)</sup>		0.11	n.a.	1996
	11	0 <sup>(1)</sup>		0.11	n.a.	1996
	13*	372		0.69*	3 (50m)	1996
	CdO-producers	11		0 <sup>(1)</sup>	0.11	n.a.
12			0 <sup>(1)</sup>	0.11	n.a.	1993
Cd-stabilisers	F		0.03	0.11	n.a.	1996
	G		0.5	0.29	n.a.	1996
	H		0.78	0.14	n.a.	1996
	I		0.1	0.13	n.a.	1996
	J		0	0.11	n.a.	1996
	K		4.1	0.69	n.a.	1996
	L		0	0.11	n.a.	1996
	M		0	0.11	n.a.	1996
	window manufacturer		0	0.11	n.a.	1996
Cd-pigments	A		0.6	0.25	n.a.	1996
	B		4.02	0.11	n.a.	1996
	C		5.9	0.15	n.a.	1996
	D		0.9	0.14	n.a.	1996
	E		13.4	0.11	n.a.	1996
Cd-plating	EU		250	2.9	n.a.	1996
Cd-alloys	EU		61.3	1.81	n.a.	1996

\* Emission to the sea;

n.a. Not available;

1) No water emissions: dry process or waste waters are recycled;

2) If total concentrations are measured, dissolved concentrations are estimated to be 33% of total Cd concentration ( $K_p = 130 \cdot 10^3 \text{ L kg}^{-1}$ ,  $C_{susp} = 15 \text{ mg L}^{-1}$ );

a) Measured at 40 m depth (emission at 30 m depth), several km away from the emission point.

### 3.1.3.1.2 The sediment

Following the standard approach as laid down in the TGD, the local concentration in the sediment is predicted based on the local concentrations in the water as

$$PEC_{local\,sediment} = K_p \, PEC_{local\,water} \cdot 10^{-3}$$

in which the  $K_p$  ( $L \, kg^{-1}_{dw}$ ) equals the solid- water partition coefficient of suspended matter. The average  $K_p$  value for suspended matter ( $130,000 \, L \, kg^{-1}_{dw}$ ) however strongly over predicts sediment concentrations. As an example, the average Cd concentrations in surface water in Europe is about  $0.14 \, \mu g \, Cd/L$  and the average sediment Cd concentration is  $1.32 \, mg \, Cd/kg_{dw}$ <sup>41</sup>. The predicted average sediment concentration using the average  $K_p$  of suspended matter is  $0.14 \cdot 130,000/1,000 = 18.2 \, mg \, Cd/kg_{dw}$  and which is about 14-fold above the average measured concentrations. As an alternative, one could use the ‘best fit’  $K_p$  of sediments, defined as the ratio of the average sediment to average water Cd concentrations. This ‘best fit’  $K_p$  yields  $10,000 \, L \, kg^{-1}_{dw} (=1.32/0.14 \cdot 1,000)$ . Another alternative is to use a measured regional PEC for the sediment to which a local added fraction is added, formally

$$PEC_{local\,sediment} = PEC_{regional\,sediment} + K_p \, C_{local\,water} \cdot 10^{-3}$$

in which the  $K_p$  ( $L \, kg^{-1}_{dw}$ ) equals the solid- water partition coefficient of suspended matter. This option has been preferred because (i) of the preference for measured rather than predicted sediment concentrations and (ii) because the contribution of the local discharge to the sediment concentrations is taken into account via suspended matter  $K_p$  in line with the TGD.

The measured PEC regional is taken as an average of 90<sup>th</sup> percentiles of surveys:  $2.66 \, mg \, Cd/kg_{dw}$  (see **Table 3.189**).

The local  $PEC_{sediment}$  are readily calculated from the data in **Table 3.83** and the above-mentioned equation and presented in **Table 3.85**. The  $C_{local\,sediment}$  ( $K_p \, C_{local\,water} \cdot 10^{-3}$ ) is included to illustrate the contribution of the local discharge onto the sediment PEC.

The local  $PEC_{sediment}$  range from 2.7 to  $707.8 \, mg \, kg^{-1}_{dw}$  for Cd-producing plants and from 2.7 to  $359.6 \, mg \, kg^{-1}$  for Cd-processing plants.

**Table 3.85** The local  $PEC_{sediment}$  for Cd-producing and –processing plants in the EU-16. The PEC’s include background Cd. All values are expressed as total Cd concentrations and thus not corrected for bioavailability

Use category	Plant n°	Production emission <sup>¶</sup>	Processing emission <sup>¶</sup>	$C_{local\,sediment}$	$PEC_{local\,sediment}$	Year
		$kg \, year^{-1}$	$kg \, year^{-1}$	$mg \, kg^{-1}_{dw}$	$mg \, kg^{-1}_{dw}$	
Cd-producers <sup>(e)</sup>	1	23.9		163.7	166.4	1996
	2	614		61.4	64.1	1996
	3*	15.7		4.4	7.1	1996

Table 3.85 continued

<sup>41</sup> Median of averages, median or geometric means (of min-max) of all European surveys listed in Tables 3.184 and 3.187. Observations near point sources and industrial activities are excluded and only the most recent data are included when data were reported for various periods. Concentrations in water refer to the dissolved fraction (see Table 3.184) but also include the data with ‘unknown fractionation’ (i.e. dissolved or not; this means that the median Cd water concentration can somewhat be overestimated).

Table 3.85 continued The local  $PEC_{\text{sediment}}$  for Cd-producing and –processing plants in the EU-16. The PEC's include background Cd. All values are expressed as total Cd concentrations and thus not corrected for bioavailability

Use category	Plant n°	Production emission¶ kg year-1	Processing emission¶ kg year-1	Clocal <sub>sediment</sub> mg kg-1dw	PEClocal <sub>sediment</sub> mg kg-1dw	Year
	4*	21.6		52.9	55.6	1996
	5	77.8		705.1	707.8	1996
	6	0.18		0.0	2.7	1996
	7*£	70		26.4	29.1	1996
	8	11		1.4	4.1	1996
	9*	17.4		1.8	4.5	1999
	10	0 <sup>(1)</sup>		0.0	2.7	1996
	11	0 <sup>(1)</sup>		0.0	2.7	1996
	13*	372		74.9	77.6	1996
CdO-producers	11		0 <sup>(1)</sup>	0.0	2.7	1996
	12		0 <sup>(1)</sup>	0.0	2.7	1993
Cd-stabilisers	F		0.03	0.1	2.8	1996
	G		0.5	22.9	25.6	1996
	H		0.78	3.5	6.2	1996
	I		0.1	1.7	4.4	1996
	J		0	0.0	2.7	1996
	K		4.1	75.3	78.0	1996
	L		0	0.0	2.7	1996
	M		0	0.0	2.7	1996
	window manufacturer		0	0.0	2.7	1996
Cd-pigments	A		0.6	18.8	21.5	1996
	B		4.02	0.1	2.8	1996
	C		5.9	5.2	7.9	1996
	D		0.9	3.8	6.5	1996
	E		13.4	0.1	2.8	1996
Cd-plating	EU		250	356.9	359.6	1996
Cd-alloys	EU		61.3	220.4	223	1996

\* Emission to the sea;

¶ Annual averages;

n.a. Not available;

1) No water emissions: waste waters are recycled;

2) No water emission: dry process;

£ Based on 1996 monitoring results (sediment analyses 0-3cm), the value of 1.9 mg Cd/kg dwt is proposed for the local exposure assessment by the company (Industry/company data submission, Aug. 2004).

### 3.1.3.1.3 Atmospheric compartment

#### Calculated local concentrations

Local PEC-values for the atmospheric compartment are calculated according to the OPS model proposed in the TGD (1996) for a general standard environment. The PEC values are represented as an average concentration at 100 m from the source. In general the atmospheric compartment receives its input from direct emission to air. Local Cd concentrations in the air are assessed by calculating the amount emitted to the air by the Cd producing and processing plants:

$$\text{Clocal}_{\text{air,ann}} = \text{Clocal}_{\text{air}} \cdot \frac{\text{Temission}}{365}$$

$$\text{Clocal}_{\text{air}} = \text{Elocal}_{\text{air}} \cdot \text{Cstd}_{\text{air}}$$

- $\text{Elocal}_{\text{air}}$  : Local direct emission rate to air during emission period ( $\text{kg d}^{-1}$ )  
 $\text{Cstd}_{\text{air}}$  : Concentration in air at source strength of  $1 \text{ kg d}^{-1}$  ( $\text{ng m}^{-3}$ ) default: 278 (TGD, 1996)  
 $\text{Temission}$  : Number of days per year that emission takes place ( $\text{d y}^{-1}$ )  
 $\text{Clocal}_{\text{air}}$  : Local concentration in air during emission period ( $\text{ng m}^{-3}$ )  
 $\text{Clocal}_{\text{air,ann}}$  : Annual average concentration in air, 100 m from point source ( $\text{ng m}^{-3}$ )

Input data are the total daily emissions of the individual Cd-producing plants and EU emission data of industry processing Cd in alloys (ERL, 1990) and plating (WS Atkins, 1998).

The calculated concentrations in air are actual contributions to the receiving atmosphere. The local PEC values are obtained by adding the regional PEC values for air to the calculated local concentration in the atmosphere.

$$\text{PEClocal}_{\text{air,ann}} = \text{Clocal}_{\text{air,ann}} + \text{PECregional}_{\text{air}}$$

- $\text{PEClocal}_{\text{air,ann}}$ : Annual average predicted environmental concentration in air ( $\text{ng m}^{-3}$ )  
 $\text{PECregional}_{\text{air}}$ : Regional concentration in the air ( $0.55 \text{ ng m}^{-3}$ ; Table 3.157)

The results of the predicted local atmospheric Cd concentrations at 100 m from the point sources are listed in **Table 3.86**. Calculated local PEC values range from 0.8 to  $1,282 \text{ ng m}^{-3}$  with the highest values emitted by Cd producing pyrometallurgical plants. For the Cd processing industry, a very high value was found for the processing of Cd in alloys. Since information on-site specific or EU level was not available, it is based on estimated EU-emission amounts. Site-specific information is needed to validate the results.

Table 3.86 Calculated local PEC<sub>air</sub> concentrations for Cd-producing and processing plants in EU-16

Use-category	Plant N°	Production emission amount <sup>fl</sup> kg year <sup>-1</sup>	Processing emission amount <sup>fl</sup> kg year <sup>-1</sup>	Number of emission days <sup>(1)</sup>	Annual average air concentration (100 m) ng m <sup>-3</sup>	PEC <sub>local,air,ann</sub> (100 m) ng m <sup>-3</sup>	Year
Cd-production	1	54		365	41	42	1996
	2	1,683		365	1,282	1,282	1996
	3	800		70	609	610	1996
	4	3.03		15	2.3	2.9	1996
	5	946		243	721	721	1996
	6	6.24		105	4.8	5.3	1996
	7	200		365	152	153	1996
	8	28.6		151	21.8	22	1996
	9	110		365	83.8	84	1996
	10	3.32		316	2.5	3.1	1996
	11	1.61		32	1.2	1.8	1996
	13	24.6		123	18.7	19	1996
	CdO-producers	11		0.30	251	0.228	0.8
12			0.31	256	0.236	0.8	1993
Cd-stabilisers	F		0.09	20	0.069	0.6	1996
	G		0.8	48	0.609	1.2	1996
	H		0.5	60	0.381	0.9	1996
	I		0.1	13	0.076	0.6	1996
	J		0.7	13	0.533	1.1	1996

Table 3.86 continued overleaf

Table 3.86 continued Calculated local PEC<sub>air</sub> concentrations for Cd-producing and processing plants in EU-16

Use-category	Plant N°	Production emission amount <sup>†</sup> kg year-1	Processing emission amount <sup>†</sup> kg year-1	Number of emission days(1)	Annual average air concentration (100 m) ng m <sup>-3</sup>	PEC <sub>local,air,ann</sub> (100 m) ng m <sup>-3</sup>	Year
	K		0.04	12	0.030	0.6	1996
	L		n.a.	155	n.a.	0.6	1996
	M		0	155	0	0.6	1996
	window manufacturer		n.a.	350	n.a.	0.6	1996
Cd-pigments	A		1.15	230	0.876	1.4	1996
	B		2.37	231	1.8	2.4	1996
	C		3.6	276	2.7	3.3	1996
	D		5.8	230	4.4	5.0	1996
	E		0.2	85	0.152	0.7	1996
Cd-plating	EU		0	155	0	0.6	1996
Cd-alloys	EU		770	62	586	587	1996

n.a. Not available;

<sup>†</sup> Annual averages;

1) B-Tables, TGD (1996) when data not available.

### Measured local concentrations

Measured atmospheric concentrations in the surroundings of the production-sites are available and are presented in **Table 3.87**. Concentrations in the air vary according to the distance from the emission point and the prevailing wind direction. Measured data range from 0.23 ng m<sup>-3</sup> to 78 ng m<sup>-3</sup>. Distances from the point source range from 100 m to 2,400 m. Calculated values of these sites vary from 0.6 to 1,300 ng m<sup>-3</sup> at a distance of 100 m from the point source. They are the sum of the calculated local atmospheric concentration, due to plant emission, and the background concentration, which is, according to the TGD (1996), the regional PEC value (0.561 ng m<sup>-3</sup>, **Table 3.157**). Due to the difference in distance between the measured and calculated values, comparison of both values for each site is not possible. Trends in the measured Cd concentrations over the last decade are presented in **Annex J**.

Table 3.87 Calculated and measured local PEC<sub>air</sub> concentrations for Cd-producing and processing plants in EU-16

Use-category	N°	Production emission amount kg y <sup>-1</sup>	Processing emission amount kg y <sup>-1</sup>	PEC <sub>local</sub> <sub>air</sub> (100 m) ng m <sup>-3</sup>	Measured ann.avg. air concentration ng m <sup>-3</sup>	Year
Cd-producers	1	54		42	44 (300m, 1993)	1996
	2	1,683		1,282	78 (600m)	1996
	3	800		610	n.a.	1996
	4	3.03		2.9	4 (1,000 m,1994)	1996
	5	946		721	30 (1,200 m)	1996
	6	6.24		5.3	1 (2,400 m)	1996
	7 <sup>E</sup>	200		153	11 (4,000 m)	1996
	8	28.6		22	11 (300m, 1996)	1996
	9	110		84	0.23(2,000 m,1993)	1996
	10	3.32		3.1	< 40 (100m)	1996
	11	1.61		1.8	n.a.	
	13	24.6		19	n.a.	1996
	CdO-producers	11		0.30	0.8	n.a.
12			0.31	0.8	5.4 (150m, 1994)	1993
Cd- stabilisers	F		0.09	0.6	n.a.	1996
	G		0.8	1.2	n.a.	1996
	H		0.5	0.9	n.a.	1996
	I		0.1	0.6	n.a.	1996
	J		0.7	1.1	n.a.	1996
	K		0.04	0.6	n.a.	1996
	L		n.a.	0.6	n.a.	1996
	M		0	0.6	n.a.	1996

Table 3.87 continued overleaf

Table 3.87 continued Calculated and measured local  $PEC_{air}$  concentrations for Cd-producing and processing plants in EU-16

Use-category	N°	Production emission amount kg y-1	Processing emission amount kg y-1	$PEC_{localair}$ (100 m) ng m <sup>-3</sup>	Measured ann.avg. air concentration ng m <sup>-3</sup>	Year
	window manufacturer		n.a.	0.6	n.a.	1996
Cd-pigments	A		1.15	1.4	n.a.	1996
	B		2.37	2.4	n.a.	1996
	C		3.6	3.3	n.a.	1996
	D		5.8	5.0	8 (200 m)	1996
	E		0.2	0.7	n.a.	1996
Cd-plating	EU		0	0.6	n.a.	1996
Cd-alloys	EU		770	587	n.a.	1996

n.a. Not available;

£ The results of recent measurements during February-May 2003 indicate figures of 0.7 to 8.50 ng Cd/m<sup>3</sup> (3 month average) (Industry/company data submission, Aug. 2004).

### 3.1.3.1.4 Terrestrial compartment

#### Calculated local concentrations

According to the TGD, the local  $PEC_{soil}$  is calculated as an average concentration over a certain time period in agricultural soil, fertilised yearly with sludge from a STP and receiving continuous aerial deposition (dry and wet) from a nearby point source, for a period of 10 years. For the terrestrial ecosystem, the concentration is calculated for a depth of 0.2 m. Sludge from Cd producing plants is however not applied to agricultural land but is recycled internally or by an external plant (IZA-Europe, pers. communication). Application of sludge from processing sites/scenarios is unlikely to take place<sup>42</sup> but may occur if the Cd is emitted via a sewer to a municipal sewage treatment plant. This route of emission is taken into account in the regional assessment as diffuse Cd flux (see Section 3.1.3.4.2). Therefore, the Cd input to soil through sludge from the Cd producing plants is omitted in these local calculations and atmospheric deposition is the only source of Cd input into the terrestrial compartment. Atmospheric deposition of Cd is calculated assuming that all Cd is deposited within an area of 100 km<sup>2</sup> around the source and that the deposition occurs in a continuous flux.

The  $PEC_{local}$  is the sum of the regional Cd concentration in soil ( $PEC_{regional}$ ) and the atmospheric deposition minus the leaching losses. The  $PEC_{local}$  is solved from the dynamic Cd balance in the 0-0.2 top layer of the soil as:

$$PEC_{local_{soil}} = \frac{D_{air}}{k} - \left( \frac{D_{air}}{k} - PEC_{regional_{soil}} \right) \exp(-kt)$$

where

$D_{air}$  = aerial deposition flux per kg of soil (mg kg<sup>-1</sup> d<sup>-1</sup>)  
 $t$  = time (3,650 days)

<sup>42</sup> In line with national and EU legislation sludges from on-site WWTP of Cd processors are likely to be classified as hazardous (e.g. see for the sector of metal treatment in IPPC, 2004; EC legislation in: EC, 1991 and EC, 2000)

$k =$  first order rate constant for removal from top soil ( $d^{-1}$ )  
 $PEC_{regional_{soil}} =$  the regional Cd concentration in soil ( $0.36 \text{ mg kg}^{-1}_{ww}$ ; **Table 3.157**) and which is calculated for an agricultural scenario assuming a realistic worst case Cd input scenario.

The aerial deposition flux is

$$D_{air} = \frac{DEP_{totalann}}{DEPTH_{soil} \cdot RHO_{soil}}$$

$DEP_{totalann} =$  annual average total deposition flux ( $\text{mg m}^{-2} \text{ d}^{-1}$ )  
 $DEPTH_{soil} =$  mixing depth of soil (0.20 m)  
 $RHO_{soil} =$  bulk density of soil ( $1,700 \text{ kg m}^{-3}$ )  
 $D_{air} =$  aerial deposition flux per kg of soil ( $\text{mg kg}^{-1} \text{ d}^{-1}$ )

$$DEP_{totalann} = 0.01 (E_{localair} + E_{stpair}) \cdot T_{emission}/365$$

$E_{localair} =$  local direct emission rate to air during emission episode ( $\text{kg d}^{-1}$ )  
 $E_{stpair} =$  local indirect emission to air from STP during episode ( $0 \text{ kg d}^{-1}$ )  
 $T_{emission} =$  number of days per year that the emission takes place  
 $DEP_{totalann} =$  annual average total deposition flux ( $\text{mg m}^{-2} \text{ d}^{-1}$ )

The factor 0.01 is used in the previous calculation to convert the source strength ( $\text{kg d}^{-1}$ ) to deposition ( $\text{mg m}^{-2} \text{ d}^{-1}$ ) assuming a deposition area of  $100 \text{ km}^2$  (TGD, 1996, p. 300).

Removal from the top soil is by leaching only and the first order rate constant is given as

$$k = \frac{F_{insoil} \cdot RAIN_{rate}/365}{K_D \cdot DEPTH_{soil} \cdot RHO_{soil}}$$

$F_{insoil} =$  fraction of rain water that infiltrates into soil (0.25)  
 $RAIN_{rate} =$  rate of wet precipitation ( $700 \text{ mm y}^{-1}$ )  
 $K_D =$  solid:liquid Cd distribution in soil ( $280 \text{ L kg}^{-1}$ , see below)  
 $k =$  pseudo first-order rate constant for leaching from soil layer ( $d^{-1}$ )

The solid-liquid Cd distribution coefficient ( $K_D$ ;  $\text{L kg}^{-1}$ ) in soil is defined as

$$K_D = \frac{[Cd]_s}{[Cd]_l}$$

in which  $[Cd]_s$  represents the Cd concentration in the solid phase of the soil ( $\mu\text{g kg}^{-1}$ ) and  $[Cd]_l$  the Cd concentration in pore water ( $\mu\text{g L}^{-1}$ ). The Cd  $K_D$  values vary strongly with soil properties. The Cd  $K_D$  values have been measured in different soils. **Table 3.10** lists a number of these studies and shows regression equations between the  $K_D$  values and soil properties. The  $K_D$  values are generally obtained from Cd adsorption studies in soil suspensions. Main methodological differences between studies are the type and concentration of the background electrolyte, the solid:liquid ratio and the equilibration time. A variation of about two orders of magnitude of the  $K_D$  of Cd between different soil types was found. The soil pH is a dominant factor controlling mobility of Cd. From the regression lines between the  $K_D$  and soil properties (see **Table 3.88**) it can be predicted that the  $K_D$  decreases between 3.2 and 5.1 fold per unit pH decrease. Some studies show that the  $K_D$  significantly increases if the soil organic matter content increases (see **Table 3.88**).

The McBride model was based on data of Gerritse and Van Driel (1984), who measured  $K_D$  values of Cd for 33 temperate soils, at three different ionic strengths of soils extractants (water extract, dilute salt extract of ionic strength (IS) 0.011M and dilute salt extract of IS 0.11M). The relationship between  $\log K_D$  and pH that was derived for the salt extract of intermediate IS (0.011M) - which best matches the IS of many soil solutions - was in best agreement with the  $\log K_D$ -pH relationships derived by Römken and Salomons (1998) and Smolders et al. (unpublished) for *in situ*  $K_D$  values (see **Table 3.88**). The  $K_D$  values in the water extract were higher than in the dilute salt extracts, which can be ascribed to a general ionic strength effect. Due to this effect, Cd concentrations in water extracts tend to underestimate the Cd concentrations in the soil solution as the IS is usually lower in a water extract than in the soil solution. It was found for 18 (contaminated) topsoils that the concentration in a water extract was on average 2.4 times lower than the Cd concentration in the pore water (Degryse F, personal communication). As McBride et al. (1997) used the water extract data of Gerritse and Van Driel (1984), their model probably overestimates *in situ*  $K_d$  values and hence underestimates Cd concentrations in the soil solution.

The best estimates on leaching losses are probably made using *in situ* pore water concentrations, and not using the soluble Cd concentrations in suspension studies. However, no large data sets on *in situ*  $K_D$  values are available. In this model  $K_D$  was assumed 280 L kg<sup>-1</sup> which is a typical value for a soil with pH 6.5 and 2% organic matter (the average predicted  $K_D$  for these characteristics is 500 L kg<sup>-1</sup> based on all equations in **Table 3.88**, and 320 L kg<sup>-1</sup> without the McBride equation).

Table 3.88 The solid-liquid Cd distribution coefficient ( $K_D$ ) in different topsoils†

$K_D$ (L kg <sup>-1</sup> )	Notes	Source
$\log K_D = -1.00 + 0.51\text{pH} + 0.51\log(\%OM)$	adsorption $K_D$ measured in 0.001M CaCl <sub>2</sub> , n=63 (Danish agricultural soils, subsoils included)	Christensen, 1989
$\log K_D = 0.89 + \log(\%OM/100) + 0.52\text{pH}$	adsorption $K_D$ in NaNO <sub>3</sub> 0.01M, n=15 (soils from New Jersey)	Lee et al., 1996
$\log K_D = -1.8 + \log(\%OM) + 0.59\text{pH}$	adsorption $K_D$ in 0.005N salts; n=33 (Dutch, French and British soils, some polluted soils included)	Gerritse and Van Driel, 1984
$\log K_D = -1.16 + 0.56\text{pH}$	<i>in situ</i> (pore-water based) $K_D$ , n=100 (unpolluted agricultural and forest soils from the Netherlands)	Römken and Salomons, 1998
$\log[Cd]_s = 3.62 - 0.50\text{pH} - 0.45\log(\%OM \cdot 10) + 0.96\log[Cd]_{\text{Tot}}$	metal concentration in water extract; n=33 (contaminated soils from various sources)	McBride et al., 1997
$\log K_D = -1.34 + 0.64\text{pH}$	<i>in situ</i> (pore-water based) $K_D$ , n=28 (unpolluted grassland soils from Belgium)	Smolders et al. (unpublished)
$\log K_D = -2.09 + 0.61\text{pH} + 0.936\log(\%C)$	adsorption $K_D$ in CaCl <sub>2</sub> 0.010M n=58 (unpolluted grassland soils from Belgium)	Smolders et al. (unpublished)

† The study of Römken and Salomons (1998) include subsurface horizons;

%OM Percentage organic matter;

%C Percentage carbon;

[Cd]<sub>s</sub> Metal concentration in water extract (µg l<sup>-1</sup>);

[Cd]<sub>Tot</sub> Total metal concentration in soil (mg kg<sup>-1</sup>).

Results of the calculations are presented in **Table 3.89**. The  $PEC_{\text{soil}}$  values range from 0.36 mg kg<sub>ww</sub><sup>-1</sup> to 0.85 mg kg<sub>ww</sub><sup>-1</sup>.

Table 3.89 Calculated total local PEC<sub>soil</sub> for Cd-producing and processing plants in EU-16. PEC's include background Cd

Use-Category	Plant N°	Emission to air <sup>†</sup> kg d <sup>-1</sup>	Number of emission days <sup>(1)</sup>	PEC <sub>local soil</sub> mg kg <sub>ww</sub> <sup>-1</sup>	Year
Cd-production	1	0.15	365	0.37	1996
	2	4.6	365	0.85	1996
	3	11.4	70	0.59	1996
	4	0.2	15	0.36	1996
	5	3.9	243	0.63	1996
	6	0.06	105	0.36	1996
	7	0.5	365	0.41	1996
	8	0.2	151	0.36	1996
	9	0.3	365	0.39	1996
	10	0.01	316	0.36	1996
	11	0.05	32	0.36	1996
	13	0.2	123	0.36	1996
	CdO-producers	11	0.001	251	0.36
12		0.001	256	0.36	1993
Cd recycling	1	0.02	260	0.36	1996
	2	0	230	0.36	1997
Cd-stabilisers	F	0.005	20	0.36	1996
	G	0.02	48	0.36	1996
	H	0.008	60	0.36	1996
	I	0.008	13	0.36	1996
	J	0.1	13	0.36	1996
	K	0.003	12	0.36	1996
	L	n.a.	155	0.36	1996
	M	0	155	0.36	1996
	window manufacturer	n.a.	350	0.36	1996
Cd-pigments	A	0.01	230	0.36	1996
	B	0.01	231	0.36	1996
	C	0.01	276	0.36	1996
	D	0.03	230	0.36	1996
	E	0.002	85	0.36	1996
Cd-plating	EU	0	155	0.36	1996
Cd-alloys	EU	12.4	62	0.58	1996

n.a. Not available;

<sup>†</sup> Annual averages; B-Tables (TGD, 1996) when data not available.

### Measured local concentrations

At this moment, there are no measured local soil concentrations submitted by the Cd producing- or processing industries.

#### **3.1.3.2 Local exposure assessment: batteries' related scenarios**

Point sources can have a major impact on the environmental concentration on a local scale. Local exposure concentrations are calculated from emission data submitted by Industry (Industry Questionnaires, 2000/2001) according to the EU-Technical Guidelines Document. (TGD, 1996). In this report local PECs are calculated for life cycle stages 1 (NiCd batteries producers) and 4 (Cd recyclers) of the life cycle of NiCd batteries. Local exposure during production of battery raw materials is not considered in this section but is addressed in the Section 3.1.3.1. Calculated values will be compared with measured concentrations near Cd emitting plants (Industry Questionnaires, 2000/2001) and where large differences occur, results are analysed and re-evaluated. For the disposal life cycle stage a generic exposure assessment is performed for incineration.

##### **3.1.3.2.1 Aquatic compartment**

#### Calculated local concentrations

Input data were submitted via Industry Questionnaires (2000/2001).

Calculation of local PEC-values for the aquatic compartment is performed according to the method described in the TGD (EC, 2003). The general lines are the same as those given in the TGD (1996, see Section 3.1.3.1.1). However, application of the revised TGD implies a number of changes. These are:

The calculation of the dilution factor is based on the given low-flow rate (or 10<sup>th</sup> percentile) of the receiving water body and on the given effluent discharge rate. Where only average river flows are available, the flow for dilution purposes should be estimated as one third of this average (EC, 2003). In the absence of both data, a default dilution factor of 10 is used for emissions to freshwater. A default dilution factor of 100 is used for emissions to the sea.

It must be noted that with the assumption of complete mixing of the effluent in the surface water no account is taken of the fact that in reality in the mixing zone higher concentrations will occur. For situations with relatively low dilution factors this mixing zone effect can be accepted. For situations with very high dilution factors, however, the mixing zones may be very long and the overall area that is impacted by the effluent before it is completely mixed can be very substantial. Therefore, in case of site-specific assessments the dilution factor that is applied for calculation of the local concentration in surface water should not be greater than 1000 (EC, 2003).

In short:

The calculated surface water concentrations are actual contributions to the receiving water. The local PEC values are obtained by adding the regional PEC value for water (modelled value) to the calculated local concentration in surface water.

$$PEC_{local\_water} = C_{local\_water} + PEC_{regional\_water}$$

$PEC_{local\_water}$ :	Predicted environmental concentration during emission episode ( $\mu\text{g/L}$ )
$C_{local\_water}$ :	Local concentration in surface water during emission episode ( $\mu\text{g/L}$ )
$PEC_{regional\_water}$ :	Regional concentration in surface water ( $0.11\mu\text{g L}^{-1}$ , calculated value, no changes made see Table 3.57) <sup>43</sup>

In the calculations, a European average value of suspended matter partitioning coefficient:  $K_p = 130,000 \text{ l/kg}$  is used.

The local PEC values of Cd in surface water are presented in **Table 3.90** and **Table 3.91**.

Table 3.90 Local PEC<sub>water</sub> for NiCd batteries producing plants and Cd recycling plants in the EU emitting to the surface water after on-site WWTP

Use category	N°	Production/processing emission (average)	Ceffluent	Dilution factor Site-specific	Clocal water Site-specific	PEClocal water Site-specific	Max. Dilution factor (revised TGD)	Clocal water D=1,000	PEClocal water D=1,000	Year
NiCd batteries		kg/y	mg L <sup>-1</sup>	-	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	-	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	
	2 <sup>a</sup>	7.3	0.12	1,178	0.034	0.15	1,000	0.041	0.15	2000
	3	30.5 (36,29)	0.12	13,542	0.0030	0.12	1,000	0.041	0.15	2000
	4	21.9 (31.88)	0.13	771	0.06	0.18	N.A.	N.A.	N.A.	2000
	6 <sup>b</sup>	No emissions to water (recycled)	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1999
	7 <sup>c</sup>	No emissions to water (recycled)	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1999
Cd recyclers <sup>d</sup>										
	1	0.126	0.45	1,889	0.08	0.19	1,000	0.153	0.27	2000
	2 <sup>d</sup>	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1999

N.A. Not applicable;

- Company 2 emits to the marine environment;
- All process wastewater is collected and sent to recycling company;
- Emissions to water from cleaning operations are disposed in alkaline solution and externally recycled;
- Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown in the submitted figures between the producing process and the recycling process was not feasible. For this reason this company have been listed with the other producers;
- No "open" treatment steps; no emissions to air. The wastewater is collected and treated off-site. No further information was available. The sludge from the treatment is land-filled.

Plant 1 and plant 5 discharge their effluent after on-site treatment into the public sewer system (STP). These discharges will undergo a dilution step in the STP. The corresponding dilution factor is calculated based on the effluent flow rate and a default sewage flow of  $2,000 \text{ m}^3/\text{day}$ . In addition to the dilution factor the cadmium removal efficiency of the STP has to be taken into

<sup>43</sup> The effect of an increase in MSW cadmium content up to  $24 \text{ mg kg}^{-1}$  dry wt. ('future' scenarios) will have only a minor influence on the currently derived PECs regional for air, water and soil (see EUSES outprints in Annex V). Therefore there is no need to revise the current PEC reg, water and the PEC reg, air in order to derive the PEC values for the future situation.

account. According to CBS (2002) a removal efficiency of 60% can be used. The final site specific dilution factor is obtained using the site specific flow rate of the receiving surface water and the effluent flow of the STP. The results of the calculations are presented in **Table 3.91**.

Table 3.91 Local PEC<sub>water</sub> for NiCd batteries producing plants in the EU emitting to the surface water after on site WWTP and followed by STP

Input	Plant N° 1	Plant N° 5
Reference year		2,000
Processing emission (kg year <sup>-1</sup> )	4.9	59.7
Effluent flow (m <sup>3</sup> /day)	127	5
Conc. effluent (mg L <sup>-1</sup> )	0.43	0.03
Size of STP (m <sup>3</sup> /day)	2,000	2,000
Removal of cadmium in STP (%)	60	60
Flow rate receiving water (m <sup>3</sup> /day)	1.9.10 <sup>6</sup>	2.2.10 <sup>6</sup>
Output		
Calculated dilution factor in STP	16.7	401
Calculated conc. effluent STP (mg L <sup>-1</sup> )	0.010	0.00003
Calculated site specific dilution factor in receiving water	894	1,101
Clocal water site specific (µg L <sup>-1</sup> )	0.0037	0.00001
PEC <sub>local</sub> water site specific	0.12	0.114
Clocal water (D = 1,000)	N/A.	0.00001
PEC <sub>local</sub> water site (D = 1,000)	N/A	0.114

N/A Not applicable.

The local PEC values -calculated on the basis of site-specific dilution factors- range from 0.11 to 0.18 µg L<sup>-1</sup> for NiCd batteries producing plants and 0.19 µg L<sup>-1</sup> for Cd recycling plants. It should be noted that the 0.11 µg L<sup>-1</sup> value -for NiCd batteries producing plant 5 - equals the regional PEC. The draft revised TGD (2002) states that in case of site-specific assessments the dilution factor that is applied for calculation of the local concentration in surface water should not be greater than 1,000 (assumption of complete mixing, mixing zones). Therefore, for NiCd producing plants 2, 3 and Cd recycling plant 1 a local concentration in surface water is calculated based on the maximum dilution factor of 1,000. The results from this exercise indicate that for these plants the PEC values in surface water equals 0.15 µg L<sup>-1</sup> for the NiCd batteries producing plants and 0.27 µg L<sup>-1</sup> for the Cd recycling plant.

### Measured local concentrations

Monitoring data from Cd-producing plants were submitted via the Industrial Questionnaire (2000/2001). In general, most of these plants have implemented a monitoring program to control the effluent concentrations. Only a limited number of measured Cd concentrations are available in the receiving surface water of the plants. Submitted measured values are generally total concentrations. In order to be able to compare measured and calculated values, total measured values are converted to dissolved values assuming a dissolved fraction of 33% of the total measured Cd concentration. In **Table 3.92** measured and calculated data are presented as dissolved concentrations.

Table 3.92 Measured local Cd concentrations in the effluent receiving water and the local PEC<sub>water</sub> concentrations for Cd-producing and processing plants in EU

Use-category	Plant N°	Production Emission amount kg year <sup>-1</sup>	Processing Emission amount kg year <sup>-1</sup>	PEC <sub>local water</sub> calculated µg L <sup>-1</sup>	Measured µg L <sup>-1</sup>	Year
NiCd-batteries	1 <sup>g</sup>		4.9	0.12	N.A.	1999
	2 <sup>a</sup>		7.3	0.15	0.153 (P <sub>90</sub> downstream of discharge)	2000
	3		30.5	0.15	N.A.	2000
	4		21.9	0.17	N.A.	2000
	5		0.07	0.11	N.A.	1999
	6 <sup>b</sup>		No emissions to water (recycled)	N/A	N.A.	1999
	7 <sup>c</sup>		No emissions to water (recycled)	N/A	N.A.	1999
Cd recycling <sup>d</sup>	1	0.126		0.16	upstream: 75.9 µg L <sup>-1f</sup> (20 m before emission point) downstream: 85.8 µg L <sup>-1</sup> (80 m after emission point)	2000
	2 <sup>e</sup>	0		N/A	N.A.	1999

N.A. Not available;

N/A Not applicable;

a) Company 2 emits to the marine environment. Measured data from the harbour;

b) All process wastewater is collected and sent to recycling company;

c) Emissions to water from cleaning operations are disposed in alkaline solution and externally recycled;

d) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown in the submitted figures between the producing process and the recycling process was not feasible. For this reason this company have been listed with the other producers;

e) No "open" treatment steps; no emissions to air. The wastewater is collected and treated off-site. No further information was available. The sludge from the treatment is land-filled;

f) It should be noted that the river already has high Cd levels (see upstream from discharge) probably due to pollution from old metallic slag heaps;

g) Company stopped NiCd production.

Most of the plants did not have measured data. For plant 2, emitting to the marine environment, measured data were reported. From these data the 90th percentile was taken resulting in a Cd concentration of 0.153 µg L<sup>-1</sup> which is in accordance with the modelled concentration. Recycling plant 1 reported measured Cd concentrations in surface water upstream and downstream from the plant for several years. Although the cadmium concentration downstream increases significantly it is highly unlikely that this increase is caused by a plant emitting 0.126 kg year<sup>-1</sup> with an average effluent flow of 5 m<sup>3</sup>/day. It is more likely that the elevated cadmium concentrations in the river are due the input from contaminated groundwater and/or run-off water originating from historical metallurgical slag heaps present at the industrial site of the former zinc processing plant. This hypothesis is supported by the increase in zinc concentration in the same order as cadmium, while the recycling plant does not emit zinc.

#### MSW incinerator: current situation (24.4% incineration)

Since the collection of site-specific data on MSW incinerators was outside the scope of this report a local scenario has been developed for a hypothetical incinerator based on the information provided in **Table 3.25** and **Table 3.33**. On average 25 incinerators are present in

one region incinerating 2,794 ktonnes of MSW per year which result in an average capacity of 111,760 tonnes MSW/plant.year. The amount of wastewater generated is of the order of 0.5-2.5 m<sup>3</sup> per tonne of municipal waste incinerated (Williams, 1998). Reimann (2002) reported a water consumption of 1.1 m<sup>3</sup>/tonne for the FGCS and 0.25 m<sup>3</sup> per tonne boiler water. Stubenvoll et al. (2002) reported amounts of waste water between 0.3-0.4 m<sup>3</sup>/tonne. If it is assumed that an incinerator is in operation for 330 days per year a daily emission between 169 and 846 m<sup>3</sup> can be calculated  $(111,760 \cdot 2.5 \text{ (or } 0.5)) / 330$ . Using these two values and assuming a default river flowrate of 18,000 m<sup>3</sup>/day (TGD default) a generic dilution factor between 22 (=18,846/846) and 107 (= 18,169/169) can be calculated.

Although it was impossible to gather site-specific information for every incinerator in Europe, for some incinerators site-specific information on type of receiving water and flow rate was available (see **Table 3.93**). The dilution factors provided in this table were calculated using the minimum effluent flow of 169 m<sup>3</sup>/ day and the maximum flow rate of 846 m<sup>3</sup>/day.

Table 3.93 Calculated site specific dilution factors for some MSW incinerators in the EU

Incinerator	Receiving water	Flow rate m <sup>3</sup> day <sup>-1</sup>	846 m <sup>3</sup> day <sup>-1</sup>	169 m <sup>3</sup> day <sup>-1</sup>
			Dilution factor	
<b>United Kingdom</b>				
Edmonton Incinerator London Waste Ltd	Thames	5,702,400	6,740	33,743
Lewisham Incinerator London	Thames	5,702,400	6,740	33,743
Stoke on Trent Incinerator MES Environmental Ltd	Trent	54,432	64	323
Nottingham Incinerator Waste Recycling Group	Trent	5,814,000	6,872	34,403
<b>France</b>				
Brive	Corrèze	864,000	1,021	5,113
Chartres	Eure	432,000	511	2,557
Toulouse	Garonne	17,280,000	20,426	102,250
Bordeaux	Garonne	60,480,000	71,489	357,871
Pau	Gave de Pau	> 57,888	> 68	344
Orléans	Loire	73,008,000	86,298	432,001
Angers	Maine	11,059,200	13,072	65,440
Chaumont (close to the source)	Marne	17,280	20	103
Créteil	Marne (at mouth in Seine)	4,242,240 – 8,320,320	5,014 – 9,835	25,103 – 49,234
Caen	Orne	2,790,720	3,299	16,514
Maubeuge	Sambre	43,200 – 259,200	51 – 306	257 – 1,534

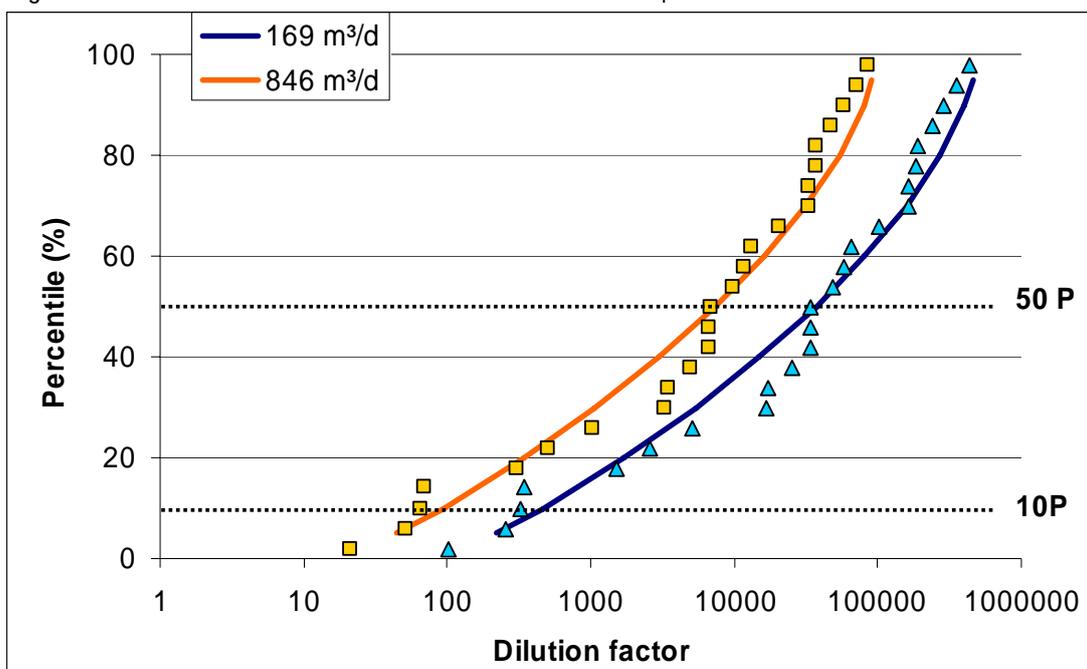
Table 3.93 continued overleaf

Table 3.93 continued Calculated site specific dilution factors for some MSW incinerators in the EU

Incinerator	Receiving water	Flow rate m <sup>3</sup> day <sup>-1</sup>	846 m <sup>3</sup> day <sup>-1</sup>	169 m <sup>3</sup> day <sup>-1</sup>
France				
Strasbourg	Rhine	9,936,000	11,745	58,794
Lyon Sud	Rhone	40,262,400 – 49,334,400	47,591 – 58,315	238,240 – 291,921
Bellegarde	Rhone	31,104,000	36,766	184,048
Lyon Nord	Saone	27,993,600 – 31,795,200	33,089 – 37,583	165,644 – 188,138
Le Mans	Sarthe	2,937,600  (à Spay, 5 km van Le Mans)	3,472	17,383
St. Thibault des Vignes Carrières/S. Guerville Issy les Moul. St Ouen Ivry Argenteuil	Seine	27,648,000	32,681	1  63,599

From the previous table it is clear that a lot of incinerators are discharging their effluents into large rivers frequently resulting in a dilution factor larger than 1,000. In order to obtain both a realistic worst case dilution factor and a typical dilution factor the cumulative distribution function of dilution factors have been elaborated and the 10<sup>th</sup> percentile and the 50<sup>th</sup> percentile are taken respectively.

Figure 3.11 Cumulative distribution function of dilution factor based on reported flowrates.



From **Figure 3.11** it can be calculated that the realistic worst case dilution factors (10<sup>th</sup> P) range between 93 and 459. Typical dilution factors (50<sup>th</sup> P) range between 7,370 and 36,840.

In order to take this variation in dilution factors over to the risk characterisation phase two scenarios are withheld:

- Realistic worst case dilution factor of 100
- Typical dilution factor of 1,000

As effluent concentration for the local PEC calculations the 90<sup>th</sup> P value has been chosen of the measured influent concentration and a removal efficiency of 98.8%.

$$\text{Effluent concentration} = 0.47 \text{ mg Cd/L (90}^{\text{th}} \text{ influent)} \cdot (1-0.988) = 0.0056 \text{ mg Cd/L}$$

In Scenario 1 (DF = 100), the amount of waste water generated is 846 m<sup>3</sup>/tonnes/day. With an effluent concentration of 0.0056 mg L<sup>-1</sup> and 330 operating days a yearly load of 1.6 kg can be calculated (846 m<sup>3</sup>/day · 330 days/year · 0.0056 mg L<sup>-1</sup> = 1.6 kg Cd/year). In a similar way the cadmium load associated with 169 m<sup>3</sup> of waste water per day (Scenario 2 with DF = 1,000) can be calculated (169 m<sup>3</sup>/day · 330 days/year · 0.0056 mg L<sup>-1</sup> = 0.3 kg Cd/year).

Table 3.94 Local PEC water (total cadmium) for MSW incineration plants in the EU.  
Scenario 1: Dilution factor 100. Scenario 2: Dilution factor 1000

	Emission	Ceffluent	Dilution factor <sup>a</sup>	Clocal water	PEClocal water
	kg year <sup>-1</sup>	mg L <sup>-1</sup>	-	µg L <sup>-1</sup>	µg L <sup>-1</sup>
Scenario 1	10 <sup>th</sup> percentile measured dilution factors				
	1.6	0.0056	100	0.019	0.13
Scenario 2	50 <sup>th</sup> percentile measured dilution factors				
	0.3	0.0056	1,000	0.0019	0.12

a) Dilution in receiving water

The Cd emissions and the calculated PEC<sub>local water</sub> in **Table 3.94** represents the impact of all cadmium containing sources in the MSW and not NiCd batteries only. PEC<sub>local surface water</sub> of 0.12 µg L<sup>-1</sup> (total cadmium) is calculated for a reasonable worst case scenario (90<sup>th</sup> P Cd concentration) with a typical dilution factor of 1,000. This value is very close to the regional background of 0.11 µg L<sup>-1</sup>. If the calculations are performed with the realistic worst case dilution factor (i.e. 100) PEC<sub>local water</sub> is 0.13 which is only slightly above the regional PEC value (0.11 µg L<sup>-1</sup>).

In order to evaluate if having NiCd batteries in the MSW stream or not significantly influences the PEC<sub>local water</sub> values, these PEC<sub>local waters</sub> have been recalculated assuming in the first scenario that NiCd batteries only contributed 10% to the overall cadmium content of the waste and in a second scenario it was assumed that Cd from NiCd batteries accounted for 50 % of the total Cd load observed in MSW (see **Table 3.95**).

Table 3.95 Local PEC water (total cadmium without the NiCd contribution) for MSW incineration plants in the EU.  
Scenario 1: Dilution factor 100. Scenario 2: Dilution factor 1,000

	Dilution factor Scenario 1	Clocal water	PEClocal water	Dilution factor Scenario 2	Clocal water	PEClocal water
		$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	-	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$
Assumption NiCd contribution: 10% of the total Cd load						
Scenario 1 & 2	100	0.017	0.13	1,000	0.002	0.11
Assumption NiCd contribution: 50% of the total Cd load						
Scenario 1 & 2	100	0.009	0.12	1,000	0.0009	0.11

a) Dilution in receiving water

From **Table 3.95** it is clear that removing the NiCd battery fraction from the MSW does not significantly reduce the PEClocal water. This is not surprisingly since on average 95% of the PEClocal water is coming from the regional background concentration, which is  $0.11 \mu\text{g L}^{-1}$  on a calculated basis.

#### MSW incinerator scenario sensitivity analysis (effluent concentration = $0.009 \text{ mg L}^{-1}$ )

As part of the sensitivity analysis (see subsection “Sensitivity analysis” under Section 3.1.2.2.5) a scenario of a incinerator with a effluent concentration of  $0.009 \text{ mg L}^{-1}$  (derived from the maximum reported influent concentration of  $0.76 \text{ mg L}^{-1}$  and assuming a removal efficiency of 98.8%) is included (see **Table 3.96**).

$$\text{Effluent concentration} = 0.76 \text{ mg Cd/L (max con. influent)} \cdot (1-0.988) = 0.009 \text{ mg Cd/L}$$

In scenario 1 (DF = 100), the amount of waste water generated is  $846 \text{ m}^3/\text{tonnes/day}$ . With an effluent concentration of  $0.009 \text{ mg L}^{-1}$  and 330 operating days a yearly load of 2.5 kg can be calculated ( $846 \text{ m}^3/\text{day} \cdot 330 \text{ days/year} \cdot 0.009 \text{ mg L}^{-1} = 2.5 \text{ kg Cd/year}$ ). In a similar way the cadmium load associated with  $169 \text{ m}^3$  of waste water per day (Scenario 2 with DF = 1,000) can be calculated ( $169 \text{ m}^3/\text{day} \cdot 330 \text{ days/year} \cdot 0.009 \text{ mg L}^{-1} = 0.5 \text{ kg Cd/year}$ ).

Table 3.96 Local PEC water (total cadmium) for MSW incineration plants in the EU

	Emission	Ceffluent	Dilution factor <sup>a</sup>	Clocal water	PEClocal water
	$\text{kg year}^{-1}$	$\text{mg L}^{-1}$	-	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$
Scenario 1	10 <sup>th</sup> percentile measured dilution factors				
	2.5	0.009	100	0.03	0.14
Scenario 2	50 <sup>th</sup> percentile measured dilution factors				
	0.5	0.009	1,000	0.003	0.12

a) Dilution in receiving water

PEClocal surface water of  $0.12 \mu\text{g L}^{-1}$  (total cadmium) is calculated for a worst case scenario (max Cd concentration) with a typical dilution factor of 1,000. This value is very close to the regional background of  $0.11 \mu\text{g L}^{-1}$ . If the calculations are performed with the realistic worst case dilution factor (i.e. 100) PEClocal water is 0.14 which is only slightly above the regional PEC value ( $0.11 \mu\text{g L}^{-1}$ ),

MSW incinerator: future situation (100% incineration)

In a similar way the cadmium emission to surface water from future incinerators can be calculated. The assumption has been made that due to expected higher cadmium content in the MSW a higher effluent concentration is expected to occur (this is the case if the removal efficiency will be kept at 98.8%). For the two future scenarios the following effluent concentrations have been used to perform the calculations (based on **Table 3.37**):

- For the scenario with 10% batteries' collection efficiency the following overall cadmium effluent concentration has been used: 0.0135 mg Cd/L (= 1.13 · 0.012)
- For the scenario with 75% collection efficiency the following overall cadmium effluent concentration has been used: 0.007 mg Cd/L (= 0.62 · 0.012)

In Scenario 1 (DF = 100) for the 10% collection scenario, the amount of waste water generated is 846 m<sup>3</sup>/tonnes/day. With an effluent concentration of 0.0135 mg L<sup>-1</sup> and 330 operating days a yearly load of 3.75 kg can be calculated (846 m<sup>3</sup>/day · 330 days/year · 0.0135 mg L<sup>-1</sup> = 3.75 kg Cd/year). In a similar way the cadmium load associated with 169 m<sup>3</sup> of waste water per day (Scenario 2 with DF = 1,000) can be calculated (169 m<sup>3</sup>/day · 330 days/year · 0.0135 mg L<sup>-1</sup> = 0.75 kg Cd/year).

In Scenario 1 (DF = 100) for the 75% collection scenario, the amount of waste water generated is 846 m<sup>3</sup>/tonnes/day. With an effluent concentration of 0.007 mg L<sup>-1</sup> and 330 operating days a yearly load of 1.9 kg can be calculated (846 m<sup>3</sup>/day · 330 days/year · 0.007 mg L<sup>-1</sup> = 1.9 kg Cd/year). In a similar way the cadmium load associated with 169 m<sup>3</sup> of waste water per day (Scenario 2 with DF = 1,000) can be calculated (169 m<sup>3</sup>/day · 330 days/year · 0.007 mg L<sup>-1</sup> = 0.4 kg Cd/year).

Table 3.97 Local PEC<sub>water</sub> for MSW incineration plants in the EU. Future scenarios: collection rate: 10% and 75% (total cadmium concentrations). Dilution Scenario 1: Dilution factor 100. Dilution Scenario 2: Dilution factor 1000

Use category	Emission kg/y	C <sub>effluent</sub> mg L <sup>-1</sup>	Dilution factor <sup>a</sup>	C <sub>local water</sub> µg L <sup>-1</sup>	PEC <sub>local water</sub> µg L <sup>-1</sup>
MSW Incineration plant			-		
10% collection Dilution Scenario 1	3.75	0.0135	100	0.045	0.16
10% collection Dilution Scenario 2	0.75	0.0135	1,000	0.0045	0.12
75% collection Dilution Scenario 1	1.9	0.007	100	0.023	0.14
75% collection Dilution Scenario 2	0.4	0.007	1,000	0.0023	0.12

a) Dilution in receiving water

A PEC<sub>local surface water</sub><sup>28</sup> of 0.12 µg L<sup>-1</sup> (total cadmium) under a collection scenario of 10% and 75% is calculated for a scenario in which a dilution factor of 1,000 is relevant. For the

<sup>28</sup> PEC<sub>reg, water, future</sub> = PEC<sub>reg, water, current</sub>. Indeed, the effect of an increase in MSW cadmium content up to 24 mg kg<sup>-1</sup> dry wt. ('future' scenarios) will have only a minor influence on the currently derived PECs regional for air, water and soil (cfr EUSES outprints in Annex V). Therefore there is no need to revise the current PEC<sub>reg, water</sub> and the PEC<sub>reg, air</sub> in order to derive the PEC values for the future situation.

realistic worst case (DF = 100) PEC local water varies between 0.14 and 0.16  $\mu\text{g L}^{-1}$  for the respective scenarios of 75% collection and 10% collection.

In case the NiCd batteries would be completely removed from the MSW stream (for the 10% collection scenario the contribution of NiCd batteries is 63% and for the 75% collection scenario a contribution of 32% is assumed) similar PEC local water values as presented in **Table 3.89**, for the assumption that NiCd batteries contributed in the current situation only 10% of the total cadmium load, are obtained.

#### Landfill current situation (leachate concentration = 5 $\mu\text{g L}^{-1}$ )

In the following paragraph the results from the local exposure assessment for a generic landfill (life cycle stage 5: disposal; landfills **Table 3.50**) are presented. Since the collection of site specific data on landfills was out of the scope of this report, local PEC values have been calculated for two hypothetical sites:

- Scenario 1: a landfill where the collected landfill leachate is discharged directly in the surface water
- Scenario 2: a landfill where the collected landfill leachate is discharged into a municipal STP before going into the surface water

The contamination of the groundwater compartment (PEC groundwater, added) due to fugitive emissions of landfills has not been quantified on a local scale in this report since no guidance is available to perform these calculations.

In the case of Scenario 1 (direct discharge to surface water) a generic dilution factor can be calculated from the leachate volume generated daily (100  $\text{m}^3/\text{day}$ , see subsection “Overall cadmium emissions from landfilling MSW” under Section 3.1.2.2.5) and the default flowing rate of a river being 18,000  $\text{m}^3/\text{day}$  resulting in a dilution factor of 180.

In Scenario 2 the landfill leachate is discharged in the public sewer system (STP). These discharges will undergo a dilution step in the STP. The corresponding dilution factor is calculated based on the landfill effluent flow rate and a default sewage flow of 2,000  $\text{m}^3/\text{day}$ . In addition to the dilution factor the cadmium removal efficiency of the STP has to be taken into account. According to CBS (2002) a removal efficiency of 60% can be used for STP’s. Finally the effluent of the STP is diluted in the receiving water. For the latter a default dilution factor of 10 can be used (based on a default flow rate of the receiving surface water of 18,000  $\text{m}^3/\text{day}$  and a default effluent flow of the STP of 2,000  $\text{m}^3$ ). The results of the calculations are presented in **Table 3.98**.

Table 3.98 Local PEC water for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is 5  $\mu\text{g L}^{-1}$ . Comparison of both scenarios

Input	Scenario 1	Scenario 2
Effluent Flow ( $\text{m}^3/\text{d}$ )	100	100
Conc. effluent ( $\mu\text{g L}^{-1}$ )	5	5
Size of STP ( $\text{m}^3/\text{d}$ )	N/A	2,000
Removal of cadmium in STP (%)	N/A	60
Flow rate receiving water ( $\text{m}^3/\text{d}$ )	18,000	18,000

Table 3.98 continued overleaf

Table 3.98 continued Local PEC water for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is  $5 \mu\text{g L}^{-1}$ . Comparison of both scenarios

Input	Scenario 1	Scenario 2
Dilution factor from STP to river	N/A	10
Output		
Calculated dilution factor in STP	N/A	21
Calculated conc. effluent STP ( $\mu\text{g L}^{-1}$ )	N/A	0.095
Calculated generic dilution factor in receiving water	180	10
Clocal water generic ( $\mu\text{g L}^{-1}$ )	0.009	0.003
PEClocal water generic	0.12	0.12

N/A Not applicable.

Table 3.99 Local PEC water for MSW landfills emitting directly to the surface water (scenario 1) or indirectly through a STP (scenario 2: STP). Cadmium leachate concentration is  $5 \mu\text{g L}^{-1}$ . Total cadmium concentrations

Use category	Ceffluent $\text{mg L}^{-1}$	Dilution factor <sup>a</sup> -	Clocal water $\mu\text{g L}^{-1}$	PEClocalwater $\mu\text{g L}^{-1}$
Scenario 1 (direct discharge, no STP)				
MSW Landfill (total cadmium)	0.005	180	0.009	0.12
Scenario 2 ( STP)				
MSW Landfill (total cadmium)	0.005	10	0.003	0.12

a) Dilution in receiving water

A PEClocal surface water of 0.12 (total cadmium) is calculated for both scenarios which is only slightly above the regional PEC ( $= 0.11 \mu\text{g L}^{-1}$ ).

In case all NiCd batteries would be removed from the MSW the influence on the PEClocal water would be negligible (see **Table 3.100**).

Table 3.100 Local PEC water for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2: STP). Cadmium leachate concentration is  $5 \mu\text{g L}^{-1}$ . Total cadmium without the NiCd contribution

Use category	Ceffluent $\text{mg L}^{-1}$	Dilution factor <sup>a</sup> -	Clocal water $\mu\text{g L}^{-1}$	PEClocalwater $\mu\text{g L}^{-1}$
Scenario 1 (direct discharge, no STP)				
MSW Landfill (NiCd batteries contributed for 10%)	0.0045	180	0.008	0.12
MSW Landfill (NiCd batteries contributed for 50%)	0.003	180	0.005	0.12

Table 3.100 continued overleaf

Table 3.100 continued Local PEC water for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2: STP). Cadmium leachate concentration is  $5 \mu\text{g L}^{-1}$ . Total cadmium without the NiCd contribution

Scenario 2 (STP)				
MSW Landfill (NiCd batteries contributed for 10%)	0.0045	10	0.003	0.12
MSW Landfill (NiCd batteries contributed for 50%)	0.003	10	0.002	0.12

a) Dilution in receiving water.

### Landfill scenario sensitivity analysis (leachate concentration = $50 \mu\text{g L}^{-1}$ )

As part of the sensitivity analysis (see subsection “Sensitivity analysis” under Section 3.1.2.2.5) a scenario of a landfill with a leachate concentration of  $50 \mu\text{g L}^{-1}$  is included. As is the case in the previous paragraph both a landfill with and without a STP is being considered.

Table 3.101 Local PEC water for landfills emitting directly to the surface water (scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is  $50 \mu\text{g L}^{-1}$

Input	Scenario 1	Scenario 2
Effluent Flow ( $\text{m}^3/\text{d}$ )	100	100
Conc. effluent ( $\mu\text{g L}^{-1}$ )	50	50
Size of STP ( $\text{m}^3/\text{day}$ )	N/A	2,000
Removal of cadmium in STP (%)	N/A	60
Flow rate receiving water ( $\text{m}^3/\text{day}$ )	18,000	18,000
Dilution factor from STP to river	N/A	10
Output		
Calculated dilution factor in STP	N/A	21
Calculated conc. effluent STP ( $\mu\text{g L}^{-1}$ )	N/A	0.95
Calculated generic dilution factor in receiving water	180	10
Clocal water generic ( $\mu\text{g L}^{-1}$ )	0.094	0.032
PEClocal water generic	0.21	0.15

N/A Not applicable.

Table 3.102 Local PECwater for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is  $50 \mu\text{g L}^{-1}$ . Total cadmium concentrations

Use category	Cleachate	Dilution factor <sup>a</sup>	Clocal water	PEClocalwater
	$\text{mg L}^{-1}$	-	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$
Scenario 1 (direct discharge, no STP)				
MSW Landfill (total cadmium)	0.05	180	0.094	0.21
Scenario 2 (STP)				
MSW Landfill (total cadmium)	0.05	10	0.032	0.15

a) Dilution in receiving water

A PEC<sub>local</sub> surface water of 0.21 µg L<sup>-1</sup> (total cadmium) is calculated for landfill sites that discharge directly in surface water. In case the landfill discharged to a STP an overall PEC of 0.15 µg L<sup>-1</sup> is obtained.

In case all NiCd batteries would be removed from the MSW the influence on the PEC<sub>local</sub> water would be negligible at the exception of the case where NiCd batteries as to their Cd content contribute to 50% of the MSW (see **Table 3.103**). In the latter case, direct discharge of leachate from MSW landfills would no longer result in risk (see **Table 3.266**).

Table 3.103 Local PEC<sub>water</sub> for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is 50 µg L<sup>-1</sup>. Total cadmium without the NiCd contribution

Use category	Cleachate	Dilution factor <sup>a</sup>	Clocal water	PEC <sub>local</sub> water
	mg L <sup>-1</sup>	-	µg L <sup>-1</sup>	µg L <sup>-1</sup>
<b>Scenario 1 (direct discharge, no STP)</b>				
MSW Landfill (NiCd batteries contributed for 10%)	0.045	180	0.085	0.20
MSW (NiCd batteries contributed for 50%)	0.025	180	0.047	0.16
<b>Scenario 2 (STP)</b>				
MSW Landfill (NiCd batteries contributed for 10%)	0.045	10	0.028	0.14
MSW Landfill MSW (NiCd batteries contributed for 50%)	0.025	10	0.016	0.13

a) Dilution in receiving water.

### 3.1.3.2.2 Sediment compartment

The PEC<sub>local</sub><sub>sediment</sub> is calculated according to the formula presented below (see Section 3.1.3.1.2):

$$\text{PEC}_{\text{local}}_{\text{sediment}} = \text{PEC}_{\text{regional}}_{\text{sediment}} + K_p \text{C}_{\text{local}}_{\text{water}} \cdot 10^{-3}$$

in which the  $K_p$  (L kg<sup>-1</sup><sub>dw</sub>) equals the solid- water partition coefficient of suspended matter ( $K_p = 130,000$  L kg<sup>-1</sup><sub>dw</sub>).

The measured PEC regional as mentioned in Section 3.1.3.4.3 is taken as an average of 90<sup>th</sup> percentiles of different surveys (Flanders, France, The Netherlands, Spain and Sweden) and is 2.66 mg kg<sup>-1</sup><sub>dry wt.</sub> (see **Table 3.189**). This value represents a realistic worst case for the EU ambient Cd concentrations in sediment (natural Cd + historical Cd) and is used as the PEC<sub>regional</sub> in the risk characterisation.

The local PEC<sub>sediment</sub> are readily calculated from the data in **Table 3.90** and the aforementioned equation and presented in **Table 3.104**. The C<sub>local</sub><sub>sediment</sub> ( $K_p \text{C}_{\text{local}}_{\text{water}} \cdot 10^{-3}$ ) is included to illustrate the contribution of the local discharge onto the sediment PEC.

The local PEC<sub>sediment</sub> range from 2.66 (i.e. the PEC<sub>regional</sub>) to 10.46 mg kg<sup>-1</sup><sub>dry wt.</sub> for NiCd batteries-producing plants and is 22.6 mg kg<sup>-1</sup><sub>dry wt.</sub> for one Cd-recycling plant. Local sediment concentrations calculated for plants 2, 3 and recycler 1 are on the basis of the maximum dilution factor of 1,000.

Table 3.104 Local PECsediment for NiCd batteries producing plants and Cd recycling plants in the EU (without correction for bioavailability)

Use category	N°	Production emission	Processing emission	Clocal sediment D=1,000 or site specific	PEClocal sediment D=1,000 or site specific	Year
NiCd batteries		kg year <sup>-1</sup>	kg year <sup>-1</sup>	mg kg <sup>-1</sup> dry wt	mg kg <sup>-1</sup> dry wt.	
	1		4.9	0.5	3.16	1999
	2 <sup>a</sup>		7.3	5.3	7.96	2000
	3		30.5	5.3	7.96	2000
	4		21.9	7.8	10.46	2000
	5		0.07	0.003	2.66	1999
	6 <sup>b</sup>		No emissions to water (recycled)	N/A	N/A	1999
	7 <sup>c</sup>		No emissions to water (recycled)	N.A	N/A	1999
Cd recyclers <sup>d</sup>	1	0.126		19.9	22.6	2000
	2 <sup>e</sup>	0		N/A	N/A	1999

N.A. Not available;

N/A Not applicable;

a) Company 2 emits to the marine environment;

b) All process wastewater is collected and sent to recycling company;

c) Emissions to water from cleaning operations are disposed in alkaline solution and externally recycled;

d) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown in the submitted figures between the producing process and the recycling process was not feasible. For this reason this company have been listed with the other producers;

e) No "open" treatment steps; no emissions to air. The wastewater is collected and treated off-site. No further information was available. The sludge from the treatment is land-filled.

### MSW incinerator: current situation

The local PEC sediment was calculated for two scenarios (dilution factor 100 and 1,000) (see **Table 3.105**)

Table 3.105 Local PECsediment for MSW incineration plants in the EU (without correction for bioavailability)

	Emission	Dilution factor <sup>a</sup>	Clocal water	Clocal sediment	PEClocal sediment
	kg year <sup>-1</sup>		µg L <sup>-1</sup>	mg kg <sup>-1</sup> dry wt.	mg kg <sup>-1</sup> dry wt.
Scenario 1	10 <sup>th</sup> percentile measured dilution factors				
	1.6	100	0.019	2.53	5.19
Scenario 2	50 <sup>th</sup> percentile measured dilution factors				
	0.3	1,000	0.0019	0.25	2.91

a) Dilution in receiving water

The Cd emissions and the calculated PEClocal sediment in **Table 3.105** represent the impact of all cadmium containing sources in the MSW and not NiCd batteries only. PEClocal sediment value of 2.91 mg kg<sup>-1</sup>. dry wt (total cadmium) is calculated for the typical scenario (dilution factor of 1,000) which is very close to the regional background of 2.66 mg kg<sup>-1</sup> dry wt. If the calculations are performed with the realistic worst case dilution factor (i.e. 100) PEClocal sediment is 5.19 mg kg<sup>-1</sup> dry wt.

Similar to the aquatic compartment the PEC<sub>local</sub>sediment has also been calculated for the assumption that all NiCd batteries would be removed from the MSW waste stream (see **Table 3.106**).

**Table 3.106** Local PEC sediment (total cadmium without the NiCd contribution) for MSW incineration plants in the EU (without correction for bioavailability). Scenario 1: dilution factor 100. Scenario 2: dilution factor 1000

	Dilution factor <sup>a</sup>	Clocal sediment	PEC <sub>local</sub> sediment	Dilution factor <sup>a</sup>	Clocal sediment	PEC <sub>local</sub> sediment
		mg kg <sup>-1</sup> dry wt.	mg kg <sup>-1</sup> dry wt.	-	mg kg <sup>-1</sup> dry wt.	mg kg <sup>-1</sup> dry wt.
Assumption NiCd contribution: 10% of the total Cd load						
Scenario 1&2	100	2.21	4.87	1,000	0.03	2.69
Assumption NiCd contribution: 50% of the total Cd load						
Scenario 1&2	100	1.17	3.93	1,000	0.13	2.79

a) Dilution in receiving water

From **Table 3.106** it is clear that removing the NiCd battery fraction from the MSW does not have a large impact on the calculated PEC sediment values. For those scenarios with a dilution factor of 1,000 the cadmium sediment concentrations are similar (2.69-2.79). If a dilution factor of 100 is applied the calculated sediment concentration is only slightly lower (3.93 versus 4.87) when it is assumed that NiCd batteries contribute for 50% of the total cadmium load.

#### MSW incinerator scenario sensitivity analysis (effluent concentration = 0.009 mg L<sup>-1</sup>)

The local PEC sediment was also calculated for the scenario developed with the maximum effluent concentration (i.e. 0.009 mg L<sup>-1</sup>) (see **Table 3.107**) as part of the sensitivity analysis.

**Table 3.107** Local PEC<sub>sediment</sub> (without correction for bioavailability) for MSW incineration plants in the EU

	Emission	Dilution factor <sup>a</sup>	Clocal water	Clocal sediment	PEC <sub>local</sub> sediment
	kg year <sup>-1</sup>		µg L <sup>-1</sup>	mg kg <sup>-1</sup> dry wt.	mg kg <sup>-1</sup> dry wt.
<u>Scenario 1</u>	10 <sup>th</sup> percentile measured dilution factors				
	2.5	100	0.03	3.95	6.6
<u>Scenario 2</u>	50 <sup>th</sup> percentile measured dilution factors				
	0.5	1,000	0.003	0.39	3.1

a) Dilution in receiving water

PEC<sub>local</sub> sediment value of 3.1 mg kg<sup>-1</sup> dry wt (total cadmium) is calculated for the typical scenario (dilution factor of 1,000) which is very close to the regional background of 2.66 mg kg<sup>-1</sup> dry wt. If the calculations are performed with the realistic worst case dilution factor (i.e. 100) PEC<sub>local</sub> sediment is 6.6 mg kg<sup>-1</sup> dry wt.

MSW incinerator: future situation

Table 3.108 Local PEC<sub>sediment</sub> (without correction for bioavailability) for a generic MSW incineration plant in the EU. Future scenarios: collection rate: 10 and 75%. Total cadmium concentrations. Dilution Scenario 1: Dilution factor 100. Dilution Scenario 2: Dilution factor 1,000

Use category	Emission	Dilution factor <sup>a</sup>	Clocal water	Clocal sediment	PEC <sub>local sediment</sub>
MSW Incineration plant	kg/y	-	µg L <sup>-1</sup>	mg kg <sup>-1</sup> dry wt	mg kg <sup>-1</sup> .dry wt
10% collection Dilution Scenario 1	3.75	100	0.0455	5.9	8.6
10% collection Dilution Scenario 2	0.75	1,000	0.0046	0.6	3.3
75% collection Dilution Scenario 1	1.9	100	0.023	4.2	6.8
75% collection Dilution Scenario 2	0.4	1,000	0.0023	0.3	3.0

a) Dilution in receiving water

The results from the local exposure assessment for MSW incineration plants predict a PEC<sub>local sediment</sub> of 3.0-3.3 mg kg<sup>-1</sup> dry wt. (total cadmium) for the different future scenarios (collection rate: 75% and 10% respectively) if a dilution factor of 1,000 is relevant. In case only a dilution factor of 100 can be applied PEC<sub>local sediment</sub> varies between 6.8 and 8.6 mg kg<sup>-1</sup> dry wt.

In case the NiCd batteries would be completely removed from the MSW stream (for the 10% collection scenario the contribution of NiCd batteries is 63% and for the 75% collection scenario a contribution of 32% is assumed) similar PEC<sub>local sediment</sub> values as presented in **Table 3.106**, for the assumption that NiCd batteries contributed in the current situation only 10% of the total cadmium load, are obtained.

Landfill current situation

Table 3.109 Local PEC sediment (without correction for bioavailability) for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2: STP). Cadmium leachate concentration is 5 µg L<sup>-1</sup>

Use category	Dilution factor <sup>a</sup>	Clocal water	Clocal sediment	PEC <sub>local sediment</sub>
	-		mg kg <sup>-1</sup> dry wt.	mg kg <sup>-1</sup> dry wt.
Scenario 1 (direct discharge, no STP) MSW Landfill (total cadmium)	180	0.009	1.17	3.8
Scenario 2 (STP) MSW Landfill (total cadmium)	10	0.003	0.39	3.1

a) Dilution in receiving water.

The results from the local exposure assessment for MSW landfills show a PEC<sub>local sediment</sub> of 3.1 mg kg<sup>-1</sup> dry wt. (total cadmium) if the leachate is sent to an STP and 3.8 mg kg<sup>-1</sup> dry wt. if there is no STP.

In case all NiCd batteries would be removed from the MSW the influence on the PEClocal sediment would be negligible (see **Table 3.110**).

Table 3.110 Local PEC sediment (without correction for bioavailability) for MSW landfills emitting directly to the surface water (scenario 1) or indirectly through a STP (scenario 2: STP). Cadmium leachate concentration is  $5 \mu\text{g L}^{-1}$ . Total cadmium without the NiCd contribution

Use category	Dilution factor <sup>a</sup>	Clocal water	Clocal sediment	PEClocal sediment
	-	$\mu\text{g L}^{-1}$	$\text{mg kg}^{-1}$ dry wt	$\text{mg kg}^{-1}$ dry wt
Scenario 1 (direct discharge, no STP)				
MSW Landfill (NiCd batteries contributed for 10%)	180	0.008	1	3.7
MSW Landfill (NiCd batteries contributed for 50%)	180	0.005	0.65	3.3
Scenario 2 (STP)				
MSW Landfill (NiCd batteries contributed for 10%)	10	0.003	0.39	3.1
MSW Landfill (NiCd batteries contributed for 50%)	10	0.002	0.26	2.9

a) Dilution in receiving water.

#### Landfill scenario sensitivity analysis (leachate concentration = $50 \mu\text{g L}^{-1}$ )

As part of the sensitivity analysis (see subsection “Sensitivity analysis” under Section 3.1.2.2.5) a scenario of a landfill with a leachate concentration of  $50 \mu\text{g L}^{-1}$  is included. As is the case in the previous paragraph both a landfill with and without a STP is being considered.

Table 3.111 Local PEC<sub>sediment</sub> (without correction for bioavailability) for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2). Cadmium leachate concentration is  $50 \mu\text{g L}^{-1}$ . Total cadmium

Use category	Dilution factor <sup>a</sup>	Clocal water	Clocal sediment	PEClocal sediment
	-	$\mu\text{g L}^{-1}$	$\text{mg kg}^{-1}$ dry wt.	$\text{mg kg}^{-1}$ dry wt.
Scenario 1 (direct discharge, no STP) MSW Landfill (total cadmium)	180	0.094	12.2	14.9
Scenario 2 (STP) MSW Landfill (total cadmium)	10	0.032	4.2	6.8

a) Dilution in receiving water.

The results from the local exposure assessment for MSW landfills with a leachate concentration of  $50 \mu\text{g Cd/L}$  show a PEClocal sediment of  $6.8 \text{ mg kg}^{-1}$  dry wt. (all waste) if the leachate is sent to an STP and  $14.9 \text{ mg kg}^{-1}$  dry wt. if there is no STP.

Table 3.112 Local PEC sediment (without correction for bioavailability) for MSW landfills emitting directly to the surface water (Scenario 1) or indirectly through a STP (Scenario 2: STP). Cadmium leachate concentration is 50  $\mu\text{g L}^{-1}$ . All cadmium without the NiCd contribution

Use category	Dilution factor <sup>a</sup>	Clocal water $\mu\text{g L}^{-1}$	Clocal sediment $\text{mg kg}^{-1}$ dry wt	PEClocal sediment $\text{mg kg}^{-1}$ dry wt
Scenario 1 (direct discharge, no STP)				
MSW Landfill (NiCd batteries contributed for 10%)	180	0.085	11.1	13.7
MSW Landfill (NiCd batteries contributed for 50%)	180	0.047	6.1	8.8
Scenario 2 (STP)				
MSW Landfill (NiCd batteries contributed for 10%)	10	0.028	3.6	6.3
MSW Landfill (NiCd batteries contributed for 50%)	10	0.016	2.1	4.7

a) Dilution in receiving water.

For the scenario with a direct discharge of a leachate cadmium concentration of 50  $\mu\text{g L}^{-1}$  the PEClocal sediment originating from cadmium emitting sources other than NiCd batteries is predicted to range between 8.8 and 13.7  $\text{mg kg}^{-1}$  dry wt. If the landfill leachate is sent to an STP for treatment the local sediment concentrations range between 4.7-6.3  $\text{mg kg}^{-1}$  dry wt.

### 3.1.3.2.3 Atmospheric compartment

#### Calculated local concentrations

Local PEC-values for the atmospheric compartment are calculated according to the OPS model proposed in the TGD (1996) for a general standard environment (see Section 3.1.3.1.3).

Input data are the total daily emissions of the individual NiCd batteries-producing plants and Cd recycling plants (Industry questionnaires 1999/2000). The calculated concentrations in air are actual contributions to the receiving atmosphere. The local PEC values are obtained by adding the regional PEC values for air to the calculated local concentration in the atmosphere.

$$\text{PEC}_{\text{local air}} = \text{C}_{\text{local air}} + \text{PEC}_{\text{regional air}}$$

$\text{PEC}_{\text{local air}}$ : predicted environmental concentration in air during emission episode ( $\text{ng/m}^3$ )

$\text{C}_{\text{local air}}$ : local concentration in the air during emission episode ( $\text{ng/m}^3$ )

$\text{PEC}_{\text{regional air}}$ : regional concentration in the air (0.561  $\text{ng/m}^3$ )

The results of the predicted local atmospheric Cd concentrations at 100 m from the point sources are listed in **Table 3.113** Reported data are based on new emission data from Industry Questionnaire, 2000/2001. Calculated local PEC values range from 0.561 to 22.6  $\text{ng/m}^3$  for NiCd batteries producers and from 0.561 to 1.91  $\text{ng/m}^3$  for Cd recycling plants. It should be noted that for producing company 1 and 3 it was stated that emissions to air were negligible and mainly through effluents. Recycler 2 also declared that there are no “open treatment” steps in its procedure, so there are no stack emissions to air.

Table 3.113 Calculated local PEC<sub>air</sub> concentrations for NiCd batteries producing plants and Cd recycling plants in the EU

Use category	Plant n°	Production emission amount (kg/y)	Processing emission amount (kg/y)	Number of emission days (d)	Annual average air concentration (100 m) ng/m <sup>3</sup>	PEC <sub>local air</sub> (100 m) ng/m <sup>3</sup>	Year
NiCd batteries							
	1		N.A.	225	N.A.	0.561	1999
	2 <sup>a</sup>		1.6	330	1.22	1.78	2000
	3 <sup>b</sup>		N.A.	315	N.A.	0.561	2000
	4		13.5	330	10.28	10.9	2000
	5		7	230	5.3	5.9	1999
	6		0.036	250	0.03	0.64	1999
	7		28.99	300	22.1	22.64	1999
Cd recyclers <sup>c</sup>							
	1	1.77		350	1.35	1.91	2000
	2 <sup>d</sup>	0		240	0	0.561	1999
Total			> 53				

N.A. Not available;

a) Company 2 emits to the marine environment;

b) Wet processes. Mainly emissions to effluents;

c) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown in the submitted figures between the producing process and the recycling process was not feasible. For this reason this company have been listed with the other producers;

d) No "open" treatment steps; no emissions to air.

### Measured local concentrations

Measured atmospheric concentrations in the surroundings of the production-sites are scarce and are presented in **Table 3.114**.

From this table it can be concluded that the measured data at a distance of 100 m from the point source for plant 4 and plant 6 are in the same order of magnitude as the calculated data (4 ng/m<sup>3</sup> versus 10.9 ng/m<sup>3</sup> and 0.7 ng/m<sup>3</sup> versus 0.64 ng/m<sup>3</sup>).

Table 3.114 Calculated and measured local PEC<sub>air</sub> concentrations for NiCd producing and Cd recycling plants in EU

Use-category	N°	Production emission amount kg year <sup>-1</sup>	Processing emission amount kg / <sup>-1</sup>	PEC <sub>local air</sub> (100 m) ng/m <sup>3</sup>	Measured ann.avg. air concentration ng/m <sup>3</sup>	Year
NiCd-batteries	1		N.A.	0.56	N.A.	1999
	2 <sup>a</sup>		1.6	1.78	N.A.	2000
	3 <sup>b</sup>		N.A.	0.56	N.A.	2000
	4		13.5	10.9	4 (100 m from plant)	2000
	5		7	5.9	N.A.	1999
	6		0.036	0.64	0.7 (0.2-2.5) (100 m from plant)	1999
	7		28.99	22.64	N.A.	1999

Table 3.114 continued overleaf

Table 3.114 continued Calculated and measured local PEC<sub>air</sub> concentrations for NiCd producing and Cd recycling plants in EU

Use-category	N°	Production emission amount kg year <sup>-1</sup>	Processing emission amount kg / <sup>-1</sup>	PEC <sub>local,air</sub> (100 m) ng/m <sup>3</sup>	Measured ann.avg. air concentration ng/m <sup>3</sup>	Year
Cd recycling <sup>c</sup>	1	1.77		1.91	N.A.	2000
	2 <sup>d</sup>	0		0.56	N.A.	1999

N.A. Not available;

a) Company 2 emits to the marine environment;

b) Wet processes. Mainly emissions to effluents;

c) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown in the submitted figures between the producing process and the recycling process was not feasible. For this reason this company have been listed with the other producers;

d) No "open" treatment steps; no emissions to air.

### MSW incinerator: current situation

In the following section the results from the local exposure assessment for MSW incineration plants (life cycle stage 5: disposal; incineration) is presented. The local air emission for incineration plants is calculated using an allocation key based on the number of incinerators in each country and the country specific air emission amounts. The results presented below are based on emission data for incineration scenario 24.4% only (realistic case); it is assumed that for incineration scenario 100% (worst case), taking into account a proportional increase in incineration plants over Europe, analogous results can be expected.

Table 3.115 Calculated local PEC<sub>air</sub> concentration for MSW incineration plant in the EU. Current situation. Total cadmium concentrations

Country	Emission amount kg year <sup>-1</sup>	Number of emissions days days	Annual average air concentration (100 m) ng/m <sup>3</sup>	PEC <sub>local air</sub> (100m) ng/m <sup>3</sup>
Austria	1.4 <sup>c</sup>	330	1.07	1.63
Belgium	3.5	330	2.7	3.2
Denmark	9.7	330	7.4	8.0
Finland	14	330	10.7	11.2
France <sup>a</sup>	16.4	330	12.5	13.1
France <sup>b</sup>	36.7	330	27.95	28.5
Germany	5	330	3.8	4.4
Italy	5.7	330	4.3	4.9
Luxembourg	22	330	16.8	17.3
The Netherlands	4.8	330	3.7	4.2
Norway	5.1	330	3.9	4.5
Portugal	1.6	330	1.2	1.8
Spain	6.8	330	5.2	5.7

Table 3.115 continued overleaf

Table 3.115 continued Calculated local PEC<sub>air</sub> concentration for MSW incineration plant in the EU.  
Current situation. Total cadmium concentrations

Country	Emission amount	Number of emissions days	Annual average air concentration (100 m)	PEC <sub>local</sub> air (100m)
	kg year <sup>-1</sup>	days	ng/m <sup>3</sup>	ng/m <sup>3</sup>
Sweden	0.2	330	0.2	0.7
UK	1.5	330	1.1	1.7
EU 10% scenario	9.1	330	6.9	7.5

- a) Generic scenario;  
 b) Based on P90 measured data;  
 c) According to the latest information (Stubenvoll et al., 2002) total Cd emissions in Austria from incinerators amount to 4.2 kg. Since there is a total of 3 plants, on average, 1.4 kg per plant is emitted.

From this table it can be concluded that the PEC<sub>local</sub> in air at a distance of 100 m from the point source of the incineration plant range between 0.7 and 28.5 ng/m<sup>3</sup> (7.5 ng/m<sup>3</sup> for the average EU situation). It should be noted that this concentration is valid for all MSW incinerated (not exclusively batteries). The influence of removing the NiCd batteries on the overall emissions is given in **Table 3.116**.

Table 3.116 Calculated local PEC<sub>air</sub> concentration for MSW incineration plant in the EU). Current situation. Total cadmium without the NiCd contribution

Country	Emission amount	Number of emissions days	Annual average air concentration (100 m)	PEC <sub>local</sub> air (100m)
	kg year <sup>-1</sup>	days	ng/m <sup>3</sup>	ng/m <sup>3</sup>
Assumption NiCd contribution: 10% of the total Cd load				
Austria	1.26	330	1.0	1.5
Belgium	3.2	330	2.4	3.0
Denmark	8.7	330	6.3	7.2
Finland	12.6	330	9.6	10.2
France <sup>a</sup>	14.7	330	11.2	11.8
France <sup>b</sup>	33	330	25.1	25.7
Germany	4.5	330	3.4	4.0
Italy	5.1	330	3.9	4.5
Luxembourg	19.8	330	15.1	15.6
The Netherlands	4.3	330	3.3	3.8
Norway	4.6	330	3.5	4.1
Portugal	1.4	330	1.1	1.6
Spain	6.1	330	4.7	5.2
Sweden	0.18	330	0.14	0.7
UK	1.4	330	1.1	1.6
EU 10% scenario	8.2	330	6.3	6.8

Table 3.116 continued overleaf

Table 3.116 continued Calculated local PEC<sub>air</sub> concentration for MSW incineration plant in the EU). Current situation. Total cadmium without the NiCd contribution

Country	Emission amount	Number of emissions days	Annual average air concentration (100 m)	PEC <sub>local</sub> air (100m)
	kg year <sup>-1</sup>	days	ng/m <sup>3</sup>	ng/m <sup>3</sup>
Assumption NiCd contribution: 50% of the total Cd load				
Austria	0.7	330	1.07	1.63
Belgium	1.8	330	1.4	1.9
Denmark	4.9	330	3.7	4.2
Finland	7	330	5.4	5.9
France <sup>a</sup>	8.3	330	6.3	6.8
France <sup>b</sup>	18.4	330	14	14.6
Germany	2.5	330	1.9	2.4
Italy	2.9	330	2.2	2.7
Luxembourg	11	330	8.4	8.9
The Netherlands	2.4	330	1.9	2.4
Norway	2.5	330	2.0	2.5
Portugal	0.8	330	0.6	1.1
Spain	3.4	330	2.6	3.1
Sweden	0.1	330	0.1	0.6
UK	0.8	330	0.6	1.1
EU 10% scenario	4.5	330	3.5	4.0

a) Generic scenario;

b) Based on P90 measured data.

Removing the contribution from NiCd batteries to the MSW (10-50%), PEC local in air range between 0.6 and 25.7 ng/m<sup>3</sup>.

For the future<sup>44</sup> and the 100% incineration scenarios it is assumed that the number of incineration plants is proportionally increased to the amount of MSW to incinerate. And since higher local air emissions due to higher cadmium content of the MSW are not expected to occur when the FGCS are working well (shift of the cadmium to incineration residues) **Table 3.111** can also be used for these scenarios.

### 3.1.3.2.4 Terrestrial compartment

#### Calculated local concentrations

According to the TGD, the local PEC<sub>soil</sub> is calculated as an average concentration over a certain time period in agricultural soil, fertilised yearly with sludge from a STP and receiving continuous aerial deposition (dry and wet) from a nearby point source, for a period of 10 years.

<sup>44</sup> PEC<sub>reg, air, future</sub> = PEC<sub>reg, air, current</sub>. Indeed, the effect of an increase in MSW cadmium content up to 24 mg kg<sup>-1</sup> dry wt. ('future' scenarios) will have only a minor influence on the currently derived PECs regional for air, water and soil (cfr EUSES outprints in Annex V). Therefore there is no need to revise the current PEC<sub>reg, water</sub> and the PEC<sub>reg, air</sub> in order to derive the PEC values for the future situation.

For the terrestrial ecosystem, the concentration is calculated for a depth of 0.2 m. Sludge from Cd producing plants is however not applied to agricultural land but is recycled internally or by an external plant (IZA-Europe, pers. communication). Application of sludge from processing sites/scenarios is unlikely to take place<sup>45</sup> but may occur if the Cd is emitted via a sewer to a municipal sewage treatment plant. This route of emission is taken into account in the regional assessment as diffuse Cd flux (no changes made, see Section 3.1.3.4.2). Therefore, the Cd input to soil through sludge from the Cd producing plants is omitted in these calculations and atmospheric deposition is the only source of Cd input into the terrestrial compartment. The fate of sludge from Cd processors is unknown. Atmospheric deposition of Cd is calculated assuming that all Cd is deposited within an area of 100 km<sup>2</sup> around the source and that the deposition occurs in a continuous flux.

The PEC<sub>local</sub> is the sum of the regional Cd concentration in soil (PEC<sub>regional</sub>) and the atmospheric deposition minus the leaching losses. The PEC<sub>local</sub> is solved from the dynamic Cd balance in the 0-0.2 m top layer of the soil as (see Section 3.1.3.4.2):

$$PEC_{local,soil} = \frac{D_{air}}{k} - \left( \frac{D_{air}}{k} - PEC_{regional,soil} \right) \exp(-kt)$$

where

D<sub>air</sub> = aerial deposition flux per kg of soil (mg kg<sup>-1</sup> days)  
 t = time (3,650 days)  
 k = first order rate constant for removal from top soil (d<sup>-1</sup>)  
 PEC<sub>regional,soil</sub> = the regional Cd concentration in soil (0.36 mg kg<sup>-1</sup> wet wt) and which is calculated for an agricultural scenario assuming a realistic worst case Cd input scenario.

Results of the calculations are presented in **Table 3.117**. The PEC<sub>soil</sub> values are 0.36 mg kg<sup>-1</sup> wet wt. - 0.37 mg kg<sup>-1</sup> wet wt. PEC<sub>soil</sub> values for NiCd batteries producers and Cd recyclers are very similar and are mainly determined by the PEC<sub>regional</sub> value for soil of 0.363 mg kg<sup>-1</sup> wet wt. Since atmospheric deposition is the only source of Cd input to the terrestrial compartment (sludge is recycled or land-filled) and emissions to air are relatively low (0.0014-0.10 kg/day; emission days: 225-350 days), this emission route is of minor importance in comparison to the regional Cd concentration in soil. Referring to the scenarios of production, processing and use (reference year: 1996) in Section 3.1.3.1.4, local PEC<sub>soil</sub> values for Cd producing plants (with higher air emissions) of 0.36-0.85 mg kg<sup>-1</sup> wet wt. were calculated.

<sup>45</sup> In line with national and EU legislation sludges from on-site wwtp of Cd processors are likely to be classified as hazardous (e.g. see for the sector of metal treatment in IPPC, 2004; EC legislation in: EC, 1991 and EC, 2000)

Table 3.117 Calculated local PECsoil for NiCd producing plants and Cd recycling plants

Use category	Plant n°	Emission to air	Number of emission days	PEClocal soil	Year
		kg/day		mg kg <sup>-1</sup> wet wt	
NiCd batteries					
	1	N.A.	225	0.36	1999
	2 <sup>a</sup>	0.005	330	0.36	2000
	3 <sup>b</sup>	N.A.	315	0.36	2000
	4	0.04	330	0.37	2000
	5	0.03	230	0.37	1999
	6	0.00014	250	0.36	1999
	7	0.097	300	0.37	1999
Cd recyclers <sup>c</sup>	1	0.01	350	0.36	2000
	2 <sup>d</sup>	0	240	0.36	1999

N.A. Not available;

a) Company 2 emits to the marine environment;

b) Wet processes; no emissions to air. Mainly emissions to effluents;

c) Only two recyclers (instead of three) have been listed under Cd-recyclers. The reason is that one company is both recycler and producer. A further breakdown in the submitted figures between the producing process and the recycling process were not feasible. For this reason this company have been listed with the other producers;

d) No "open" treatment steps; no emissions to air.

### Measured local concentrations

At this moment, only company 3 reported measured local soil concentrations of <math> < 12 \text{ mg kg}^{-1}</math> dry wt.

### MSW incinerator: current situation

In the following section the results from the local exposure assessment for the terrestrial compartment for MSW incineration plants (life cycle stage 5: disposal; incineration) are presented. The only route of exposure for the terrestrial compartment is aerial deposition since it is assumed that the sludge from the on-site wastewater treatment plant is land-filled. As mentioned previously the local air emission for incineration plants is calculated using an allocation key based on the number of incinerators in each country and the country specific air emission amounts.

From **Table 3.118** it can be concluded that the local PEC soil surrounding incineration plants in the EU range from  $0.363 \text{ mg kg}^{-1}$  wet wt to  $0.374 \text{ mg kg}^{-1}$  wet wt. (total cadmium) which is almost similar to the regional PEC soil concentration of  $0.363 \text{ mg kg}^{-1}$  wet wt. Removing NiCd batteries in the MSW will not significantly reduce the cadmium soil concentration (calculations not shown).

Table 3.118 Calculated total local PECsoil for MSW incineration plants

Country	Emission amount	Number of emissions days	Clocalsoil	PEClocal soil
	kg year <sup>-1</sup>	days	mg kg <sup>-1</sup> wwt	mg kg <sup>-1</sup> wwt.
Austria	1.4 <sup>c</sup>	330	0.00041	0.363
Belgium	3.5	330	0.0012	0.364
Denmark	9.7	330	0.0028	0.366
Finland	14	330	0.0041	0.367
France <sup>a</sup>	16.4	330	0.0048	0.368
France <sup>b</sup>	36.7	330	0.0107	0.374
Germany	5	330	0.0015	0.365
Italy	5.7	330	0.0017	0.363
Luxembourg	22	330	0.0064	0.369
The Netherlands	4.8	330	0.0014	0.364
Norway	5.1	330	0.0015	0.364
Portugal	1.6	330	0.0005	0.363
Spain	6.8	330	0.0020	0.365
Sweden	0.2	330	0.00006	0.363
UK	1.5	330	0.0004	0.363
EU 10% scenario	9.1	330	0.0027	0.366

- a) Generic scenario;  
b) Based on P90 measured data;  
c) According to the latest information (Stubenvoll et al., 2002) total Cd emissions in Austria from incinerators amount to 4.2 kg. Since there is a total of 3 plants, on average 1.4 kg per plant is emitted.

### Landfills

The leachate from landfills may be treated in municipal treatment plants from which sludge may be applied to land. Figures for the amounts going to agricultural land have been added to the tables in the assessment, but no calculations of soil concentrations have been included (there is no calculation of soil levels related to landfill, as there are no air emissions).

Regulations on the metals content of sludges for agriculture come into play here (see Section 2.3). Moreover, as the case in (the 'global' RAR related) Section 3.1.3.1.4, the TRAR/batteries' related sections does not include local 'sludge application scenario'. Only diffuse emissions (averaged over whole EU) are considered in the assessment. The contribution of sludge application to (arable) land is considered and included in the PEC, reg, soil see Section 3.1.3.4.2.

### 3.1.3.3 Local exposure: all scenarios: update data (reference year 2002)

#### 3.1.3.3.1 Aquatic compartment: calculated PECs

##### Surface water

##### *Introduction*

Calculation of local PEC-values for the aquatic compartment is performed according to the method described in the TGD (EC, 2003; see also Section 3.1.3.2.1). Input data were submitted via the Industry Questionnaire (2004).

##### *Cd metal and Cd oxide production*

##### *Cd metal production*

An overview of the calculated local Cd concentrations in surface water is presented in **Table 3.119**. From this table it can be concluded that for Cd metal producers in Europe:

- Daily emissions to surface water vary between 0.001 kg Cd/day (site 6) and 0.16 kg Cd/day (site 7; year 2002).
- Update information for on-site WWTP cadmium removal efficiency is not provided.
- Total Cd concentrations in on-site WWTP effluent vary between 0.0007 mg L<sup>-1</sup> (annual mean site 6, direct discharge to large tide influenced river) and 0.05 mg L<sup>-1</sup> (annual mean site 7, discharge to the sea; year 2002).
- Dilution factors vary between 2.3 (site specific dilution factor ditch, site 1) and 1,000 (maximum site specific dilution factor large river, site 6). Site specific dilution factors were derived for 2 sites. Production-site 7 discharges its wastewater to a marine environment for which a default dilution factor of 100 is applied.
- Local dissolved Cd concentrations in water vary between 0.0002 µg L<sup>-1</sup> (site 6, large tidal river, maximum dilution factor of 1,000) and 0.53 µg L<sup>-1</sup> (site 1, ditch, very small dilution factor).
- Calculated PEC<sub>total</sub> levels in surface water vary between 0.11 µg L<sup>-1</sup> (calculated regional background<sub>total</sub> = 0.11 µg L<sup>-1</sup>) and 0.64 µg L<sup>-1</sup>.

Table 3.119 The local PEC<sub>water</sub> (dissolved fraction) for Cd metal producing plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>¶</sup>	Concentration in effluent	Type of receiving water	Dilution Factor	Clocal <sub>water</sub>	PEClocal <sub>water</sub>	Year
	kg d <sup>-1</sup>	mg l <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>	
1	0.03 <sup>(c)</sup>	0.004	ditch	2.3	0.53	0.64	2002
6	0.001	0.0007	Tide influenced river	1,000 <sup>(b)</sup> (ss: 11,087)	0.0002	0.11	2002
7*	0.16*	0.05	sea	100 <sup>(a)*</sup>	0.17*	0.28*	2002
7*	0.10*	0.03	sea	100 <sup>(a)*</sup>	0.10*	0.21*	2004

a) Default dilution factor: 10 (freshwater), 100 (sea water);

b) Site specific dilution factor restricted to a maximum of 1,000 (revised TGD - EC, 2003);

c) The total emission in 2002 consists of discharge of effluent from water purification plant and discharge of other water from the plant area (historic contaminated). Since 2005, the discharge from water from the plant area has been stopped; since then all waste water is treated in the purification plant;

ss Site specific dilution factor;

\* Emission to the sea: values are only indicative; no assessment is done for the marine environment;

¶ Annual averages.

### Cd oxide production

An overview of the calculated local Cd concentrations in surface water is presented in **Table 3.120**. From this table it can be concluded that for Cd oxide producers in Europe:

- Due to the fact that the production of cadmium oxide is a totally dry process; discharge of waste water from the site does not take place.
- As a result the PEC<sub>local</sub> in surface water is 0.11 µg L<sup>-1</sup> (calculated regional background).

Table 3.120 The local PEC<sub>water</sub> (dissolved fraction) for Cd oxide producing plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>¶</sup>	Concentration in effluent	Type of receiving water	Dilution Factor	Clocal <sub>water</sub>	PEClocal <sub>water</sub>	Year
	kg d <sup>-1</sup>	mg l <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>	
12	0 <sup>(a)</sup>	0	n.a.	n.a.	0	0.11	2002

¶ Annual averages;

n.a. Not applicable;

a) No emission to water; thermal/dry process.

### Production and recycling of NiCd batteries

#### Production of NiCd batteries

An overview of the calculated local Cd concentrations in surface water is presented in **Table 3.121**. From this table it can be concluded that for NiCd battery producers in Europe:

- Daily emissions to surface water vary between 0.03 kg Cd/day (site 2) and 0.07 kg Cd/day (site 4).
- Update information for on-site WWTP cadmium removal efficiency is not provided.
- Total Cd concentrations in on-site WWTP effluent vary between 0.06 mg L<sup>-1</sup> (annual mean site 3, direct discharge to large river) and 0.11 mg L<sup>-1</sup> (annual mean site 2, discharge to the sea).

- Dilution factors are set to 1,000 (maximum site specific dilution factor, site 2, 3, 4). Site specific dilution factors were derived for 3 sites.
- Local dissolved Cd concentrations in water vary between  $0.02 \mu\text{g L}^{-1}$  (site 3, river, maximum dilution factor of 1,000) and  $0.04 \mu\text{g L}^{-1}$  (site 2, sea, maximum dilution factor of 1,000).
- Calculated PEC<sub>total</sub> levels in surface water vary between  $0.13 \mu\text{g L}^{-1}$  (calculated regional background<sub>total</sub> =  $0.11 \mu\text{g L}^{-1}$ ) and  $0.15 \mu\text{g L}^{-1}$ . Please note that in this update, annual mean effluent concentrations -as provided by industry- are used for PEC<sub>local</sub> water derivation, as opposed to the original TRAR on NiCd batteries (see Section 3.1.3.2.1), in which P90 effluent concentrations were calculated based on monthly average concentrations.

Table 3.121 The local PEC<sub>water</sub> (dissolved fraction) for NiCd batteries producing plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>†</sup>	Concentration in effluent	Type of receiving water	Dilution Factor	C <sub>local</sub> <sub>water</sub>	PEC <sub>local</sub> <sub>water</sub>	Year
	kg d <sup>-1</sup>	mg l <sup>-1</sup>			μg L <sup>-1</sup>	μg L <sup>-1</sup>	
2*/2bis	0.03*	0.11	sea	1,000 <sup>(b)</sup> (ss: 1,326)*	0.04	0.15	2002
3	0.04	0.06	Tide influenced river	1000 <sup>(b)</sup> (ss: 25,951)	0.02	0.13	2002
4	0.07	0.10	river	1,000 <sup>(b)</sup> (ss: 1,850)	0.03	0.14	2002
6	No update data						
7	No update data						

\* Emission to the sea: values are only indicative; no assessment is done for the marine environment;

<sup>†</sup> Annual averages;

b) Site specific dilution factor restricted to a maximum of 1,000 (revised TGD - EC, 2003); ss: site specific dilution factor.

### Recycling of NiCd batteries

An overview of the calculated local Cd concentrations in surface water is presented in **Table 3.122**. From this table it can be concluded that for NiCd battery recyclers in Europe:

- Daily emissions to surface water vary between 0 kg Cd/d (Cd recycling plant 2; off-site treatment of waste water) and 0.0007 kg Cd/d (site 1, year 2002 value). All waste waters from site 2 are collected and treated off-site in an external waste water treatment plant. Recent -year 2004- measurements for site 1 indicate that waste water emissions are reduced by a factor two due to various measures taken to conform to ISO 14000. Please note that emission information and PEC<sub>local</sub><sub>water</sub> for site 2bis is already included in the NiCd battery producing section since waste water emissions could not be split between the NiCd-battery manufacturing and the recycling plant.
- Update information for on-site WWTP cadmium removal efficiency is not provided.
- Total Cd concentrations in on-site WWTP effluent vary between 0 mg L<sup>-1</sup> (site 2) and 0.37 mg L<sup>-1</sup> (90P site 1, year 2002, discharge to river). Please note that the 90P Cd concentration in the effluent of site 1 is reduced to 0.24 mg L<sup>-1</sup> in the year 2004.
- The dilution factor for site 1 is set to 1,000 (maximum site specific dilution factor; TGD - EC, 2003). Site specific dilution factors were derived for this site (site 1).

- Calculated PEC<sub>total</sub> levels in surface water vary between 0.11 µg L<sup>-1</sup> (site 2, calculated regional background<sub>total</sub> = 0.11 µg L<sup>-1</sup>) and 0.24 µg L<sup>-1</sup> (site 1, year 2002 data). On the basis of year 2004 information for site 1, a PEC<sub>local<sub>water</sub></sub> of 0.19 µg L<sup>-1</sup> is calculated.

Table 3.122 The local PEC<sub>water</sub> (dissolved fraction) for NiCd batteries recycling plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>†</sup>	Concentration in effluent	Type of receiving water	Dilution Factor	C <sub>local<sub>water</sub></sub>	PEC <sub>local<sub>water</sub></sub>	Year
	kg d <sup>-1</sup>	mg l <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>	
1	0.0007	0.37 (90P) 0.16 (avg)	river	1,000 <sup>(b)</sup> (ss: 2,672)	0.13	0.24	2002
1	0.0003	0.24 (90P) 0.1 (avg)	river	1,000 <sup>(b)</sup> (ss: 3,443)	0.08	0.19	2004
2	0 <sup>(a)</sup>	0	n.a.	n.a.	0	0.11	2002
2bis	See data on-site 2/2bis in Table 3.21						

<sup>†</sup> Annual averages;

n.a. Not applicable;

a) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant;

b) Site specific dilution factor restricted to a maximum of 1,000 (revised TGD - EC, 2003); ss: site specific dilution factor.

### Production of Cd containing pigments

An overview of the calculated local Cd concentrations in surface water is presented in **Table 3.123**. From this table it can be concluded that for Cd pigment producers in Europe:

- Daily emissions to surface water vary between 0.003 kg Cd/day (site A) and 0.02 kg Cd/day (site C). Please note that for site C year 2004 data have also been provided; emission to surface water is 0.01 kg/d (as opposed to 0.02 kg/day for year 2003).
- Update information for on-site WWTP cadmium removal efficiency is not provided.
- Total Cd concentrations in on-site WWTP effluent vary between 0.02 mg L<sup>-1</sup> (annual mean for the sites A and B, direct discharge to river) and 0.12 mg L<sup>-1</sup> (annual mean site C, direct discharge to river). Site C reports a 90P effluent concentration of 0.08 mg L<sup>-1</sup> for the year 2004.
- Dilution factors vary between 24 (site specific factor river, site A) and 1,000 (maximum site specific dilution factor river, site B). Site specific dilution factors were derived for all sites.
- Local dissolved Cd concentrations in water vary between 0.01 µg L<sup>-1</sup> (site B, river, maximum dilution factor of 1,000) and 0.27 µg L<sup>-1</sup> (site A, river, site specific dilution factor). Note that for site C C<sub>local<sub>water</sub></sub> for the year 2003 and 2004 are similar; i.e. 0.14 µg L<sup>-1</sup>. Different dilution factors have been calculated for both years due to the large difference in effluent discharge rates: year 2003: 156 m<sup>3</sup>/day; year 2004: 240 m<sup>3</sup>/day. Since for the year 2004 a higher effluent discharge is reported, the subsequent dilution in the receiving water is smaller.
- Calculated PEC<sub>total</sub> levels in surface water vary between 0.12 µg L<sup>-1</sup> (calculated regional background<sub>total</sub> = 0.11 µg L<sup>-1</sup>) and 0.38 µg L<sup>-1</sup>.

Table 3.123 The local  $PEC_{\text{water}}$  (dissolved fraction) for Cd pigments production plants in the EU-16. PEC's include background Cd

N°	Processing emission <sup>†</sup>	Concentration in effluent	Type of receiving water	Dilution factor	$C_{\text{local water}}$	$PEC_{\text{local water}}$	Year
	kg d <sup>-1</sup>	mg l <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>	
A	0.003	0.02	river	24	0.27	0.38	2003
B	0.01	0.02	river	1,000 <sup>(b)</sup> (ss: 3378)	0.01	0.12	2003
C	0.02	0.12	river	289	0.14	0.25	2003
C	0.01	0.08 (90P) 0.05 (avg)	river	189	0.14	0.25	2004

<sup>†</sup> Annual averages;

Avg Average

90P 90th percentile

b) Site specific dilution factor restricted to a maximum of 1,000 (revised TGD - EC, 2003); ss: site specific dilution factor.

### Production of Cd containing stabilisers

An overview of the calculated local Cd concentrations in surface water is presented in **Table 3.124**. From this table it can be concluded that for Cd stabiliser producers in Europe:

- Daily emissions to surface water vary between 0.003 kg Cd/day (site X) and 0.01 kg Cd/day (site Y).
- Update information for on-site WWTP cadmium removal efficiency is not provided.
- Total Cd concentrations in on-site WWTP effluent vary between < 0.001 mg L<sup>-1</sup> (maximum value, site Y, discharge to canal, external laboratory detection limit) and < 0.005 mg L<sup>-1</sup> (maximum value, site X, discharge to municipal STP). Taking into account a second treatment step for site X (STP: 60% removal) and extra dilution of 5.4 in a municipal STP lowers the Cd concentration from < 0.005 mg L<sup>-1</sup> to < 0.00037 mg L<sup>-1</sup>.
- Dilution factors vary between 246 (site specific factor river, site Y) and 417 (site specific dilution factor river, site X). Site specific dilution factors were derived for 2 sites.
- Local dissolved Cd concentrations in water vary between 0.0003 µg L<sup>-1</sup> (site X, river after STP, site specific dilution factor) and 0.007 µg L<sup>-1</sup> (site Y, canal, site-specific dilution factor, based on detection limit internal laboratory).
- Calculated  $PEC_{\text{total}}$  levels in surface water vary between 0.11 µg L<sup>-1</sup> (calculated regional background<sub>total</sub> = 0.11 µg L<sup>-1</sup>) and 0.12 µg L<sup>-1</sup>.

Table 3.124 The local  $PEC_{water}$  (dissolved fraction) for Cd stabilisers production plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>¶</sup>	Concentration in effluent	Type of receiving water	Dilution Factor	$C_{local_{water}}$	$PEC_{local_{water}}$	Year
	kg d <sup>-1</sup>	mg l <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>	
X	0.003	On-site WWTP: < 0.005  Municipal STP: < 0.00037 <sup>(a)</sup>	river after municipal STP	417	0.0003	0.11	2002
Y	0.01	< 0.005 <sup>(b)</sup>	canal	246	0.007	0.12	2002
Y	0.01	< 0.001 <sup>(c)</sup>	canal	246	0.001	0.11	2002

¶ Annual averages;

- a) Cd concentration in effluent from municipal STP; calculated from Cd concentration in effluent from on-site WWTP; taking into account removal at STP: 60%; extra dilution= 5.4 (ratio of effluent discharge rate STP: default 2000 m<sup>3</sup>/day and on-site WWTP discharge rate: 370 m<sup>3</sup>/day);
- b) Analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;
- c) Analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

### Use of Cd/CdO in alloys, plating and other uses

For these uses, no update information was submitted to the Rapporteur.

### Calculation of Predicted Environmental Concentration for Sewage Treatment Plants ( $PEC_{STP}$ )

The first step in the assessment of the local PEC values in the aquatic environment is the determination of the site-specific effluent concentration after on-site WWTP treatment. If not available, it is calculated from reported daily releases to surface water and local effluent discharge rate.

$$C_{local_{effluent}} = \frac{EMISSION_{local_{water}} \times 10^6}{EFFLUENT_{local_{STP}}}$$

$C_{local_{effluent}}$ : Concentration in effluent water (mg L<sup>-1</sup>)  
 $EMISSION_{local_{water}}$ : Local emission rate to water (kg/day)  
 $EFFLUENT_{local_{STP}}$ : Effluent discharge rate of local STP (l/day)

If no effluent discharge rate is submitted, a default value of 2,000 m<sup>3</sup>/day is used.

In case measured Cd concentrations in WWTP effluent are available, 90th percentile values are preferably used to account for a realistic worst case situation. If not available, annual means are used.

Additional removal of Cd needs to be considered if the industrial waste water undergoes an additional treatment in a municipal STP.

Since site specific information on type of WWTP, removal efficiency, Cd concentration in sludge and destination of sludge is not provided in the recently submitted industry questionnaires (2004), the paragraph extracted from Section 3.1.2.2.1 is still considered as valid for Cd metal/CdO producing and processing plants (see below).

“Wastewater treatment at Cd-producing and -processing plants involves filtration and precipitation. Liquid effluents from the different stages during production and processing of Cd are collected and treated with sodium carbonate at alkaline pH to precipitate Cd. Filtration aids

and flocculating agents are added. The sludge is then filtered from the solution. The filtrate is neutralised prior to discharge to the environment. At industrial non-ferrous metal producing sites and waste water treatment plants (WWTP) a cadmium removal efficiency of at least 90% is reported based on physico-chemical techniques only, to achieve total cadmium concentrations within the range 1 – 0.1 mg L<sup>-1</sup> (IPPC report, 2000). EUSES calculations give a corroborating removal rate (WS Atkins, 1998 and RPA, 2001): the Simple Treat model run with the K<sub>p</sub> value of 130,000 l/kg yields the following distribution in the waste water treatment plant: 90% in sludge and 10% in water.

However, for municipal STP in practice, the average removal efficiency can vary widely from > 80% (based on measurements of influent and effluent cadmium concentrations and the water flows; VMM, pers. com. 2002) to 60% (CUWVO, 1986; in: CBS/Milieucompendium, 2000). The latter, lower figure will be used in this report”.

*Calculation of the STP concentration for evaluation inhibition to microorganisms (EC, 2003)*

The removal of a chemical in the STP is computed from a simple mass balance. For the aeration tank, this implies that the inflow of sewage (raw or settled, depending on the equipment with a primary sedimentation tank) is balanced by the following removal processes: degradation, volatilisation and outflow of activated sludge into the secondary settler. Activated sludge flowing out of the aeration tank contains the chemical at a concentration similar to the aeration tank, which is the consequence of complete mixing. It consists of two phases: water, which is virtually equal to effluent flowing out of the solids-liquid separator (this is called the effluent of the STP), and suspended particles, which largely settle to be recycled into the aeration tank. Assuming steady state and complete mixing in all tanks (also the aeration tank), the effluent concentration approximates the really dissolved concentration in activated sludge. It is assumed that only the dissolved concentration is bioavailable, i.e. the actual concentration to which the microorganisms in activated sludge are exposed. For the risk characterisation of a substance upon micro-organisms in the STP, it can therefore be assumed that homogeneous mixing in the aeration tank occurs which implies that the dissolved concentration of a substance is equal to the effluent concentration:

$$PEC_{stp} = C_{local\_effluent}$$

C<sub>local\_effluent</sub>: Total concentration of substance in STP effluent (mg L<sup>-1</sup>)  
 PEC<sub>stp</sub>: PEC for microorganisms in the STP (mg L<sup>-1</sup>)

*Cd metal production*

An overview of PEC<sub>WWTP/STP</sub> is given in **Table 3.125**. From this table it can be concluded that the PEC<sub>WWTP</sub> for Cd metal producing plants varies between 0.7 µg L<sup>-1</sup> and 50 µg L<sup>-1</sup> (dissolved fraction).

Table 3.125 The local PEC<sub>WWTP/STP</sub> (total fraction) for Cd metal producing plants in the EU-16

N°	Production emission <sup>¶</sup>	On-site WWTP Off-site municipal STP	Removal efficiency	PEC <sub>WWTP</sub> /PEC <sub>STP</sub> (dissolved fraction)	Year
	kg d <sup>-1</sup>		%	µg L <sup>-1</sup>	
1	0.03	On-site WWTP (physico-chemical as pre-treatment, biological BDS and SRB as polishing) <sup>(a)</sup>	n.d.	3.6	2002
6	0.001	On-site WWTP	n.d.	0.7	2002
7*	0.16*	On-site WWTP	n.d.	50	2002
7*	0.10*	Site WWTP	n.d.	30	2004

a) WWTP with physico-chemical pre-treatment followed by biological process based on fully adapted, specialised and dedicated micro-organisms. Cannot be compared with STPs based on 'standard' microorganisms communities;

\* Emission to the sea;

¶ Annual averages;

n.d. No data available.

### *Cd oxide production*

Since the production of cadmium oxide is a totally dry process; discharge of waste water from the site does not take place.

Table 3.126 The local PEC<sub>WWTP/STP</sub> (total fraction) for Cd oxide producing plants in the EU-16

N°	Production emission <sup>¶</sup>	On-site WWTP Off-site municipal STP	Removal efficiency	PEC <sub>WWTP</sub> /PEC <sub>STP</sub> (dissolved fraction)	Year
	kg d <sup>-1</sup>		%	µg L <sup>-1</sup>	
12	0 <sup>(a)</sup>	n.a.	n.a.	0	2002

¶ Annual averages;

n.a. Not applicable;

a) No emission to water; thermal/dry process.

### *Production of NiCd batteries*

An overview of PEC<sub>WWTP/STP</sub> is given in **Table 3.127**. From this table it can be concluded that the PEC<sub>WWTP</sub> for NiCd battery producing plants vary between 63 µg L<sup>-1</sup> and 107 µg L<sup>-1</sup> (dissolved fraction).

Table 3.127 The local PEC<sub>WWTP/STP</sub> (total fraction) for NiCd batteries producing plants in the EU-16

N°	Production emission <sup>¶</sup>	On-site WWTP Off-site municipal STP	Removal efficiency	PEC <sub>WWTP</sub> /PEC <sub>STP</sub> (dissolved fraction)	Year
	kg d <sup>-1</sup>		%	µg L <sup>-1</sup>	
2*/2bis	0.03	On-site WWTP	n.d.	107	2002
3	0.04	On-site WWTP	n.d.	63	2002

Table 3.127 continued overleaf

Table 3.127 continued The local  $PEC_{WWTP/STP}$  (total fraction) for NiCd batteries producing plants in the EU-16

N°	Production emission <sup>¶</sup>	On-site WWTP Off-site municipal STP	Removal efficiency	$PEC_{WWTP}/PEC_{STP}$ P (dissolved fraction)	Year
	kg d <sup>-1</sup>		%	µg L <sup>-1</sup>	
4	0.07	On-site WWTP	n.d.	103	2002
6	No update data				
7	No update data				

\* Emission to the sea;

¶ Annual averages;

n.d. No data available.

### Recycling of NiCd batteries

An overview of  $PEC_{WWTP/STP}$  is given in **Table 3.128**. Update data are available for site 1 and site 2. For the latter site, the waste waters are collected and transported to be treated in an external waste water treatment plant. Therefore no site emissions occur. For site 1, the  $PEC_{WWTP}$  is 370 µg L<sup>-1</sup>(90P, year 2002). For the year 2004, a lower  $PEC_{WWTP}$  of 240 µg L<sup>-1</sup>(90P) is reported.

Table 3.128 The local  $PEC_{WWTP/STP}$  (total fraction) for NiCd batteries recycling plants in the EU-16

N°	Production emission <sup>¶</sup>	On-site WWTP Off-site municipal STP	Removal efficiency	$PEC_{WWTP}/PEC_{STP}$ (dissolved fraction)	Year
	kg d <sup>-1</sup>		%	µg L <sup>-1</sup>	
1	0.0004	On-site WWTP	n.d.	370 (90P)	2002
1	0.0002	On-site WWTP	n.d.	240 (90P)	2004
2	0 <sup>(a)</sup>	n.a.	n.a.	0	2002
2bis	See data on-site 2/2bis in Table 3.127				

¶ Annual averages;

n.d. No data available;

n.a. Not applicable;

a) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant.

### Production of Cd containing pigments

An overview of  $PEC_{WWTP/STP}$  is given in **Table 3.129**. From this table it can be concluded that the  $PEC_{WWTP}$  for Cd pigments producing plants vary between 19 µg L<sup>-1</sup> and 121 µg L<sup>-1</sup> (dissolved fraction).

Table 3.129 The local PEC<sub>WWTP/STP</sub> (total fraction) for Cd pigments producing plants in the EU-16

N°	Processing emission <sup>¶</sup>	On-site WWTP Off-site municipal STP	Removal efficiency	PEC <sub>WWTP</sub> /PEC <sub>STP</sub> (dissolved fraction)	Year
	kg d <sup>-1</sup>		%	µg L <sup>-1</sup>	
A	0.003	On-site WWTP	n.d.	19	2003
B	0.01	On-site WWTP	n.d.	19	2003
C	0.02	On-site WWTP	n.d.	121	2003
C	0.01	On-site WWTP	n.d.	80	2004

¶ Annual averages;  
n.d. No data available.

### *Production of Cd containing stabilisers*

An overview of PEC<sub>WWTP/STP</sub> is given in **Table 3.130**. From this table it can be concluded that the PEC<sub>WWTP</sub> for Cd stabiliser producing plants vary between 5 µg L<sup>-1</sup> and 19 µg L<sup>-1</sup> (dissolved fraction). The PEC<sub>STP</sub> for stabiliser plant X –discharging to a municipal STP- is 0.4 µg L<sup>-1</sup>.

Table 3.130 The local PEC<sub>WWTP/STP</sub> (total fraction) for Cd stabiliser producing plants in the EU-16

N°	Production emission <sup>¶</sup>	On-site WWTP Off-site municipal STP	Removal efficiency	PEC <sub>WWTP</sub> /PEC <sub>STP</sub> (dissolved fraction)	Year
	kg d <sup>-1</sup>		%	µg L <sup>-1</sup>	
X	0.003	On-site WWTP	n.d.	5	2002
X		Off-site municipal STP	60	0.4 <sup>(a)</sup>	2002
Y	0.01	On-site WWTP	n.d.	< 5 <sup>(b)</sup>	2002
	1.01	On-site WWTP	n.d.	< 1 <sup>(c)</sup>	2002

¶ Annual averages;  
n.d. No data available;  
a) PEC<sub>STP</sub> calculated taking into account 60% removal at STP and extra dilution at municipal STP of 5.4 (ratio of effluent discharge rate STP: default 2000 m<sup>3</sup>/day and on-site WWTP discharge rate: 370 m<sup>3</sup>/day);  
b) Effluent analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;  
c) Effluent analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

### *Use of Cd/CdO in alloys, plating and other uses*

For these uses, no update information was submitted to the Rapporteur.

### Calculation of PEC<sub>sediment</sub>

The PEC<sub>local\_sediment</sub> is calculated according to the formula presented below (see Section 3.1.3.1.2):

$$PEC_{local\_sediment} = PEC_{regional\_sediment} + K_p C_{local\_water} \cdot 10^{-3}$$

in which the K<sub>p</sub> (L kg<sup>-1</sup><sub>dw</sub>) equals the solid- water partition coefficient of suspended matter (K<sub>p</sub> = 130,000 l/kg).

The measured PEC regional is taken as an average of 90<sup>th</sup> percentiles of surveys: 2.66 mg Cd/kg<sub>dw</sub> (no changes made; **Table 3.189**, value not corrected for bioavailability).

The local  $PEC_{\text{sediment}}$  are readily calculated from the data in **Table 3.119-Table 3.124** and the above-mentioned equation and presented in **Table 3.131-Table 3.136**. The  $C_{\text{local}}_{\text{sediment}}$  ( $K_p C_{\text{local}}_{\text{water}} \cdot 10^{-3}$ ) is included to illustrate the contribution of the local discharge onto the sediment PEC.

### *Cd metal production*

- Local Cd concentrations in sediment vary between  $0.03 \text{ mg kg}^{-1} \text{ dw}$  (site 6, tide influenced river, maximum dilution 1,000) and  $68.8 \text{ mg kg}^{-1} \text{ dw}$  (site 1, ditch). Elevated Cd concentrations in surface water lead to high concentrations in sediment due to the methodology used to calculate the  $C_{\text{sediment}}$  (see partitioning on the basis of  $C_{\text{surface water}}$ , see subsection “Calculation on  $PEC_{\text{sediment}}$ ” under Section 3.1.3.3).
- Calculated  $PEC_{\text{total}}$  levels in sediment vary between  $2.7 \text{ mg kg}^{-1} \text{ dw}$  (measured regional background<sub>total</sub> =  $2.66 \text{ mg kg}^{-1} \text{ dw}$ ) and  $71.5 \text{ mg kg}^{-1} \text{ dw}$ .

Table 3.131 The local  $PEC_{\text{sediment}}$  (without correction for bioavailability) for Cd metal producing plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>¶</sup>	$C_{\text{local}}_{\text{water}}$	$C_{\text{local}}_{\text{sediment}}$	$PEC_{\text{local}}_{\text{sediment}}$	Year
	$\text{kg d}^{-1}$	$\mu\text{g L}^{-1}$	$\text{mg kg}^{-1} \text{ dw}$	$\text{mg kg}^{-1} \text{ dw}$	
1	0.03	0.53	68.8	71.5	2002
6 <sup>(b)</sup>	0.001	0.0002	0.03	2.7	2002
7 <sup>*(a)</sup>	0.16	0.17*	21.9	24.5	2002
7 <sup>*(a)</sup>	0.10	0.10*	13.6	16.2	2004

a) Default dilution factor: 10 (freshwater), 100 (sea water);

b) Site specific dilution factor restricted to a maximum of 1,000 (revised TGD - EC, 2003);

\* Emission to the sea: values are only indicative; no assessment is done for the marine environment;

¶ Annual averages.

### *Cd oxide production*

- Since no emissions to water take place at the CdO producing plant, the  $C_{\text{local}}_{\text{sediment}}$  and  $PEC_{\text{local}}_{\text{sediment}}$  is  $0 \text{ mg kg}^{-1} \text{ dw}$  and  $2.7 \text{ mg kg}^{-1} \text{ dw}$  respectively.

Table 3.132 Local  $PEC_{\text{sediment}}$  (without correction for bioavailability) for Cd oxide producing plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>¶</sup>	$C_{\text{local}}_{\text{water}}$	$C_{\text{local}}_{\text{sediment}}$	$PEC_{\text{local}}_{\text{sediment}}$	Year
	$\text{kg d}^{-1}$	$\mu\text{g L}^{-1}$	$\text{mg kg}^{-1} \text{ dw}$	$\text{mg kg}^{-1} \text{ dw}$	
12	0 <sup>(a)</sup>	0	0	2.7	2002

¶ Annual averages;

a) No emission to water; thermal/dry process.

### *Production of NiCd batteries*

- Local Cd concentrations in sediment vary between  $2.8 \text{ mg kg}^{-1} \text{ dw}$  (site 3, tide influenced river, maximum dilution 1,000) and  $4.7 \text{ mg kg}^{-1} \text{ dw}$  (site 2, sea, maximum dilution 1,000).
- Calculated  $PEC_{\text{total}}$  levels in sediment vary between  $5.5 \text{ mg kg}^{-1} \text{ dw}$  (measured regional background<sub>total</sub> =  $2.66 \text{ mg kg}^{-1} \text{ dw}$ ) and  $7.4 \text{ mg kg}^{-1} \text{ dw}$ . Please note that site 2 is involved in

both production and recycling of NiCd batteries. No split in aquatic emissions could be done. Please note that in this update document, annual mean effluent concentrations, as provided by industry, are used for PEC<sub>local</sub> water derivation, and consequently also the derivation of PEC<sub>local</sub> sediment, as opposed to the original TRAR on NiCd batteries (see Section 3.1.3.2.1), in which P90 effluent concentrations were calculated based on monthly average concentrations.

Table 3.133 The local PEC<sub>sediment</sub> (without bioavailability correction) for NiCd batteries producing plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>†</sup>	Clocal <sub>water</sub>	Clocal <sub>sediment</sub>	PEC <sub>local</sub> <sub>sediment</sub>	Year
	kg d <sup>-1</sup>	µg L <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>	
2 <sup>*(b)</sup> /2bis	0.03*	0.04	4.7	7.4	2002
3 <sup>(b)</sup>	0.04	0.02	2.8	5.5	2002
4	0.07	0.03	4.5	7.2	2002
6	No update data				
7	No update data				

\* Emission to the sea: values are only indicative; no assessment is done for the marine environment;

† Annual averages;

b) Site specific dilution factor restricted to a maximum of 1,000 (revised TGD - EC, 2003).

### Recycling of NiCd batteries

- Local Cd concentrations in sediment vary between 0 mg kg<sup>-1</sup> dw (site 2, no direct, local on-site emissions to water) and 16.3 mg kg<sup>-1</sup> dw (site 1, river, maximum dilution 1,000, year 2002 data).
- Calculated PEC<sub>total</sub> levels in sediment vary between 2.66 mg kg<sup>-1</sup> dw (measured regional background<sub>total</sub> = 2.66 mg kg<sup>-1</sup> dw) and 19.0 mg kg<sup>-1</sup> dw.

Table 3.134 The local PEC<sub>sediment</sub> (without correction for bioavailability) for NiCd batteries recycling plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>†</sup>	Clocal <sub>water</sub>	Clocal <sub>sediment</sub>	PEC <sub>local</sub> <sub>sediment</sub>	Year
	kg d <sup>-1</sup>	µg L <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>	
1	0.0007	0.13	16.3	19.0	2002
1	0.0003	0.08	10.6	13.2	2004
2 <sup>(a)</sup>	0	0	0	2.7	2002
2bis	See data on-site 2/2bis in Table 3.133				

† Annual averages;

a) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant.

### Production of Cd containing pigments

- Local Cd concentrations in sediment vary between 0.8 mg kg<sup>-1</sup> dw (site B, river, max. dilution 1,000) and 34.7 mg kg<sup>-1</sup> dw (site A, river). Please note that update emission information (90P) submitted for site C for the year 2004 gives similar results for Clocal<sub>sediment</sub>: 18.7 mg kg<sup>-1</sup> dw as opposed to 18.4 mg kg<sup>-1</sup> dw.

- Calculated PEC<sub>total</sub> levels in sediment vary between 3.5 mg kg<sup>-1</sup> dw (measured regional background<sub>total</sub> = 2.66 mg kg<sup>-1</sup> dw) and 37.4 mg kg<sup>-1</sup> dw.

Table 3.135 The local PEC<sub>sediment</sub> (without correction for bioavailability) for Cd pigments production plants in the EU-16. PEC's include background Cd

N°	Processing emission <sup>¶</sup>	Clocal <sub>water</sub>	Clocal <sub>sediment</sub>	PEClocal <sub>sediment</sub>	Year
	kg d <sup>-1</sup>	µg L <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>	
A	0.003	0.27	34.7	37.4	2003
B <sup>(b)</sup>	0.01	0.01	0.8	3.5	2003
C	0.02	0.14	18.4	21.0	2003
C	0.01	0.14	18.7	21.3	2004

¶ Annual averages;

b) Site specific dilution factor restricted to a maximum of 1,000 (revised TGD - EC, 2003).

#### *Production of Cd containing stabilisers*

- Local Cd concentrations in sediment vary between 0.04 mg kg<sup>-1</sup> dw (site X, river after STP, site specific dilution factor) and 0.9 mg kg<sup>-1</sup> dw (site Y, canal).
- Calculated PEC<sub>total</sub> levels in sediment vary between 2.7 mg kg<sup>-1</sup> dw (measured regional background<sub>total</sub> = 2.66 mg kg<sup>-1</sup> dw) and 3.6 mg kg<sup>-1</sup> dw.

Table 3.136 The local PEC<sub>sediment</sub> (without correction for bioavailability) for Cd stabilisers production plants in the EU-16. PEC's include background Cd

N°	Production emission <sup>¶</sup>	Clocal <sub>water</sub>	Clocal <sub>sediment</sub>	PEClocal <sub>sediment</sub>	Year
	kg d <sup>-1</sup>	µg L <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>	
X <sup>(a)</sup>	0.003	0.0003	0.04	2.7	2002
Y	0.01	0.007 <sup>(b)</sup>	0.9	3.6	2002
Y	0.01	0.001 <sup>(c)</sup>	0.2	2.8	2002

¶ Annual averages;

a) Cd concentration in effluent from municipal STP; calculated from Cd concentration in effluent from on-site WWTP; taking into account removal at STP: 60%; extra dilution: 2000 m<sup>3</sup>/day/370 m<sup>3</sup>/day = 5.4;

b) Effluent analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;

c) Effluent analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

#### *Use of Cd/CdO in alloys, plating and other uses*

For these uses, no update information was submitted to the Rapporteur.

#### Summary of calculated PECs for surface water

In **Table 3.137** a summary is given of the calculated Clocal and PECs in WWTP/STP, surface water and sediment for Cd metal and CdO producing and processing sectors. A detailed description of the results for each sector is provided in subsections “Surface water”, “Calculation of predicted environmental concentration for sewage treatment plants (PEC<sub>stp</sub>)” and “Calculation on PEC<sub>sediment</sub>” under Section 3.1.3.3 of this document.

Table 3.137 Summary of calculated PECs in surface water for Cd/CdO producing/processing sectors. Clocalsediment and PEClocalsediment are not corrected for bioavailability

N°	PEC <sub>WWTP</sub> /PEC <sub>STP</sub> (total fraction)	Clocal <sub>water</sub>	PEClocal <sub>water</sub>	Clocal <sub>sediment</sub>	PEClocal <sub>sediment</sub>
	µg L <sup>-1</sup>	µg L <sup>-1</sup>	µg L <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>
<b>Cd metal production</b>					
1	3.6 (c)	0.53	0.64	68.8	71.5
6	0.7	0.0002	0.11	0.03	2.7
7*	50	0.17*	0.28*	21.9	24.5
7* (year 2004 data)	30	0.10*	0.21*	13.6	16.2
<b>Cd oxide production</b>					
12 <sup>(a)</sup>	0	0	0.11	0	2.7
<b>NiCd battery production</b>					
2*/2bis	107	0.04	0.15	4.7	7.4
3	63	0.02	0.13	2.8	5.5
4	103	0.03	0.14	4.5	7.2
6	No update data	No update data	No update data	No update data	No update data
7	No update data	No update data	No update data	No update data	No update data
<b>NiCd battery recycling</b>					
1	370	0.13	0.24	16.3	19.0
1 (year 2004 data)	240	0.08	0.19	10.6	13.2
2 <sup>(b)</sup>	0	0	0.11	0	2.7
2bis	See data on-site 2/2bis under NiCd battery production				
<b>Cd pigments production</b>					
A	19	0.27	0.38	34.7	37.4
B	19	0.01	0.12	0.8	3.5
C	121	0.14	0.25	18.4	21.0
C (year 2004 data, 90P)	80	0.14	0.25	18.7	21.3
<b>Cd stabiliser production</b>					
X WWTP	5				
X STP	0.4	0.0003	0.11	0.04	2.7
Y	< 5 <sup>(d)</sup>	0.007	0.12	0.9	3.6
Y	< 1 <sup>(e)</sup>	0.001	0.11	0.18	2.8

\* Emission to the sea: values are only indicative; no assessment is done for the marine environment;

a) No emission to water; thermal/dry process;

b) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant;

c) Effluent concentration from biological based wastewater purification system contains fully adapted, specialised and dedicated micro-organisms. Cannot be compared with STPs based on 'standard' micro-organisms communities;

d) Effluent analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;

e) Effluent analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

Measured data in the aquatic compartment*Surface water*

Table 3.138 Summary of calculated versus measured levels in surface water for Cd/CdO producing/processing sectors

N°	Emission amount	PEC <sub>local water</sub> Calculated Dissolved Cd	Measured <sup>(1)</sup> (estimated dissolved Cd unless stated differently)	Remarks	Year
	kg d <sup>-1</sup>	µg L <sup>-1</sup>	µg L <sup>-1</sup>		
<b>Cd metal production</b>					
1	0.03	0.64	1.0	25 m downstream from discharge point; spot sampling: 3 times/week, analytical method NEN 6426, Ditch is influenced by historical contamination, pH: 7.7-7.9	2002-2003
6	0.001	0.11	n.d.		
7*	0.16*	0.28	0.1-1.65 µg L <sup>-1</sup> (total Cd)  0.08-1.3 µg L <sup>-1</sup> (estimated dissolved fraction in seawater)	different sampling points nearest to the outlets of the WWTPs, year 2002, concentration of suspended matter in seawater: 0.5-4 mg L <sup>-1</sup> (avg 2 mg L <sup>-1</sup> ), dissolved concentration is estimated to be 79% of total concentration (K <sub>p</sub> =130,000 l/kg, C <sub>susp</sub> =2 mg L <sup>-1</sup> ) (external laboratory data, NIVA).	2002
7*	0.10*	0.21	0.16-0.36 µg L <sup>-1</sup> (total Cd)  0.13-0.28 µg L <sup>-1</sup> (estimated dissolved fraction in seawater)	different sampling points nearest to the outlets of the WWTPs, year 2004, concentration of suspended matter in seawater: 0.5-4 mg L <sup>-1</sup> (avg 2 mg L <sup>-1</sup> ), dissolved concentration is estimated to be 79% of total concentration (K <sub>p</sub> =130,000 l/kg, C <sub>susp</sub> =2 mg L <sup>-1</sup> ) (external laboratory data, NIVA).	2004
<b>Cd oxide production</b>					
12 <sup>(a)</sup>	0	0.11	n.d.		2002
<b>NiCd battery production</b>					
2*/2bis	0.03*	0.15	n.d.		2002
3	0.04	0.13	n.d.		2002
4	0.07	0.14	n.d.		2002
6	No update data				
7	No update data				

Table 3.138 continued overleaf

Table 3.138 continued Summary of calculated versus measured levels in surface water for Cd/CdO producing/processing sectors

N°	Emission amount	PEC <sub>local water</sub> Calculated Dissolved Cd	Measured <sup>(1)</sup> (estimated dissolved Cd unless stated differently)	Remarks	Year
	kg d <sup>-1</sup>	µg L <sup>-1</sup>	µg L <sup>-1</sup>		
<b>NiCd battery recycling</b>					
1	0.0007	0.24	19.8	200 m downstream from discharge point, year 2002,  River is influenced by contamination; i.e. infiltration and run-off waters from old metallurgical slag heaps.  Upstream conc: 9.9 µg dissolved Cd/l; 200 m upstream from discharge point.	2002
1	0.0003	0.19	10.6	200 m downstream from discharge point, year 2004,  River is influenced by contamination; i.e. infiltration and run-off waters from old metallurgical slag heaps.  Upstream conc: 13.9 µg dissolved Cd/l; 200 m upstream from discharge point.	2004
2 <sup>(b)</sup>	0	0.11	n.d.		2002
2bis	See data on-site 2/2bis under NiCd battery production				
<b>Cd pigments production</b>					
A	0.003	0.38	n.d.		2003
B	0.01	0.12	n.d.		2003
C	0.02	0.25	n.d.		2003
<b>Cd stabiliser production</b>					
X WWTP	0.003				
X STP		0.11	n.d.		2002
Y	0.01	0.12 <sup>(b)</sup>	< 1.65 µg L <sup>-1</sup>	upstream and downstream value, < 5 µg total Cd/l = dl, ICP, pH: 7.9; hardness: 120-123 mg CaCO <sub>3</sub> /l; DOC: 7-11 mg L <sup>-1</sup>	2002
Y	0.01	0.11 <sup>(c)</sup>	< 1.65 µg L <sup>-1</sup>	upstream and downstream value, < 5 µg total Cd/l = dl, ICP, pH: 7.9; hardness: 120-123 mg CaCO <sub>3</sub> /l; DOC: 7-11 mg L <sup>-1</sup>	2002

\* Emission to the sea: values are only indicative; no assessment is done for the marine environment n.d.: no data available; dl: detection limit

1) If total concentrations are measured, dissolved concentrations are estimated to be 33% of total Cd concentration (K<sub>p</sub> = 130 103 L kg<sup>-1</sup>, C<sub>susp</sub> = 15 mg L<sup>-1</sup>);

a) No emission to water; thermal/dry process;

b) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant;

b) Effluent analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;

c) Effluent analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

*Sediment*

Table 3.139 Summary of calculated versus measured levels in sediment for Cd/CdO producing/processing sectors (without correction for bioavailability)

N°	Emission amount	PEC <sub>local</sub> <sub>sediment</sub> calculated	Measured	Remarks	Year
	kg d <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>		
<b>Cd metal production</b>					
1	0.03	71.5	upstream: 5 mg kg <sup>-1</sup> dw At discharge point: 1.6 mg kg <sup>-1</sup> dw	(Recent) dredging occurred downstream of the discharge point. Ditch is influenced by historical contamination. TOC: < 1% AVS: U: 23.7 µmol/g dw D: 2.6 µmol/g dw (sampling: 25.11.2002, 100m upstream and downstream discharge point) (EURAS, 2003; external laboratory)	2002-2003
6	0.001	2.7	0.64 mg kg <sup>-1</sup> dw (300 m upstream) 1.14 mg kg <sup>-1</sup> dw (1,800 m downstream)	n.d.	2002
7*	0.16*	24.5	At discharge point: 1.1 mg kg <sup>-1</sup> dw; further in the open sea: 2.1-3.2 mg kg <sup>-1</sup> dw	jarosite discharge prior to 1986; since deposition in mountain caverns, significant decrease in top 1-cm sediment concentrations (external laboratory data, NIVA).	1996 (measured data) 2002 (calculated PEC)
7*	0.10*	16.2	At discharge point: 1.1 mg kg <sup>-1</sup> dw; further in the open sea: 2.1-3.2 mg kg <sup>-1</sup> dw	jarosite discharge prior to 1986; since deposition in mountain caverns, significant decrease in top 1-cm sediment concentrations (external laboratory data, NIVA).	1996 (measured data) 2002 (calculated PEC)
<b>Cd oxide production</b>					
12 <sup>(a)</sup>	0	2.7	n.d.	n.d.	2002

Table 3.39 continued overleaf

Table 3.139 continued Summary of calculated versus measured levels in sediment for Cd/CdO producing/processing sectors (without correction for bioavailability)

N°	Emission amount	PEClocal <sub>sediment</sub> calculated	Measured	Remarks	Year
	kg d <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>		
<b>NiCd battery production</b>					
2*/2bis	0.03*	7.4	n.d.	The sediments of the harbour are heavily contaminated by industrial activity in the vicinity of the harbour. The total amount of metals present in the sediments is estimated to 1,000 tonnes. No relationship between the present metal emissions and the metal content of the harbour sediments can be established.	2002
3	0.04	5.5	n.d.	n.d.	2002
4	0.07	7.2	4.6	3 km downstream from discharge point, year 2001 data  3.3 mg kg <sup>-1</sup> dw; 100 m upstream from discharge point; year 2001 data.	2002
6	No update data				
7	No update data				
<b>NiCd battery recycling</b>					
1	0.0007	19.0	133	200 m downstream from discharge point, year 2002 River is influenced by contamination; i.e. infiltration and run-off waters from old metallurgical slag heaps.  Upstream conc: 55 mg kg <sup>-1</sup> dw; 200 m upstream from discharge point.	2002
1	0.0003	13.2	224	200 m downstream from discharge point, year 2002 River is influenced by contamination; i.e. infiltration and run-off waters from old metallurgical slag heaps.  Upstream conc: 88 mg kg <sup>-1</sup> dw; 200 m upstream from discharge point.	2004
2 <sup>(b)</sup>	0	2.7	n.d.	n.d.	2002
2bis	See data on-site 2 under NiCd battery production				

Table 3.39 continued overleaf

Table 3.139 continued Summary of calculated versus measured levels in sediment for Cd/CdO producing/processing sectors (without correction for bioavailability)

N°	Emission amount	PEC <sub>local</sub> <sub>sediment</sub> calculated	Measured	Remarks	Year
	kg d <sup>-1</sup>	mg kg <sup>-1</sup> <sub>dw</sub>	mg kg <sup>-1</sup> <sub>dw</sub>		
Cd pigments production					
A	0.003	37.4	n.d.	n.d.	2003
B	0.01	3.5	n.d.	n.d.	2003
C	0.02	21.0	n.d.	n.d.	2003
Cd stabiliser production					
X WWTP	0.003				
X STP		2.7	n.d.	n.d.	2002
Y	0.01	3.6 <sup>(c)</sup>	n.d.	n.d.	2002
Y	0.01	2.8 <sup>(d)</sup>	n.d.	n.d.	2002

\* Emission to the sea: values are only indicative; no assessment is done for the marine environment;

¶ Annual averages; n.d.: no data available; TOC: total organic carbon; AVS: acid volatile sulfides; U: upstream; D: downstream;

a) No emission to water; thermal/dry process;

b) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant;

c) Effluent analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;

d) Effluent analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

#### Comparison of PECs with measured data

Measured Cd concentrations in surface water, presented in **Table 3.138**, are available for Cd metal production-site 1 and 7, Cd recycling site 1 and Cd stabiliser production-site Y.

- The dissolved Cd concentration of 1 µg L<sup>-1</sup> measured in the ditch downstream from the discharge point of Cd metal production-site 1 is in the same range as the predicted concentration of 0.64 µg L<sup>-1</sup>. The measured data should however be treated with caution due to the 'large influence of historic contamination in the ditch surrounding this site' (company statement).
- Measured Cd concentrations in the receiving marine environment are available for Cd metal production-site 7. Measurements are performed at several locations: nearby the discharge point and some kilometres away from the emissions point in the open sea. Total Cd concentrations varying between 0.1 µg L<sup>-1</sup> and 1.65 µg L<sup>-1</sup> are reported. The concentration of suspended solids in the seawater is on average 2 mg L<sup>-1</sup> (0.5-4 mg L<sup>-1</sup>). On the basis of this information, dissolved concentrations can be estimated from total concentrations as 79% of total Cd concentration ( $K_p = 130 \cdot 10^3 \text{ L kg}^{-1}$ ,  $C_{\text{susp}} = 2 \text{ mg L}^{-1}$ ). Dissolved Cd concentrations varying between 0.08 µg L<sup>-1</sup> and 1.3 µg L<sup>-1</sup> are calculated. The maximum measured dissolved Cd concentration of 1.3 µg L<sup>-1</sup> is situated a factor of five above the PEC<sub>local</sub><sub>water</sub> derived for this site of 0.28 µg L<sup>-1</sup> (dissolved fraction).
- Cd recycler site 1 reports measured total Cd concentrations in the receiving river 200 m downstream from the discharge point of 60 µg total Cd/l (i.e. 19.8 µg dissolved Cd/l) (year 2002). The site reports that these data are influenced by historical contamination; i.e. infiltration and run-off waters from old metallurgical slag heaps in front of the plant. Therefore they should be treated with caution. The measured dissolved Cd concentration in the river of 19.8 µg L<sup>-1</sup> is eighty fold the calculated PEC<sub>water</sub> (0.24 µg L<sup>-1</sup>). Data for the year 2004 indicate that although there is a decline in Cd concentrations in the receiving river i.e.

10.6  $\mu\text{g L}^{-1}$ , the measured value is still a factor of 60 above the modelled PEC of 0.19  $\mu\text{g L}^{-1}$ . It should be noted however that the upstream measurement for this site is 13.9  $\mu\text{g Cd/l}$  which is in the same order of magnitude as the downstream measurement.

- Cd stabiliser site Y reports measured total Cd concentrations in the receiving river of  $< 5 \mu\text{g L}^{-1}$  ( $5 \mu\text{g L}^{-1}$  being the detection limit). This value corresponds to  $< 1.65 \mu\text{g}$  dissolved Cd/l. The calculated  $\text{PEC}_{\text{local,water}}$  of 0.12  $\mu\text{g L}^{-1}$  is situated a factor of 14 below the measured Cd concentration of 1.65  $\mu\text{g L}^{-1}$ . It should be noted however that the measured value is a maximum.

In conclusion, it can be noted that only limited measured information is (made) available.

Moreover, submitted measured data are stated by the companies to be (heavily) influenced by other sources (incl. historic contamination e.g. by infiltration from deposited waste).

In general measured Cd concentrations in surface water are situated above the modelled local values for the receiving surface water.

It should be noticed that in general the analytical methods (detection limit  $> 0.10 \mu\text{g L}^{-1}$ ) used are not adequate to accurately and reliably measure (very low) concentrations in the environment.

The measured (estimated dissolved) concentrations, including ‘background’ concentrations, range from 0.08 to 1.3  $\mu\text{g L}^{-1}$  for cadmium production-sites. The range of calculated local  $C_{\text{water}}$  and PEC values in water is respectively 0.00026 – 0.53  $\mu\text{g/l}$  and 0.11-0.64  $\mu\text{g L}^{-1}$  (the latter figures including the calculated 0.11  $\mu\text{g L}^{-1}$  regional background level). Comparison of these local measured data for sites emitting to surface water with the calculated local  $\text{PEC}_{\text{water}}$  values of the corresponding sites shows good corroboration (the difference is maximum a factor 3.5 lower to factor 4.6 higher).

The measured data for NiCd battery recycler (site 1; for 2002 and 2004) 19.8 - 10.6  $\mu\text{g L}^{-1}$  are two orders of magnitude higher as the corresponding calculated  $C_{\text{local,water}}$  and PEC values for this site are 0.13 - 0.08  $\mu\text{g L}^{-1}$  and 0.24 – 0.19  $\mu\text{g L}^{-1}$  (factors up to 152 - 132 difference).

For other sectors/plants no comparison is possible due to lack of measured data.

Both calculated and measured values will be taken forward to the risk characterisation bearing however in mind the limitations of these values.

Measured Cd concentrations in sediment (without correction for bioavailability), presented in **Table 3.139**, are available for Cd metal production-site 1, 6 and 7, NiCd battery manufacturing site 4 and Cd recycling site 1.

- For Cd metal production-site 1, the measured Cd concentration in sediment sampled upstream and at the discharge point is 5  $\text{mg kg}^{-1}$  dw and 1.6  $\text{mg kg}^{-1}$  dw respectively. Measured Cd concentrations are situated a factor of 14-45 below the  $\text{PEC}_{\text{local, sediment}}$  of 71.5  $\text{mg kg}^{-1}$  dw. This site also submitted information on AVS and organic carbon content of the sediments. Using these data, the exposure assessment could further be refined. As the methodology to perform the bioavailability correction for Cd is still under development, the correction will be performed in a next phase of the update RA process.
- Cd metal production-site 6 provides recent upstream and downstream measurements in sediments of 0.64  $\text{mg Cd/kg dw}$  and 1.14  $\text{mg Cd/kg dw}$  respectively (year 2002). As for site 1, the measured Cd concentrations are 2.4-4.2 times below the calculated  $\text{PEC}_{\text{local, sediment}}$  of 2.7  $\text{mg kg}^{-1}$  dw.

- For Cd metal production-site 7, discharging to a marine environment, Cd concentrations in sediment are reported near the discharge point for the year 1996:  $1.1 \text{ mg kg}^{-1} \text{ dw}$  and in the open sea:  $2.1\text{-}3.2 \text{ mg kg}^{-1} \text{ dw}$ . The same observation is made as for the other Cd metal producing plants. Measured Cd concentrations are situated 7.7-22.3 times below the modelled sediment concentration i.e.  $24.5 \text{ mg kg}^{-1} \text{ dw}$ .
- NiCd battery manufacturing site 4 provides recent upstream and downstream measurements in sediments of  $3.3 \text{ mg kg}^{-1} \text{ dw}$  and  $4.6 \text{ mg kg}^{-1} \text{ dw}$  respectively (year 2001). The measured Cd concentrations are situated below, but in the same order of magnitude as the calculated PEC<sub>local</sub> sediment of  $7.2 \text{ mg kg}^{-1} \text{ dw}$ . Please note that the downstream sample is situated 3 km from the discharge point.
- Cd recycling site 1 provides recent upstream and downstream measurements in sediments of  $55 \text{ mg kg}^{-1} \text{ dw}$  and  $133 \text{ mg kg}^{-1} \text{ dw}$  respectively (year 2002). The measured Cd concentrations are 3-7 fold the calculated PEC<sub>local</sub> sediment of  $19.0 \text{ mg kg}^{-1} \text{ dw}$ . Please note that the measured data are influenced by historical contamination (infiltration and run-off waters from old metallurgical slag heaps). The sediment data for the year 2004 show an increase in Cd concentrations: upstream concentration:  $88 \text{ mg kg}^{-1} \text{ dw}$ ; downstream value  $224 \text{ mg kg}^{-1} \text{ dw}$ . These data are 7-17 fold the modelled value of  $13.2 \text{ mg kg}^{-1} \text{ dw}$ .

In conclusion, it is noted that only limited measured information is (made) available.

Moreover, it is stated by the companies that submitted measured data are (heavily) influenced by other sources (including historic contamination e.g. by infiltration from deposited waste).

In general, measured values are situated below the corresponding modelled PEC<sub>local</sub><sub>sediment</sub>.

This may be due to the fact that the calculated PEC<sub>sediment</sub>, derived using the partitioning methodology and  $K_{p\text{suspended solids}}$ , overestimates the real situation.

The measured concentrations in sediment (in the range  $1.1$  to  $5 \text{ mg kg}^{-1} \text{ dw}$ ) are for the Cd metal producers a factor 4.2 to 22.3 lower than the calculated values (range  $2.7$  to  $71.5 \text{ mg kg}^{-1} \text{ dw}$ ). C<sub>local</sub> sediment varies between 0.03 and  $68.8 \text{ mg kg}^{-1} \text{ dw}$ . Only for one site (site 1): more detailed information on AVS and SEM concentrations on Cd, Cu and Pb are available.

For NiCd battery producers no comparison is possible due to lack of representative measured data (i.e. data for site 4 are not considered valid/useful given the distance from the discharge point).

For the NiCd recycler's site 1 measured data are a factor 7 to 17 higher than the calculated values. C<sub>local</sub><sub>sediment</sub> is  $10.6$  to  $16.3 \text{ mg kg}^{-1} \text{ dw}$ . Measurements only relate to Cd concentration in sediment. No data are available on AVS and SEMs on other metals, neither the sampling date(s).

For other sectors/plants no comparison is possible due to lack of measured data.

Both calculated and measured data will be taken forward to the risk characterisation bearing however in mind the limitations of these values.

### 3.1.3.3.2 Terrestrial compartment

#### Calculated PEC for soil

Calculations are made following the equations given in Section 3.1.3.1.4.

The local  $PEC_{soil}$  are readily calculated from the release data and the above-mentioned equation and are presented in **Table 3.140-Table 3.145**.

### *Cd metal production*

- Daily stack emissions to air vary between 0.03 kg Cd/d (site 6) and 0.15 kg Cd/d (site 7).
- Calculated annual average deposition rates vary between  $2.74 \cdot 10^{-4}$  mg/m<sup>2</sup>/day and  $1.48 \cdot 10^{-3}$  mg/m<sup>2</sup>/day
- The main exposure route is aerial deposition for Cd metal producers; sludge from the on-site waste water treatment system is not applied to agricultural land but is recycled or land-filled (industry information).
- Calculated added local concentrations in soil vary between 0.003 mg kg<sup>-1</sup> ww (site 6) and 0.02 mg kg<sup>-1</sup> ww (site 7).
- Calculated  $PEC_{local}$  in soil vary between 0.36 mg kg<sup>-1</sup> ww (calculated regional background soil = 0.36 mg kg<sup>-1</sup> ww) and 0.38 mg kg<sup>-1</sup> ww (based on calculated aerial deposition rates). For site 7, the selected measured annual average aerial deposition rate of 0.008 mg/m<sup>2</sup>/day was used for  $PEC_{soil}$  derivation. The  $PEC_{soil}$  level, on the basis of measured deposition rates, for this site is 0.45 mg kg<sup>-1</sup> ww. Please note that using measured deposition rates for  $PEC_{local,soil}$  derivation addresses a reasonable worst case situation. Measured deposition data are influenced by blown up dust and other undefined inputs.

Table 3.140 Calculated total local  $PEC_{soil}$  for Cd-metal producing plants in EU-16.  $PEC$ 's include background Cd

N°	Emission to air <sup>†1</sup>	Number of emission days	$C_{local,soil}$	$PEC_{local,soil}$ (modelled aerial deposition rates)	$PEC_{local,soil}$ (measured aerial deposition rates)	Year
	kg d <sup>-1</sup>		mg kg <sub>ww</sub> <sup>-1</sup>	mg kg <sub>ww</sub> <sup>-1</sup>		
1	0.08 <sup>(a)(b)</sup>	365	0.01	0.37	-	2002
6	0.03 <sup>(a)(c)</sup>	365	0.003	0.36	-	2002
7	0.15 <sup>(a)(d)</sup>	365	0.02	0.38	0.45	2002

<sup>†1</sup> Annual averages;

a) Cd emission from whole plant (including Zn and/or Pb production);

b) Total emissions: stack + diffuse emissions; diffuse emissions: 60-70% of total; stack emissions: 30-40% of total emissions;

c) All emissions from point sources and fugitive emissions from roof openings for the whole zinc production process. Emissions from cadmium production are difficult to separate;

d) Total emissions from the zinc smelter; approximately 90 emission points to air. Approximately 90% of the emission comes from 20% of the emission points which all are equipped with abatement systems (demisters or scrubbers).

### *Cd oxide production*

- Daily stack emission to air is 0.026 kg Cd/day (year 2005; in-house methods) and 0.045 kg/day (year 2004; stack air measurements performed by external laboratory).
- The calculated annual average deposition rate is  $1.81 \cdot 10^{-4}$  mg/m<sup>2</sup>/day (year 2005) and  $3.19 \cdot 10^{-4}$  mg/m<sup>2</sup>/day (year 2004).
- The main exposure route is aerial deposition for Cd oxide producers.
- Calculated added local concentration in soil is 0.002 mg kg<sup>-1</sup> ww (year 2005) and 0.003 mg kg<sup>-1</sup> ww (year 2004).

- Calculated  $PEC_{local}$  in soil is  $0.36 \text{ mg kg}^{-1} \text{ ww}$  (calculated regional background soil =  $0.36 \text{ mg kg}^{-1} \text{ ww}$ ).

Table 3.141 Calculated total local  $PEC_{soil}$  for Cd-oxide producing plants in EU-16.  $PEC$ 's include background Cd ( $0.36 \text{ mg kg}^{-1} \text{ ww}$ )

N°	Emission to air <sup>¶</sup>	Number of emission days	$C_{local_{soil}}$	$PEC_{local_{soil}}$	Year
	$\text{kg d}^{-1}$		$\text{mg kg}_{ww}^{-1}$	$\text{mg kg}_{ww}^{-1}$	
12	0.026 <sup>(a)</sup>	256	0.002	0.36	2005
12	0.045 <sup>(b)</sup>	256	0.003	0.36	2004

¶ Annual averages;

- a) Cd in stack emissions is recently measured (year 2005); average Cd concentration:  $55 \mu\text{g}/\text{m}^3$  (punctual measurement; in-house methods);
- b) Cd in stack emissions measured by external laboratory (year 2004); average Cd concentration:  $97 \mu\text{g}/\text{m}^3$ .

### Production of NiCd batteries

- Daily stack emissions to air vary between 0.01 (site 4) and 0.02 kg Cd/day (site 2, battery manufacturing plant only). Site 3 did not provide any emission information, since air emissions are not monitored (not obliged in permit).
- The calculated annual average deposition rates vary between  $9.59 \cdot 10^{-5}$  (site 4) and  $1.37 \cdot 10^{-4} \text{ mg}/\text{m}^2/\text{day}$  (site 2)
- The main exposure route is aerial deposition for NiCd battery producers; sludge from the on-site waste water treatment system is not applied to agricultural land but is recycled or land-filled (industry information).
- Calculated added local concentration in soil is  $0.001 \text{ mg kg}^{-1} \text{ ww}$  (site 2, 4).
- Calculated  $PEC_{local}$  in soil is  $0.36 \text{ mg kg}^{-1} \text{ ww}$  (calculated regional background soil =  $0.36 \text{ mg kg}^{-1} \text{ ww}$ ) (site 2, 4).

Table 3.142 Calculated total local  $PEC_{soil}$  for NiCd batteries producing plants in EU-16.  $PEC$ 's include background Cd

N°	Emission to air <sup>¶</sup>	Number of emission days	$C_{local_{soil}}$	$PEC_{local_{soil}}$	Year
	$\text{kg d}^{-1}$		$\text{mg kg}_{ww}^{-1}$	$\text{mg kg}_{ww}^{-1}$	
2	0.02 <sup>(a)</sup>	330	0.001	0.36	2002
3	n.d. <sup>(b)</sup>	330	n.d.	n.d.	2002
4	0.01	344	0.001	0.36	2002
6	No update data				
7	No update data				

¶ Annual averages;

n.d. No data available;

- a) Emission from battery manufacturing only; air emissions are broken down between two plants; battery manufacturing and Cd recycling;
- b) Air emissions are not monitored. No requirement in the permit since the plant runs a wet process, therefore most emissions are releases in the water.

*Recycling of NiCd batteries*

- Daily stack emissions to air vary between  $5.3 \cdot 10^{-6}$  kg Cd/d (site 2) and 0.01 kg Cd/day (site 1, year 2002 data).
- Calculated annual average deposition rates vary between  $5.21 \cdot 10^{-8}$  mg/m<sup>2</sup>/day and  $1.09 \cdot 10^{-4}$  mg/m<sup>2</sup>/day
- The main exposure route is aerial deposition for Cd recyclers; sludge from the on-site waste water treatment system is not applied to agricultural land but is recycled or land-filled (industry information).
- Calculated added local concentrations in soil vary between  $5.6 \cdot 10^{-7}$  mg kg<sup>-1</sup> ww (site 2) and 0.0012 mg kg<sup>-1</sup> ww (site 1, year 2002 data).
- Calculated PEC<sub>local</sub> in soil is 0.36 mg kg<sup>-1</sup> ww (calculated regional background soil = 0.36 mg kg<sup>-1</sup> ww).

Table 3.143 Calculated total local PECsoil for NiCd batteries recycling plants in EU-16. PEC's include background Cd

N°	Emission to air <sup>†</sup>	Number of emission days	C <sub>local</sub> <sub>soil</sub>	PEC <sub>local</sub> <sub>soil</sub>	Year
	kg d <sup>-1</sup>		mg kg <sub>ww</sub> <sup>-1</sup>	mg kg <sub>ww</sub> <sup>-1</sup>	
1	0.01	355	0.0012	0.36	2002
1	0.003	336	0.0003	0.36	2004
2	$5.3 \cdot 10^{-6(a)}$	360	$5.6 \cdot 10^{-7}$	0.36	2002
2bis	0.003 <sup>(b)</sup>	330	0.0003	0.36	2002

<sup>†</sup> Annual averages;

a) Submitted air emissions are checked versus the analysis report and proved to be correct. Air emissions are that low due to the fact that in air emission no considerable amount of Cd can be found (conc. 2.5 µg/m<sup>3</sup>) and the fact that the gas stream is very low due to technical reasons (78 m<sup>3</sup>/hours maximum);

b) Emissions from Cd recycling unit on the site of battery manufacturing plant 2.

*Production of Cd containing pigments*

- Daily stack emissions to air vary between 0.01 kg Cd/day (site A, C) and 0.02 kg Cd/day (site B).
- Calculated annual average deposition rates vary between  $6.85 \cdot 10^{-5}$  mg/m<sup>2</sup>/day and  $1.53 \cdot 10^{-4}$  mg/m<sup>2</sup>/day
- The main exposure route is aerial deposition for Cd pigments producers. Sludge from the treatment of waste water is land-filled.
- Calculated added local concentrations in soil vary between 0.0007 mg kg<sup>-1</sup> ww (site A) and 0.002 mg kg<sup>-1</sup> ww (site B).
- Calculated PEC<sub>local</sub> in soil is 0.36 mg kg<sup>-1</sup> ww (calculated regional background soil = 0.36 mg kg<sup>-1</sup> ww).

Table 3.144 Calculated total local PECsoil for Cd pigments producing plants in EU-16. PEC's include background Cd

N°	Emission to air <sup>†</sup>	Number of emission days	C <sub>local soil</sub>	PEC <sub>local soil</sub>	Year
	kg d <sup>-1</sup>		mg kg <sub>ww</sub> <sup>-1</sup>	mg kg <sub>ww</sub> <sup>-1</sup>	
A	0.01	230	0.0007	0.36	2003
B	0.02	318	0.002	0.36	2003
C	0.01	250	0.0008	0.36	2003

<sup>†</sup> annual averages Production of Cd containing stabilisers.

- Daily stack emissions to air vary between 0.002 kg Cd/day (site Y) and 0.003 kg Cd/day (site X).
- Calculated annual average deposition rates vary between  $2.74 \cdot 10^{-6}$  mg/m<sup>2</sup>/day and  $1.75 \cdot 10^{-5}$  mg/m<sup>2</sup>/day
- The main exposure route is aerial deposition for Cd stabiliser producers. Although site X discharges its waste water to a municipal STP; the sludge is not applied to agricultural soil (see subsection “Calculated PEC for soil” under Section 3.1.3.3.2). Site-specific information on the destination of sludge is not available.
- Calculated added local concentrations in soil vary between  $2.9 \cdot 10^{-5}$  mg kg<sup>-1</sup> ww (site Y) and 0.0002 mg kg<sup>-1</sup> ww (site X).
- Calculated PEC<sub>local</sub> in soil is 0.36 mg kg<sup>-1</sup> ww (calculated regional background soil = 0.36 mg kg<sup>-1</sup> ww).

Table 3.145 Calculated total local PECsoil for Cd stabiliser producing plants in EU-16. PEC's include background Cd

N°	Emission to air <sup>†</sup>	Number of emission days	C <sub>local soil</sub>	PEC <sub>local soil</sub>	Year
	kg d <sup>-1</sup>		mg kg <sub>ww</sub> <sup>-1</sup>	mg kg <sub>ww</sub> <sup>-1</sup>	
X	0.003	220	0.0002	0.36	2002
Y	0.002	50	$2.9 \cdot 10^{-5}$	0.36	2002

<sup>†</sup> Annual averages.

#### *Use of Cd/CdO in alloys, plating and other uses*

For these uses, no update information was submitted to the Rapporteur.

#### Measured levels in soil

There are no measured local soil concentrations submitted by the Cd/CdO producing- or processing industries.

Measured aerial deposition rates are available for the Cd metal producing sites. A comparison between calculated and measured deposition levels is provided in **Table 3.153** (see subsection “Measured levels” under Section 3.1.3.3.3).

### 3.1.3.3 Atmospheric compartment

#### Calculation of PEC<sub>local,air</sub>

Local PEC-values for the atmospheric compartment are calculated according to the OPS model proposed in the TGD (EC, 2003) for a general standard environment.

Input data are the total daily emissions of the individual Cd-producing and processing plants (Industry questionnaires, 2004).

The calculated concentrations in air are actual contributions to the receiving atmosphere. The local PEC values are obtained by adding the regional PEC values for air to the calculated local concentration in the atmosphere.

$$PEC_{local,air,ann} = C_{local,air,ann} + PEC_{regional,air}$$

PEC<sub>local,air,ann</sub>: annual average predicted environmental concentration in air (ng m<sup>-3</sup>)  
 PEC<sub>regional,air</sub>: regional concentration in the air (0.55 ng m<sup>-3</sup>; **Table 3.157**)

The results of the predicted local atmospheric Cd concentrations at 100 m from the point sources are listed in **Table 3.146-Table 3.149**.

#### Cd metal production

- Daily stack emissions to air vary between 0.03 kg Cd/day (site 6) and 0.15 kg Cd/day (site 7). Please note that in general for the Cd metal production-sites the total emissions are reported i.e. emissions from stack and diffuse sources. Moreover, emissions due to refining/production of other non-ferro metals may be included (to different extent from site to site).
- Calculated annual average Cd concentrations at a distance of 100 m from the point source vary between 7.6 ng/m<sup>3</sup> (site 6) and 41.3 ng/m<sup>3</sup> (site 7).
- Calculated PEC<sub>local,air</sub> values vary between 8.2 and 41.8 ng/m<sup>3</sup> (calculated regional background = 0.55 ng/m<sup>3</sup>).

Table 3.146 Calculated total local PEC<sub>air</sub> for Cd-metal producing plants in EU-16. PEC's include background Cd

N°	Emission to air	Number of emission days	Annual average air concentration	PEC <sub>local,air,ann</sub>	Year
	kg d <sup>-1</sup>		(100 m) ng m <sup>-3</sup>	(100 m) ng m <sup>-3</sup>	
1	0.08 <sup>(a)(b)</sup>	365	23.2	23.7	2002
6	0.03 <sup>(a)(c)</sup>	365	7.6	8.2	2002
7	0.15 <sup>(a)(d)</sup>	365	41.3	41.8	2002

<sup>†</sup> Annual averages;

a) Cd emission from whole plant (including Zn and/or Pb production);

b) Total emissions: stack + diffuse emissions; diffuse emissions: 60-70% of total; stack emissions: 30-40% of total emissions;

c) All emissions from point sources and fugitive emissions from roof openings for the whole zinc production process. Emissions from cadmium production are difficult to separate;

d) Total emissions from the zinc smelter; approximately 90 emission points to air. Approximately 90% of the emission comes from 20% of the emission points which all are equipped with abatement systems (demisters or scrubbers).

*Cd oxide production*

- The daily stack emissions to air for CdO production-site 12 amount to 0.026 kg/day (year 2005, in house methods). On the basis of Cd measurements in the stacks, performed by an external laboratory, an emission amount of 0.045 kg/day could be calculated for the year 2004.
- The calculated annual average Cd concentration at a distance of 100 m from the point source is 5.0 ng/m<sup>3</sup> (year 2005) and 8.9 ng/m<sup>3</sup> (year 2004).
- The calculated PEC<sub>local air</sub> is 5.6 ng/m<sup>3</sup> (year 2005) and 9.4 ng/m<sup>3</sup> (year 2004).

Table 3.147 Calculated total local PEC<sub>air</sub> for Cd-oxide producing plants in EU-16. PEC's include background Cd

N°	Emission to air	Number of emission days	Annual average air concentration	PEC <sub>local air,ann</sub>	Year
	kg d <sup>-1</sup>		(100 m) ng m <sup>-3</sup>	(100 m) ng m <sup>-3</sup>	
12 <sup>(a)</sup>	0.026	256	5.0	5.6	2005
12 <sup>(b)</sup>	0.045	256	8.9	9.4	2004

¶ Annual averages;

a) Cd in stack emissions is recently measured (year 2005); average Cd concentration: 55 µg/m<sup>3</sup> (punctual measurement, in-house methods);

b) Cd in stack emissions measured by external laboratory (year 2004); average Cd concentration: 97 µg/m<sup>3</sup>.

*Production of NiCd batteries*

- Daily stack emissions to air vary between 0.01 kg Cd/day (site 4) and 0.02 kg Cd/day (site 2, battery manufacturing plant only). Data are not available for site 3 since there is no requirement to monitor air emissions.
- The calculated annual average Cd concentration at a distance of 100 m from the point source vary between 2.7 ng/m<sup>3</sup> (site 4) and 3.8 ng/m<sup>3</sup> (site 2).
- Calculated PEC<sub>local air</sub> varies between 3.2 ng/m<sup>3</sup> and 4.4 ng/m<sup>3</sup> (calculated regional background = 0.55 ng/m<sup>3</sup>).

Table 3.148 Calculated total local PEC<sub>air</sub> for NiCd battery producing plants in EU-16. PEC's include background Cd

N°	Emission to air	Number of emission days	Annual average air concentration	PEC <sub>local air,ann</sub>	Year
	kg d <sup>-1</sup>		(100 m) ng m <sup>-3</sup>	(100 m) ng m <sup>-3</sup>	
2	0.02 <sup>(a)</sup>	330	3.8	4.4	2002
3	n.d. <sup>(b)</sup>	330	n.d.	n.d.	
4	0.01	344	2.7	3.2	2002
6	No update data				
7	No update data				

¶ Annual averages;

n.d. No data available;

a) Emission from battery manufacturing only; air emissions are broken down between two plants; battery manufacturing and Cd recycling;

b) Air emissions are not monitored. No requirement in the permit since the plant runs a wet process, therefore most emissions are releases in the water.

*Recycling of NiCd batteries*

- Daily stack emissions to air vary between  $5.3 \cdot 10^{-6}$  kg Cd/day (site 2) and 0.01 kg Cd/day (site 1, year 2002 data). Year 2004 data for site 1 show a significant reduction in air emissions -i.e. 0.003 kg Cd/y- as a result of measures taken to obtain an ISO 14000 certificate (building coverage, aspiration devices). The reported very low air emissions of site 2 are verified and proved to be correct (very low Cd concentrations and gas flow rate; analysis done by extern laboratory).
- The calculated annual average Cd concentrations at a distance of 100 m from the point source vary between 0.001 ng/m<sup>3</sup> (site 2) and 3.0 ng/m<sup>3</sup> (site 1).
- Calculated PEC<sub>local,air</sub> vary between 0.6 ng/m<sup>3</sup> and 3.6 ng/m<sup>3</sup> (calculated regional background = 0.55 ng/m<sup>3</sup>).

Table 3.149 Calculated total local PEC<sub>air</sub> for NiCd battery recycling plants in EU-16. PEC's include background Cd

N°	Emission to air <sup>†</sup>	Number of emission days	Annual average air concentration	PEC <sub>local,air,ann</sub>	year
	kg d <sup>-1</sup>		(100 m) ng m <sup>-3</sup>	(100 m) ng m <sup>-3</sup>	
1	0.01	355	3.0	3.6	2002
1	0.003	336	0.69	1.2	2004
2	$5.3 \cdot 10^{-6(a)}$	360	0.001	0.6	2002
2bis	0.003 <sup>(b)</sup>	330	0.6	1.2	2002

<sup>†</sup> Annual averages;

- a) Submitted air emissions are checked versus the analysis report and proved to be correct. Air emissions are that low due to the fact that in air emission no considerable amount of Cd can be found (conc. 2.5 µg/m<sup>3</sup>) and the fact that the gas stream is very low due to technical reasons (78 m<sup>3</sup>/hour maximum);
- b) Emissions from Cd recycling unit on the site of battery manufacturing plant 2.

*Production of Cd containing pigments*

- Daily stack emissions to air vary between 0.01 kg Cd/day (site A, C) and 0.02 kg Cd/day (site B).
- Calculated annual average Cd concentrations at a distance of 100 m from the point source vary between 1.9 ng/m<sup>3</sup> (site A, C) and 4.3 ng/m<sup>3</sup> (site B).
- Calculated PEC<sub>local,air</sub> values vary between 2.5 and 4.8 ng/m<sup>3</sup> (calculated regional background = 0.55 ng/m<sup>3</sup>).

Table 3.150 Calculated total local PEC<sub>air</sub> for Cd pigment producing plants in EU-16. PEC's include background Cd

N°	Emission to air <sup>†</sup>	Number of emission days	annual average air concentration	PEC <sub>local,air,ann</sub>	Year
	kg d <sup>-1</sup>		(100 m) ng m <sup>-3</sup>	(100 m) ng m <sup>-3</sup>	
A	0.01	230	1.9	2.5	2002
B	0.02	318	4.3	4.8	2002
C	0.01	250	2.2	2.8	2002

<sup>†</sup> annual averages Production of Cd containing stabilisers.

- Daily stack emissions to air vary between 0.002 kg Cd/day (site Y) and 0.003 kg Cd/day (site X).

- Calculated annual average Cd concentrations at a distance of 100 m from the point source vary between 0.08 ng/m<sup>3</sup> (site Y) and 0.5 ng/m<sup>3</sup> (site X).
- Calculated PEC<sub>local,air</sub> values vary between 0.6 and 1.0 ng/m<sup>3</sup> (calculated regional background = 0.55 ng/m<sup>3</sup>).

Table 3.151 Calculated total local PEC<sub>air</sub> for Cd stabiliser producing plants in EU-16. PEC's include background Cd

N°	Emission to air <sup>†</sup>	Number of emission days	Annual average air concentration	PEC <sub>local,air,ann</sub>	Year
	kg d <sup>-1</sup>		(100 m) ng m <sup>-3</sup>	(100 m) ng m <sup>-3</sup>	
X	0.003	220	0.5	1.0	2002
Y	0.002	50	0.08	0.6	2002

<sup>†</sup> Annual averages.

### *Use of Cd/CdO in alloys, plating and other uses*

For these uses, no site-specific update information was submitted in time to the Rapporteur.

### Measured levels

Table 3.152 Summary of calculated versus measured levels in air for Cd/CdO producing/processing sectors

N°	Emission amount	PEC <sub>local,air</sub> Calculated (100 m)	Measured ann.avg. air concentration	Remarks	Year
	kg d <sup>-1</sup>	ng m <sup>-3</sup>	ng m <sup>-3</sup>		
<b>Cd metal production</b>					
1	0.08	23.7	5.6	300 m from emission point, measured with pourbaix (isokinetic) low volume sampler, year 2003 data.	2003: measured 2002: modelled
6	0.03	8.2	1.8	300 m NNW of Cd refinery (border of the site). Sampling device: DIGITEL DHA-80 (Riemer Messtechnik), high volume sampler, 500 l/min, 24 hours; pore size: 5µm (in-house analysis). Data are influenced by neighbouring harbour and industrial activities.	2002
7	0.15	41.8	8.5 (± 14.94 st.dev.) (450 m NNW) 0.97 (± 1.06 st. dev.) (626 m SW)	3 month period; 4 sampling points; 14 measurements per point; ICP-MS, NILU method U-22, Norwegian Institute of Air research (NILU), year 2003 data (external laboratory)	2003: measured 2002: modelled

Table 3.152 continued overleaf

Table 3.152 continued Summary of calculated versus measured levels in air for Cd/CdO producing/processing sectors

N°	Emission amount	PECLocal <sub>air</sub> Calculated (100 m)	Measured ann.avg. air concentration	Remarks	Year
	kg d <sup>-1</sup>	ng m <sup>-3</sup>	ng m <sup>-3</sup>		
<b>Cd oxide production</b>					
12	0.026	5.6	n.d.	n.d.	2005
12	0.045	9.4	n.d.	n.d.	2004
<b>NiCd battery production</b>					
2	0.02	4.4	n.d.	n.d.	2002
3	No data	No data	4	200 m from stack, downwind. Measurements are carried out according to NFX 43.261 and NFX 43.006.	
4	0.01	3.2	0.3	50 m from property line to the NW; in direction of prevailing wind	2002
6	No update data				
7	No update data				
<b>NiCd battery recycling</b>					
1	0.01	3.6	126 (300 m N) 37 (300 m S) wind direction: from N or from S	Cd in PM 10; Sampling apparatus: High Volume System (Digitel DA 80); flow rate: 500 l/mn, 24 hours/day, more than 350 d/y. Analytical method: ICP, spectrophotometer.	2002
1	0.003	1.2	21 (300m N)* 15 (300m S) wind direction: from N or from S	Cd in PM 10; Sampling apparatus: High Volume System (Digitel DA 80); flow rate: 500 l/mn, 24 hours/day, more than 350 d/y. Analytical method: ICP, spectrophotometer	2004
2	5.3 · 10 <sup>-6</sup>	0.6	n.d.	n.d.	2002
2bis	0.003	1.2	n.d.	n.d.	2002
<b>Cd pigments production</b>					
A	0.01	2.5	n.d.	n.d.	2003
B	0.02	4.8	n.d.	n.d.	2003
C	0.01	2.8	n.d.	n.d.	2003

Table 3.152 continued overleaf

Table 3.152 continued Summary of calculated versus measured levels in air for Cd/CdO producing/processing sectors

N°	Emission amount	PEClocal <sub>air</sub> Calculated (100 m)	Measured ann.avg. air concentration	Remarks	Year
	kg d <sup>-1</sup>	ng m <sup>-3</sup>	ng m <sup>-3</sup>		
Cd stabiliser production					
X	.	1.0	n.d.	Cd concentration in air of the surroundings of the plant is considered to be negligible or very close to zero.	2002
Y	0.002	0.6	n.d.	n.d.	2002

n.d. No data available;

\* The reduction in air concentrations in 2004, as compared to 2002, is a result of the measures taken to reduce point and diffuse air emissions from the site (improvement in building coverage/aspiration device and improved air treatment systems (two rows of filters) (ISO 14000 certificate).

Reduction in emission data of 2002 (and possibly later year(s)) compared to previously reported and assessed data of 1996 should be seen in the light of the information given in Section 3.1.2.3 and per sector in the paragraph starting with 'significant changes in production/emission reduction measures'.

Table 3.153 Summary of calculated versus measured aerial deposition levels for Cd/CdO producing/processing sectors

N°	Emission amount	Aerial deposition calculated	Aerial deposition measured	Remarks	Year
	kg d <sup>-1</sup>	mg/m <sup>2</sup> .day	mg/m <sup>2</sup> .day		
Cd metal production					
1	0.08	$8.33 \cdot 10^{-4}$	0.1	average of 8 sampling points, average distance 1 km, deposition measurements with Bergerhoff collecting measurements, year 1996-1998). No individual data for points provided. The data are influenced by excavation activities on the plant area.	2002-2003
6	0.03	$2.74 \cdot 10^{-4}$	6.4 mg/m <sup>2</sup> .d (300 m NNW) 4.5 mg/m <sup>2</sup> .d (1.2 km ENE) 2.4 mg/m <sup>2</sup> .d (750 m S) 2.7 mg/m <sup>2</sup> .d (1 km WNW) 1.7 mg/m <sup>2</sup> .d (1.2 km SW)	sampling in accordance with VDI 2119, Bergerhoff system, duration 1 month. Data are influenced by neighbouring harbour and industrial activities.	2002
7	0.15	0.0015	0.008	location: 500 m NNW, NILU, method ISO/DIS 4222.2 standard, n=12	2002

Table 3.153 continued overleaf

Table 3.153 continued Summary of calculated versus measured aerial deposition levels for Cd/CdO producing/processing sectors

N°	Emission amount	Aerial deposition calculated	Aerial deposition measured	Remarks	Year
	kg d <sup>-1</sup>	mg/m <sup>2</sup> .d	mg/m <sup>2</sup> .d		
<b>Cd oxide production</b>					
12	0.026	1.81 · 10 <sup>-4</sup>	n.d.		2005
12	0.045	3.19 · 10 <sup>-4</sup>	n.d.		2004
<b>NiCd battery production</b>					
2	0.02	1.37 · 10 <sup>-4</sup>	n.d.		2002
3	n.d.	n.d.	n.d.		2002
4	0.01	9.59 · 10 <sup>-5</sup>	n.d.		2002
6	No update data				
7	No update data				
<b>NiCd battery recycling</b>					
1	0.01	1.09 · 10 <sup>-4</sup>	n.d.		2002
1	0.003	2.49 · 10 <sup>-5</sup>	n.d.		2004
2	5.3 · 10 <sup>-6</sup>	5.21 · 10 <sup>-8</sup>	n.d.		2002
2bis	0.003	2.33 · 10 <sup>-5</sup>	n.d.		
<b>Cd pigments production</b>					
A	0.01	6.85 · 10 <sup>-5</sup>	n.d.		2003
B	0.02	1.53 · 10 <sup>-4</sup>	n.d.		2003
C	0.01	7.95 · 10 <sup>-5</sup>	n.d.		2003
<b>Cd stabiliser production</b>					
X	0.003	1.75 · 10 <sup>-5</sup>	n.d.		2002
Y	0.002	2.74 · 10 <sup>-6</sup>	n.d.		2002

n.d. No data available

### Comparison of PECs with measured data

Measured Cd concentrations in air, presented in **Table 3.152**, are available for Cd metal production-site 1, 6 and 7; NiCd battery producing site 3, 4 and Cd recycling site 1.

- For metal production-site 1, the measured annual average Cd concentration in air at a distance of 300 m from the emission point is 5.6 ng/m<sup>3</sup>. The sampling is performed with a pourbaix low volume sampler (year 2003 data). The measured value is a factor of 4 below the modelled air concentration determined at 100 m from the emission point i.e. 23.7 ng/m<sup>3</sup>.
- Metal production-site 6 reports measured annual average air concentration at a distance of 300 m NNW of the border of the site of 1.8 ng/m<sup>3</sup> (sampling device used: high volume sampler; 500 l/min, 24 hours, pore size: 5 µm). The measured value is situated a factor of 4.6 below the modelled PEC<sub>air</sub> of 8.2 ng/m<sup>3</sup> (100 m from site). Please note that these data are influenced by neighbouring industrial activities.

- Measured Cd concentrations in the surrounding air compartment are available for Cd metal production-site 7. Measurements are performed at two different locations: 450 m NNW of site:  $8.5 \pm 14.9 \text{ ng/m}^3$  and 626 m SW of the site:  $0.97 \pm 1.06 \text{ ng/m}^3$  (year 2003 data). The highest measured concentrations are situated a factor of 4.9 below the modelled PECs. Measurements are performed according to NILU method U-22; and analysed by ICP-MS (National Environment Institute, 2003).
- Although NiCd battery producer 3 reports that there are no air emission data available (not required); measured Cd concentrations at a distance of 200 m from the stack are reported:  $4 \text{ ng/m}^3$  (measurements carried out according to National standards NFX 43.261 and NFX 43.006).
- Battery manufacturing site 4 reports a measured annual Cd concentration in air of  $0.3 \text{ ng/m}^3$  at a distance of 50 m from the property line in the prevailing wind direction. The measured value is a factor of 10 below the modelled  $\text{PEC}_{\text{air}}$  at 100 m from the site of  $3.2 \text{ ng/m}^3$ .
- Measured Cd concentrations in the surrounding air compartment are available for NiCd battery recycling site 1. Measurements are performed at two different locations: 300 m N of site:  $126 \text{ ng/m}^3$  and 300 m S of the site:  $37 \text{ ng/m}^3$  (year 2002). The wind direction is from North or South. The sampling is performed with a high volume sampler, flow rate: 500 l/min, 24 hours/day, > 350 days/year; analytical method: ICP, spectrophotometer, Cd in PM10. The highest measured concentration is situated a factor of 35 above the modelled PEC of  $3.6 \text{ ng/m}^3$ . The lowest concentration is situated a factor of 10 above the modelled  $\text{PEC}_{\text{air}}$ . Year 2004 data indicate that Cd concentrations in air are reduced in comparison with previous years:  $21 \text{ ng/m}^3$  (300 m N) and  $15 \text{ ng/m}^3$  (300 m S) respectively. These values are situated a factor of 12.5-17.5 above the modelled air concentrations. The plant indicates that impact from other industrial sources is probable (but cannot be quantified).

In conclusion, only limited measured information is (made) available.

Moreover, measured data are stated by the companies to be (very probably) influenced by other sources (e.g. other industrial sources, traffic etc.). However, only for one site, Cd metal producer site 7, the identification and approximate contribution of these other sources could be made based on the results of an extensive air monitoring programme. For recycler site 1 similar investigations are in preparation in collaboration with the national authority.

In general, the measured annual air concentration at a certain distance from the site is situated below the modelled  $\text{PEC}_{\text{local,air}}$ . This may be due to the different distances from the source (the calculated value assumes 100 m whereas the measured values were at 300 – 450 m) or different reference years (e.g. 2003 measured versus 2002 for the calculated).

For the three production companies of cadmium metal, measured concentrations, including 'background' concentrations, range from  $1.8$  to  $8.6 \text{ ng/m}^3$ . The range of calculated local  $C_{\text{air}}$  and PEC values in air is  $8.2 - 41.8 \text{ ng/m}^3$ . For corresponding sites a comparison of these local monitoring data with the calculated local  $C_{\text{air}}$  values shows that the calculated  $C_{\text{air}}$  is a factor 4 to 5 higher than the measured concentration at the respective site.

For battery producers some comparison is only possible for site 4 where the calculated value  $3.2 \text{ ng/m}^3$  is a factor 10.6 higher than the (limitedly documented) measured data ( $0.3 \text{ ng/m}^3$ ).

The measured cadmium concentrations in air near the NiCd recyclers (site 1), ranging from  $37$  to  $126 \text{ ng/m}^3$  (2002) and from  $15$  to  $21 \text{ ng/m}^3$  (2004) are a factor 17.5 to 35 higher than the calculated local  $C_{\text{air}}$  for this site ( $0.6$  to  $3 \text{ ng/m}^3$ ).

Both calculated and measured data will be taken forward to risk characterisation bearing however in mind the limitations of these values.

Measured aerial deposition rates, presented in **Table 3.153**, are available for Cd metal production-site 1, 6 and 7.

- For metal production-site 1, the measured annual average deposition rates at a distance of 1 km from the emission point is 0.1 mg/m<sup>2</sup>.day (year 1996-1998 data). The measured data are situated two orders of magnitude above the modelled deposition rates of  $8.33 \cdot 10^{-4}$  mg/m<sup>2</sup>.day (year 2002 data, based on stack emissions only). The sampling is performed at 8 different sampling points, located on average 1 km from the site. Bergerhoff collection methods are used to perform the sampling. It should be noted that the measured data are influenced by excavation activities in the plant area.
- Metal production-site 6 reports measured annual average deposition rates at different locations: 6.4 mg/m<sup>2</sup>.day (300 m NNW); 4.5 mg/m<sup>2</sup>.day (1.2 km ENE); 2.4 mg/m<sup>2</sup>.day (750 m S); 2.7 mg/m<sup>2</sup>.day (1 km WNW) and 1.7 mg/m<sup>2</sup>.day (1.2 km SW). Relevant values (1.7-4.5 mg/m<sup>2</sup>.day; within 1,000 m range as described in the TGD) are situated three orders of magnitude above the modelled aerial deposition value for the site of  $2.74 \cdot 10^{-3}$  mg/m<sup>2</sup>.day. The sampling is performed in accordance with national guidelines VDI 2119 using Bergerhoff system, duration: 1 month. Please note that the deposition monitoring data are influenced by neighbouring harbour and industrial activities.
- Metal production-site 7 reports a measured annual average deposition rate of 0.008 mg/m<sup>2</sup>.day measured at 500 m NNW of the site. The measured Cd deposition rate is five fold the deposition rate modelled by EUSES (i.e. 0.0015 mg/m<sup>2</sup>.day). The sampling is performed in accordance with ISO/DIS 4222.2 standard.

In conclusion, since metal production-sites 1 and 6 indicate that:

- the reported measured deposition rates are influenced by excavation activities on the plant area (site 1) and neighbouring harbour and industrial activities (site 6);
- fugitive emissions from both sites are reported to be minor in comparison with stack emissions (site 1) or are already included in the stack air emission estimation (site 6);
- the data from site 1 are rather outdated (1996-1998) (and in the meantime: excavation activities at the site are stopped),

It is judged that the measured aerial deposition rates for sites 1 and 6 do not fulfil the reliability and relevance criteria for further use of the data in PEC<sub>local,soil</sub> modelling. Hence only the average aerial deposition rate reported for site 7 is taken forward for modelling purposes.

#### **3.1.3.3.4 Secondary poisoning**

No changes made.

### 3.1.3.4 Regional and continental exposure assessment

#### 3.1.3.4.1 Regional and continental concentrations calculated according to the TGD

Calculation of the regional environmental exposure concentration is based on both point and diffuse sources over a wider (regional) area. The regional PEC also provides the Cd background concentration (anthropogenic and natural) that is incorporated in the calculation of the local PEC.

The point Cd emissions are rather well documented (see Section 3.1.3.1). Some diffuse Cd emissions can also be rather well quantified such as Cd input from fertilisers or the total losses to the air based on deposition data (see **Table 3.178** and **Table 3.180**). Total Cd emissions during use and from disposal of Cd containing products are more difficult to quantify. Emissions of Cd from waste incineration and land-filling have been estimated in the TRAR/batteries' related sections.

Data of the OECD 1995 questionnaire (Pearse, 1996) and, for The Netherlands, the RIVM 1997 data are used for calculating the regional and continental PEC values in the various environmental compartments. These data were not complete and the missing data were completed with emission data that were estimated by ERL (ERL, 1990), or other sources as indicated in **Tables 3.154, 3.155** and **3.156**.

Annual atmospheric emissions in the EU-16 amount to at least 124 tonnes Cd (see **Table 3.154**). This value does not include natural sources of Cd emission ( $15 \text{ tonnes y}^{-1}$ , ERL 1990) such as emissions from Mount Etna, sea spray, forest fires, weathering of Cd rich soils, etc. The contribution of the natural sources is included in the background which is added to the continental PEC's (see Section 3.1.1). The emission of the EU non-ferrous metal producers and of Cd processors is 14.4 tonnes Cd. This value corresponds well with the sum of the emissions of these industries estimated in each country. The major sources of atmospheric Cd emissions in the environment are oil/coal combustion (43%) and iron and steel production (24.7%). Large differences are noticed in estimated Cd emissions from oil/coal combustion. As an example ERL estimates 7.1 tonnes Cd emission from oil/coal combustion for the UK whereas the OECD data estimate 48.2 tonnes Cd emission for the UK (Pearse, 1996) and Berdowski et al. (1998) 4.5 tonnes Cd/year. Total Cd emission in the EU from oil/coal combustion is 49.3 tonnes (ERL, 1990) or 54 (see **Table 3.154**, data of Berdowski et al. (1998) and ERL (1990)). A roughly estimated EU average value of measured deposition is  $1 \text{ g Cd g ha}^{-1} \text{ y}^{-1}$  (see **Table 3.180**). This is equivalent to 356 tonnes Cd on the EU wide area. This value indicates that the atmospheric Cd emissions (including natural) are about 2 fold underestimated. On the other hand, net deposition may also be overestimated because even wet-only deposition data can include Cd that is resuspended from soil. Analytical quality of measured data is also a major issue in this assessment. The EU average Cd deposition rate is predicted about  $0.4 \text{ g Cd ha}^{-1} \text{ y}^{-1}$  (see **Table 3.180**) and which is equivalent to  $0.06 \text{ } \mu\text{g Cd/Lin}$  collected rain water (assume 700 mm rainfall  $\text{y}^{-1}$ ). Limits of quantification of Cd in water samples are often about  $0.05 \text{ } \mu\text{g Cd/Lin}$  monitoring programmes.

Annual emissions in water are at least 39 tonnes Cd (see **Table 3.155**). The available data are not comparable between EU countries since not all emissions were taken into account in each country. As an example, the Swedish Cd emission from municipal wastewater is 0.3 tonnes Cd/year. An extrapolation of this number to the EU on population basis, yields 12.7 tonnes Cd/year. It is unknown to what extent this value reflects a net emission to water.

Waste water contains natural Cd (e.g. surface water contains  $0.05\mu\text{g L}^{-1}$ , dissolved natural Cd, see Section 3.1.3.4.3) and carry Cd that is recycled within the environment (dust, organic matter, etc.). Data on Cd emission from waste water treatment plants in the different EU countries are scarcely available. The older data provided by ERL (ERL, 1990) estimated Cd emissions from non ferrous metal producers and Cd processors as large as 72 tonnes Cd/year. The updated data (Pearse, 1996) yield estimated emissions of only 11.1 tonnes Cd/year (see **Table 3.155**, all data refer to emissions after the STP). Stormwater and combined sewer overflows may not be entirely covered. Emissions to water through runoff from soil are not accounted in **Table 3.155**. The anthropogenic part of these emissions is, however, included in the PECwater calculations because the model (EUSES 1.0) assumes that a fraction of the emissions to soil is released to water. The natural part of these processes is included via the background Cd concentration that is added to the predicted added concentrations (see Section 3.1.1. Emissions of Cd to water from natural processes are estimated to be of the same order of magnitude or even larger than the anthropogenic emissions. The natural background of Cd (dissolved fraction only) is estimated  $0.05\mu\text{g L}^{-1}$  for the entire of Europe. At default values of water volumes in the European continent ( $320 \cdot 10^9\text{ m}^3$ ) and the mean residence time of 166 days, this natural flux is equivalent to 35 tonnes Cd year<sup>-1</sup> (dissolved Cd) or about 100 tonnes Cd year<sup>-1</sup> (total). Natural Cd in water is obviously not all derived from runoff and erosion because other biogeochemical processes, such as fluxes of natural organic transfer, introduce metals into freshwater bodies.

Fertiliser Cd and atmospheric deposition are the major sources of Cd in agricultural **soils**. Soils receive a considerable fraction of total Cd emitted to the atmosphere. The fraction surface area that is agricultural soil in EU is 0.27, therefore  $0.27 \cdot 124$  tonnes Cd (34 tonnes Cd) emitted annually ends up in agricultural soils. Fertiliser Cd is estimated to be 231 tonnes y<sup>-1</sup> in the EU. The amount of Cd used in agriculture through sludge application is at least 13.6 tonnes y<sup>-1</sup> (see **Table 3.156**).

The Cd released to natural and industrial soil is assumed to consist of atmospheric deposition only. The fraction natural soil (surface based) is 0.6 and the fraction industrial soil is 0.1. Emissions to the natural soils are therefore  $0.6 \cdot 124 = 74$  tonnes Cd/year and to industrial soil  $0.1 \cdot 126 = 12.4$  tonnes Cd/year.

Table 3.154 Direct atmospheric Cd emission in the EU-16 (tonnes Cd/y). Data combined from different source documents as indicated in footnotes. Note that EU totals of the non-ferrous metals producers do not match the sum of the emissions of each country. The EU totals are the most recent data and are based on confidential questionnaires

	Cd alloys <sup>5</sup> and batteries production and recycling <sup>12</sup>	Cd/CdO production	Other non- ferrous metals	Production of iron and steel	Oil/coal combustion	Processing phosphates	Municipal incineration <sup>13</sup>	Wood/peat combustion	Other (cement, glass prod., traffic)
Austria	0 <sup>5</sup>	0.14 <sup>11</sup>		0.14 <sup>11</sup>	2.0 <sup>11</sup>		0.086	1.4 <sup>4</sup>	2.9 <sup>11</sup>
Belgium	0 <sup>5</sup>	2 <sup>4,11</sup>		1.9 <sup>11</sup>	3 <sup>11</sup>	0.1 <sup>4</sup>	0.063		0.8 <sup>11</sup>
Denmark	0.02 <sup>5</sup>	0 <sup>9</sup>		0.2	0.45 <sup>11</sup>		0.300		1.4 <sup>11</sup>
Finland	n.d. <sup>5</sup>	0.4 <sup>11</sup>		0.7 <sup>4</sup>	0.9 <sup>11</sup>	n.d.	0.014		1.6 <sup>11</sup>
France	0.24 <sup>5</sup>	0.23 <sup>11</sup>		3.9 <sup>5,11</sup>	7.4 <sup>11</sup>	0.03 <sup>11</sup>	1.92		0.02 <sup>4</sup>
Germany	0.18 <sup>5</sup>	5.3 <sup>11</sup>		10.5 <sup>11</sup>	14.23 <sup>11</sup>		0.300		1.4 <sup>11</sup>
UK	0.26 <sup>5</sup>	6.7 <sup>11</sup>		2.9 <sup>11</sup>	4.47 <sup>11</sup>	0.03 <sup>4</sup>	0.019		1.4 <sup>11</sup>
Greece	0 <sup>5</sup>	0.02 <sup>11</sup>		0.7 <sup>11</sup>	1.6 <sup>11</sup>		0 <sup>5</sup>		2.25 <sup>11</sup>
Ireland	0 <sup>5</sup>	0.05 <sup>11</sup>		0.23 <sup>11</sup>	0.6 <sup>11</sup>		0 <sup>5</sup>		0.7 <sup>11</sup>
Italy	0.04 <sup>5</sup>	2.2 <sup>5</sup>		4.6 <sup>5</sup>	6.3 <sup>5</sup>		0.351		> 0.4 <sup>5,11</sup>
Luxemburg				0.9 <sup>11</sup>	0.24 <sup>11</sup>		0.022		
The Netherlands	0.01 <sup>5</sup>	0.85 <sup>6,8</sup>			0.3 <sup>11</sup>		0.053		0.7 <sup>11</sup>
Norway	n.d.	0.26 <sup>11</sup>		0.28 <sup>11</sup>	0.13 <sup>11</sup>	n.d.	0.041	n.d.	1.5 <sup>11</sup>
Portugal	0 <sup>5</sup>	0.02 <sup>11</sup>		0.34 <sup>11</sup>	1.4 <sup>11</sup>		0.003		1.2 <sup>11</sup>

Table 3.154 continued overleaf

Table 3.154 continued Direct atmospheric Cd emission in the EU-16 (tonnes Cd/y). Data combined from different source documents as indicated in footnotes. Note that EU totals of the non-ferrous metals producers do not match the sum of the emissions of each country. The EU totals are the most recent data and are based on confidential questionnaires

	Cd alloys <sup>5</sup> and batteries production and recycling <sup>12</sup>	Cd/CdO production	Other non-ferrous metals	Production of iron and steel	Oil/coal combustion	Processing phosphates	Municipal incineration <sup>13</sup>	Wood/peat combustion	Other (cement, glass prod., traffic)	
Spain	0.01 <sup>5</sup>	0.04 <sup>11</sup>		2.34 <sup>11</sup>	10.5 <sup>11</sup>	0.57 <sup>11</sup>	0.054		> 2.8 <sup>5,11</sup>	
Sweden	n.d.	1.4 <sup>4,11</sup>		1.2 <sup>11</sup>	0.4 <sup>11</sup>		0.005	0.3 <sup>4</sup>		
EU total	0.853 <sup>5,12</sup>	3.9 <sup>2</sup>	9.7 <sup>3</sup>	31	54	0.7	3.2	1.7	> 19	TOTAL
% of total	0.6%	3.1%	7.7%	24.7%	43.0%	0.6%	2.6% <sup>11</sup>	1.4%	15.1%	> 124

n.d. No data;

- 1) Norwegian Zn producer's data (1994-1996);
- 2) Industry questionnaire of 1997;
- 3) Industry update based on 1995-1996 data and subtracting the emissions from Cd/CdO industry (Van Assche, 1998);
- 4) OECD Cd questionnaire, 1995 (Pearse, 1996);
- 5) Emission data by ERL (1990);
- 6) RIVM, 1997;
- 7) Data from 1991 and given by Pearse (1996);
- 8) This value is estimated to consist of 0.05 tonnes Cd from non-ferrous industry and 0.8 tonnes Cd from iron and steel production;
- 9) No non-ferrous metals producing industry in DK;
- 10) Cd-Bilanz 1994 (Umweltd Bundesamt, 1996);
- 11) Berdowsky et al., 1998;
- 12 & 13) Measured and modelled emissions (see TRAR/batteries' related sections).

Table 3.155 Cd emissions in the EU-16 to water (tonnes Cd/y). Data combined from different source documents as indicated in footnotes. Note that EU totals of the non-ferrous metals producers and of country totals do not match the sum of the emissions of each country. The EU totals are the most recent data and are based on confidential questionnaires

	Cd plating <sup>12</sup> & batteries production & recycling <sup>15</sup>	Cd/CdO production	Other non-ferrous metals	Production of iron and steel	Oil/coal combustion/traffic	Processing phosphates	Municipal incineration <sup>13</sup>	MSW operational landfills <sup>14</sup>	Metal mining	Other (chem. industry, municipal wastewater)	TOTAL
Austria				n.d.			0.004	0.004	0		0.008
Belgium		0.5 <sup>4</sup>		0.4 <sup>4</sup>		1.8 <sup>4</sup>	0.012	0.0074	0		2.7
Denmark		0 <sup>9</sup>		0.1 <sup>5</sup>			0.016	0.001	0		0.1
Finland		0.1 <sup>4</sup>		n.d.	n.d.	n.d.	0.001	0.007	n.d.		0.1
France		2.4 <sup>4</sup>		0.1 <sup>4</sup>		7.3 <sup>4</sup>	0.097	0.096			9.8
Germany		0.2 <sup>10</sup>		6.3 <sup>5</sup>			0.108	0.99			6.5
UK		0.6 <sup>1</sup>		3.0 <sup>5</sup>			0.023	0.114			3.6
Greece		0.1 <sup>5</sup>		0.1 <sup>5</sup>	-.5	-.5	0	0.014	n.d.	-.5	0.2
Ireland		0 <sup>5</sup>		< 0.05	-.5	-.5	0	0.006	n.d.	-.5	< 0.05
Italy		0.025 <sup>1</sup>		3.6 <sup>5</sup>			0.018	0.085			3.6
The Netherlands		0.4 <sup>6</sup>			0.1 <sup>6</sup>	x <sup>11</sup>	0.035	0.006	0	0.8 <sup>6</sup>	1.3
Norway		0.9 <sup>1</sup>		n.d.			0.003	0.008	0		0.9
Portugal		0.1 <sup>5</sup>		0.1 <sup>5</sup>	-.5	-.5	0.003	0.011	n.d.		0.2
Spain		>2.5		1.8 <sup>5</sup>	-.5	-.5	0.012	0.072	n.d.		> 4.3
Sweden		0.1 <sup>4</sup>		0.1 <sup>4</sup>	-.4	-.4	0.013	0.017	1.1 <sup>4</sup>	0.3 <sup>4</sup>	1.6
EU total	0.2 <sup>12</sup> +0.065 <sup>15</sup>	1.2 <sup>2</sup>	9.7 <sup>3</sup>	> 15.6	> 0.1	9.1	0.354	0.55	> 1.1	> 1.2	> 39.2

n.d. No data;

- 1) Zn producer's data of these countries(1994-1996);
- 2) Industry questionnaire of 1997;
- 3) Industry update based on 1995-1996 data and subtracting the emissions from Cd/CdO industry (Van Assche, 1998);
- 4) OECD Cd questionnaire, 1995 (Pearse, 1996);
- 5) Emission data by ERL (1990);
- 6) Milieucompendium, 2001;
- 7) Data from 1988 and given by Pearse (1996);
- 8) This value is estimated to consist of 0.05 tonnes Cd from non-ferrous industry and 0.8 tonnes Cd from iron and steel production;
- 9) No non-ferrous metals producing industry in DK;
- 10) Cd-Bilanz 1994 (Umweltd Bundesamt, 1996);
- 11) Gypsum waste from the P fertiliser industry (15 tonnes Cd in 1985), this is expected to decrease to 1.2 tonnes in 1994 and 0 tonnes in 2000 (Speed, 1993);
- 12) WS Atkins (1998);
- 13), 14) and 15) Data from the TRAR/batteries' related sections.

Table 3.156 Annual Cd input into agricultural soils from phosphate fertilisers and sludge in European countries. Underlined values are used when different values were available for the same country

	Cd from phosphate fertilisers	Cd from sludge <sup>3</sup>
	tonnes y <sup>-1</sup>	tonnes y <sup>-1</sup>
Austria	2.9 <sup>1</sup>	0.1
Belgium	1.5 <sup>6</sup>	>6
Denmark	0.707 <sup>6</sup>	0.12
Finland	0.2 <sup>1</sup>	0.07
Finland		<u>0.042<sup>5</sup></u>
France	92 <sup>2</sup>	1.58
Germany		1.27
Germany	20.4 <sup>1</sup>	2.4 <sup>1</sup>
Germany <sup>¶</sup>	22.1 <sup>4</sup>	3.2 <sup>4</sup>
Greece	10 <sup>2</sup>	
Ireland	7.4 <sup>6</sup>	0.01
Italy	44 <sup>2</sup>	
The Netherlands	3 <sup>1</sup>	0.4
Norway	0.072 <sup>6</sup>	
Portugal	5 <sup>2</sup>	
Spain	30 <sup>2</sup>	
Sweden	1.1 <sup>1</sup>	0.1
Sweden		0.13 (1996)
UK	11.3 <sup>1</sup>	1.88 (1996)
EU total	231	> 13.6

- 1) Data based on the OECD questionnaire (Pearse, 1996);
- 2) Landner et al. (1996), data from 1990;
- 3) Source: report from the commission to the council and the European Parliament on the implementation of community waste legislation Directive 86/278/EEC on sewage sludge for the period 1995-1997, data from 1997 unless otherwise stated;
- 4) Kiene (1999);
- 5) Finnish Environment Institute (1997);
- 6) Hutton et al. (2001).

Computations of continental exposure concentrations are made by means of multimedia fate models based on the fugacity concept. These models are box models, consisting of a number of compartments, air, water, sediment and soil, which are considered homogeneous and well mixed. A chemical released into the model is distributed between the compartments according to the properties of both the chemical and the model environment. For metals the following types of fate processes are distinguished in the continental assessment:

- emission direct and indirect (STP)

<sup>¶</sup> The current average Cd content in P fertilisers might also be 35 mg Cd/kg P<sub>2</sub>O<sub>5</sub> or 79 mg Cd/kg P (personal communication). At an application rate of 407,000 tonnes P fertiliser per year, this makes a Cd input of 32 tonnes Cd/year

- advective transport: deposition, run-off, and erosion.

The input of chemicals is regarded in the model as continuous and equivalent to continuous diffuse emission. For metals, all individual compounds are assumed to transform into the ionic species. The results from the models are steady-state concentrations, which can be regarded as estimates of long-term average exposure levels (TGD, 1996).

In the **continental** model, it is assumed that all Cd emissions enter into the continental environment. It is also assumed that no inflow of air and water across the boundaries of the continent occurs. Continental exposure concentrations are calculated based on the combined anthropogenic Cd emissions from all EU-16 countries (**Tables 3.154 - 3.156**) and on the background level of Cd

$$PEC_{\text{continental}} = C_{\text{continental}} + \text{background Cd}$$

The  $C_{\text{continental}}$  is the Cd concentration at continental scale that is related to Cd emissions by man (EUSES 1.0 calculations, see below). Background Cd is, by definition, the natural background for surface water and air and is the ambient Cd concentration measured in areas away from point source for soils and sediments (see Section 3.1.1).

**Regional** calculations are performed using a similar box model for a generic regional environment. This environment is not an actual region, but a hypothetical site with predefined environmental characteristics, the so-called 'standard environment'. A general standard region is represented by a typical densely populated area with an area of  $200 \cdot 200 \text{ km}^2$  and 20 million inhabitants, located in the margin of Western Europe (sum of EU Member States = continental scale). By default, it is assumed that 10% of the European production and use of Cd takes place within this area. Therefore:

$$\text{continental emission} = 90\% \text{ of total European emission}$$

$$\text{regional emission} = 10\% \text{ of total European emission}$$

The  $PEC_{\text{regional}}$  is calculated from

$$PEC_{\text{regional}} = C_{\text{regional}} + PEC_{\text{continental}}$$

The  $C_{\text{regional}}$  is the Cd concentration at regional scale that is related to Cd emissions by man (EUSES 1.0 calculations, see below).

For the soil compartment, however, a second model was used in which country specific Cd emission data were used (see Section 3.1.3.4.2).

$C_{\text{continental}}$  and  $C_{\text{regional}}$  are calculated with EUSES 1.0 (1997). The output of the model gives in fact the predicted added environmental concentrations at continental and regional scale ( $PEC_{\text{con,add}}$  and  $PEC_{\text{reg,add}}$ ). Therefore  $C_{\text{continental}}$  is considered as the calculated  $PEC_{\text{con,add}}$ , and  $C_{\text{regional}}$  is calculated as the difference between  $PEC_{\text{reg,add}}$  and  $PEC_{\text{con,add}}$ .

In the model calculations, the use of the physico-chemical properties of Cd are not appropriate, and estimated partition coefficients for soil, sediments and suspended matter are used instead (TGD Appendix VIII, 1996). The solid/liquid distribution coefficient in soil,  $K_D$ , was set to  $280 \text{ L kg}^{-1}$  (see Section 3.1.3.1.4), the solid/water partition coefficient,  $K_p$ , of sediment and suspended matter were both set at  $130 \cdot 10^3 \text{ L kg}^{-1}$  (see Section 3.1.3.1.1, European average). The sensitivity of  $PEC_{\text{water}}$  and  $PEC_{\text{sed}}$  to the choice of  $K_p$  is tested with additional model calculations, assuming the  $K_p$  of sediment and suspended matter equal to  $17 \cdot 10^3 \text{ L kg}^{-1}$  or  $224 \cdot 10^3 \text{ L kg}^{-1}$ . The

concentration of suspended solids was set to 15 mg L<sup>-1</sup> in each scenario, both for the continental and the regional compartment.

Volatilisation is ignored for Cd, therefore the Henry-coefficient was set to 0 Pa m<sup>3</sup> mol<sup>-1</sup>. Most of the Cd present in the atmosphere will be bound to aerosols. The vapour pressure was set to 10<sup>-10</sup> Pa to ensure that the metal fraction associated to aerosols was equal to one. Biotic and abiotic degradation rates were considered not to be relevant and set to zero.

Two models are used to estimate the Cd concentration in agricultural soil. The first method follows the procedure of the TGD (1996) and is calculated by EUSES 1.0 (1997). The second model is based on the mass balance of Cd including detailed Cd immision onto soil (country based) from fertilisers, sludge and atmospheric deposition and including output through leaching and plant uptake. This model is described in detail in Section 3.1.3.4.2.

In the TGD model (Model I for soil), input sources for soil contamination include direct emission to soil, deposition from the atmosphere and emission of sewage sludge to agricultural soil. Three types of soil are distinguished: agricultural, natural and industrial. The Cd emissions from agricultural practice (fertilisers) are assumed not to affect natural or industrial soil. The diffuse Cd emissions from atmospheric deposition, traffic etc. are distributed between these 3 types of soil proportionally to the surface areas of the three types of soil. According to the TGD (1996) the fraction of surface area that is agricultural soils is 0.27, the fraction natural soil 0.6, and the fraction industrial soil 0.1.

The continental and calculated regional emission data and resulting regional PEC values are presented in **Table 3.157** (details see **Annex I**). The calculated values are averages for a general regional and general continental environment.

Table 3.157 Emission values, total concentration and total PEC values for the regional and continental environment

Input continental (anthropogenic):	
amount released to air	111.6 tonnes y <sup>-1</sup>
amount released to surface water	35.2 tonnes y <sup>-1</sup>
amount released to agricultural soil <sup>(1)</sup>	207.9 tonnes y <sup>-1</sup> + 12.2 tonnes y <sup>-1</sup> (sludge application)
amount released to natural soil <sup>(1)</sup>	0 tonnes y <sup>-1</sup>
amount released to industrial soil <sup>(1)</sup>	0 tonnes y <sup>-1</sup>
Input regional (anthropogenic):	
amount released to air	12.4 tonnes y <sup>-1</sup>
amount released to surface water	3.9 tonnes y <sup>-1</sup>
amount released to agricultural soil <sup>(1)</sup>	23.1 tonnes y <sup>-1</sup> + 1.4 tonnes y <sup>-1</sup> (sludge application)
amount released to natural soil <sup>(1)</sup>	0 tonnes y <sup>-1</sup>
amount released to industrial soil <sup>(1)</sup>	0 tonnes y <sup>-1</sup>

Table 3.157 continued overleaf

Table 3.157 continued Emission values, total concentration and total PEC values for the regional and continental environment

Results		C_continental concentration	background <sup>(2)</sup>	C_regional
Concentration in air	ng m <sup>-3</sup>	0.15	0	0.40
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.175	0.266	1.43 (not used)*
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.018	0.266	0.048 (not used)*
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.018	0.266	0.048 (not used)*
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
Concentration in surface water	µg L <sup>-1</sup>	0.01	0.05	0.05
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.48	0.77	2.64
K <sub>p</sub> sediment/suspended matter = 17 10 <sup>3</sup> L kg <sup>-1</sup>				
Concentration in surface water	µg L <sup>-1</sup>	0.06	0.05	0.24
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.39	0.77	1.54
K <sub>p</sub> sediment/suspended matter = 224 10 <sup>3</sup> L kg <sup>-1</sup>				
Concentration in surface water	µg L <sup>-1</sup>	0.006	0.05	0.03
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.48	0.77	2.76
PEC values		PEC continental		PEC regional
PEC air	ng m <sup>-3</sup>	0.15		0.55
PEC agricultural soil	mg kg <sup>-1</sup> <sub>wwt</sub>	0.441		0.363 (model 2)*
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.284		0.322
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.284		0.322
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.06 (selected)		0.11 (selected)
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	1.25 (selected)		3.88 (selected)
K <sub>p</sub> sediment/suspended matter = 17 10 <sup>3</sup> L kg <sup>-1</sup>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.11		0.35
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	1.16		2.70
K <sub>p</sub> sediment/suspended matter = 224 10 <sup>3</sup> L kg <sup>-1</sup>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.06		0.09
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	1.25		4.01

\* See note in text for discussion;

1) Not including atmospheric deposition;

2) Natural (water and air) or ambient (soil and sediment) background Cd, see Section 3.1.3.4.3.

The estimated C<sub>regional</sub> for agricultural soils is high and exceeds ambient Cd concentrations (see Section 3.1.3.4.4). The PEC's calculated by EUSES 1.0 refer to the 'steady state' concentrations in the environment. Cadmium has a very long residence time in soil (elimination half-life is about 380 years with default parameters) and, therefore, steady state may not be achieved within the next centuries. The assumption in the model is that 10% of the continental emissions take place within the area of a standard regional system, i.e. 10% of the continental emissions (mainly diffuse emissions) are deposited in only 1% of the total European area. Fertiliser application is the dominant source of Cd in agricultural soils (**Table 3.156** and **Table 3.157**) and is 231 tonnes

Cd  $y^{-1}$ . The fraction of surface area that is agricultural is 0.27; therefore the area of agricultural soil in that region is  $0.27 \cdot 4 \cdot 10^4 \text{ km}^2 = 1.08 \cdot 10^4 \text{ km}^2$ . The predicted emission of Cd through fertiliser at the regional scale is 10% of 231 tonnes  $y^{-1}$  or the flux is  $23.1 \text{ tonnes}/(1.08 \cdot 10^4 \text{ km}^2) = 25.5 \text{ g Cd ha } y^{-1}$ . This is about tenfold higher than the emission data found for most European countries (see **Table 3.178**). The parameter values in EUSES could be adjusted but there are a number of reasons to use alternative (existing) soil mass balances (see Section 3.1.3.4.2) rather than EUSES (e.g. modelling the transient state rather than the steady state, modelling Cd losses from background Cd due to crop off take and leaching, etc.). Input and output parameters of the alternative model will be selected to represent different land use (agricultural) scenarios in EU. Therefore,  $PEC_{\text{regional,soil}}$  for agricultural soils will be calculated with an alternative model and the outcome of this model ( $=0.36 \text{ mg Cd/kg}_{\text{ww}}$ ) will be used instead of the values given in **Table 3.15**. The  $PEC_{\text{regional,soil}}$ , calculated with the alternative model is lower than the  $PEC_{\text{continental,soil}}$ , that is calculated with EUSES (see **Table 3.157**). This is unusual but is inherent to the EUSES assumption that Cd output from soil (leaching) is calculated for the added Cd only, i.e. it assumes that ambient Cd in soil cannot be removed from soil. This is incorrect as the availability of added and ambient Cd is not strongly different (see Section 3.2.3) and ambient Cd in soil is the major source of Cd in leachates and crop Cd. The alternative model (see Section 3.1.3.4.2) assumes that all Cd in soil (natural background and historic additions and current additions) can be equally lost from soil by leaching or crop off take, leading to higher Cd output than estimated by EUSES. The EUSES calculations, will, however be used to estimate the  $PEC_{\text{regional,soil}}$  for natural soils and industrial soils because the alternative model has not been used to derive specific values for such soils. No fertiliser emissions take place on these soils, i.e. the regional emissions for natural and industrial soils in EUSES may represent realistic values in contrast with agricultural soils (see above). Even though the EUSES predicted values refer to steady state conditions for the industrial and natural soils (i.e. concentration in a far future), these choices will not affect the conclusion of this risk assessment as will be shown in Section 3.3.

Increasing the  $K_p$  value of suspended matter and sediment by a factor 13, from  $17 \cdot 10^3 \text{ l kg}^{-1}$  to  $224 \cdot 10^3 \text{ l kg}^{-1}$ , decreases the predicted regional Cd concentration in surface water by a factor 4, from  $0.35 \text{ } \mu\text{g L}^{-1}$  to  $0.09 \text{ } \mu\text{g L}^{-1}$ , which corresponds to the background concentration. The  $PEC_{\text{sediment}}$  only increases by a factor 1.5. At lower  $K_p$ , more Cd remains in solution (higher Cd concentration in dissolved fraction) and less Cd will be sorbed on particles (lower Cd concentration in sediment/suspended matter).

Varying the solid-liquid Cd distribution coefficient ( $K_D$ ) in soil tenfold above or below the selected value strongly affects the  $PEC_{\text{soil}}$  values as calculated with EUSES, but affects the  $PEC_{\text{water}}$  by maximally 20%. The  $PEC_{\text{soil}}$  values predicted with EUSES are sensitive to the  $K_D$  because EUSES predicts concentrations at steady states which are reached after varying periods depending on the  $K_D$  (which control the output). In other words,  $PEC_{\text{soils}}$  compared for different  $K_D$  values are compared at different times after contamination.

Cadmium disposal scenarios have been calculated in the Targeted Risk Assessment Report on batteries (see batteries' related sections).

#### Contribution of batteries' related life-cycle steps

In order to compare the global regional Cd emissions with the regional/continental Cd emissions during the life cycle of NiCd batteries an overview of these releases is given in **Tables 3.158-3.167**. The regional/continental cadmium emission of the disposal phase originating from all products containing cadmium in MSW can be found in **Table 3.35** (incineration current situation), **Table 3.39** (incineration future situation) and **Table 3.55** (landfills).

Table 3.158 Summary of regional releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (realistic scenario: 24.4% incineration and 75.6% land-filling. Scenario 10 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>				
	Air	Water	Urban/ind. soil/agr. soil	Ground-water	Total release
1 Manufacturing of NiCd batteries and/or battery packs	29	35.4	0	0	64.4
2 Incorporation into battery powered devices and applications	0	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	1.8	0.1	0	0	1.9
5. Disposal (10-50% NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (24.4%)</li> <li>▪ Land-filling (75.6%)</li> </ul>	32-162 N/A	4-18 5-24	N/A 6-28	N/A 1-6	36-180 12-62
<b>Total</b>	<b>63-193</b>	<b>45-78</b>	<b>6-28</b>	<b>1-6</b>	<b>115-308</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;  
N/A Not applicable.

Table 3.159 Summary of regional releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case scenario: 100% incineration. Scenario 10 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	29	35.4	0	64.4
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	1.8	0.1	0	1.9

Table 3.159 continued overleaf

Table 3.159 continued Summary of regional releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case scenario: 100% incineration. Scenario 10 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
5. Disposal (10-50% NiCd batteries contribution)				
▪ Incineration (100%)	140-701	14-72	N/A	154-773
▪ Land-filling (0%)	N/A	N/A	N/A	N/A
<b>Total</b>	<b>171-730</b>	<b>50-108</b>	<b>0</b>	<b>220-839</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.160 Summary of regional releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case scenario: 100% land-filling. Scenario 10 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>				
	Air	Water	Urban/ind. soil/agr. soil	Ground-water	Total release
1 Manufacturing of NiCd batteries and/or battery packs	29	35.4	0	0	64.4
2 Incorporation into battery powered devices and applications	0	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/	/
4 Recycling					
▪ Collection					
▪ Processing	1.8	0.1	0	0	1.9
▪ Recovery					
5. Disposal (10-50% NiCd batteries contribution)					
▪ Incineration (0%)	N/A	N/A	N/A	N/A	N/A
▪ Land-filling (100%)	N/A	7-26	6-30	1-6	14-62
<b>Total</b>	<b>31</b>	<b>43-62</b>	<b>6-30</b>	<b>1-6</b>	<b>81-129</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.161 Summary of regional releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 13.2 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	29	35.4	0	64.4
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	1.8	0.1	0	1.9
5. Disposal (32 % NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (100%)</li> <li>▪ Land-filling (0%)</li> </ul>	449 N/A	62 N/A	N/A N/A	511 N/A
<b>Total</b>	<b>480</b>	<b>98</b>	<b>0</b>	<b>577</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.162 Summary of regional releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 24 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Regional releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	29	35.4	0	64.4
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	1.8	0.1	0	1.9
5. Disposal (63 % NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (100%)</li> <li>▪ Land-filling (0%)</li> </ul>	883 N/A	218 N/A	N/A N/A	1,101 N/A
<b>Total</b>	<b>914</b>	<b>254</b>	<b>0</b>	<b>1,167</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.163 Summary of continental releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (realistic scenario: 24.4 % incineration and 75.6 % land-filling. Scenario 10 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Continental releases in kg year <sup>-1</sup>				
	Air	Water	Urban/ind. soil/agr. soil	Ground-water	Total release
1 Manufacturing of NiCd batteries and/or battery packs	22	29.6	0	0	51.6
2 Incorporation into battery powered devices and applications	0	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	0	0	0	0	0
5 Disposal (10-60% NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (24.4 %)</li> <li>▪ Land-filling (75.6 %)</li> </ul>	291-1,455 N/A	32-158 44-220	N/A 50-250	N/A 11-52	323-1,613 105-522
<b>Total</b>	<b>313-1,477</b>	<b>106-408</b>	<b>50-250</b>	<b>11-52</b>	<b>479-2,187</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.164 Summary of continental releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case: 100% incineration- Scenario 10 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Continental releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	22	29.9	0	51.6
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	0	0	0	0
5 Disposal (10-50% NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (100%)</li> <li>▪ Land-filling (0%)</li> </ul>	1,262-6,308 N/A	130-649 N/A	N/A N/A	1,392-6,957 N/A
<b>Total</b>	<b>1,284-6,330</b>	<b>160-679</b>	<b>0</b>	<b>1,444-7,009</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.165 Summary of continental releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (worst case scenario: 100% land-filling-Scenario 10 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Continental releases in kg year <sup>-1</sup>				
	Air	Water	Urban/ind. soil/agr. soil	Ground-water	Total release
1 Manufacturing of NiCd batteries and/or battery packs	22	29.6	0	0	51.6
2 Incorporation into battery powered devices and applications	0	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	0	0	0	0	0
5 Disposal (10-50 % NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (0%)</li> <li>▪ Land-filling (100%)</li> </ul>	N/A N/A	N/A 50-238	N/A 54-272	N/A 12-57	N/A 116-567
<b>Total</b>	<b>22</b>	<b>80-268</b>	<b>54-272</b>	<b>12-57</b>	<b>168-619</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.166 Summary of continental releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 13.2 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Continental releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	22	29.6	0	51.6
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	0	0	0	0
5 Disposal (32 % NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (100%)</li> <li>▪ Land-filling (0%)</li> </ul>	4,037 N/A	554 N/A	N/A N/A	4,591 N/A
<b>Total</b>	<b>4,059</b>	<b>584</b>	<b>0</b>	<b>4,643</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

Table 3.167 Summary of continental releases in kg year<sup>-1</sup> of Cd to different environmental compartments during the total life cycle of a NiCd battery (Future scenario: 100% incineration. Scenario 24 mg kg<sup>-1</sup> dry wt.)

Life cycle stages	Continental releases in kg year <sup>-1</sup>			
	Air	Water	Urban/ind. soil/agr. soil	Total release
1 Manufacturing of NiCd batteries and/or battery packs	22	29.6	0	51.6
2 Incorporation into battery powered devices and applications	0	0	0	0
3 Use, recharging and maintenance by end users	/	/	/	/
4 Recycling <ul style="list-style-type: none"> <li>▪ Collection</li> <li>▪ Processing</li> <li>▪ Recovery</li> </ul>	0	0	0	0
5 Disposal (54% NiCd batteries contribution) <ul style="list-style-type: none"> <li>▪ Incineration (100%)</li> <li>▪ Land-filling (0%)</li> </ul>	7,948 N/A	1,960 N/A	N/A N/A	9,908 N/A
<b>Total</b>	<b>7,970</b>	<b>1,990</b>	<b>0</b>	<b>9,960</b>

/ No direct emissions. Indirect cadmium emissions associated with the energy consumption used to recharge the batteries are deemed negligible;

N/A Not applicable.

The  $C_{\text{continental}}$  and  $C_{\text{regional}}$  for the NiCd battery life cycle are calculated with EUSES 1.0. Three different scenarios are considered (realistic case: 24.4% incineration; 75.6% land-filling, worst case incineration: 100% incineration, 0% land-filling and worst case land-filling: 100% land-filling, 0% incineration). The contribution from the NiCd batteries to MSW varies between 0.1 and 0.5 for the current scenarios. In addition the future scenarios with a battery contribution of 32% and 63% have also been calculated. The output of the model gives in fact the predicted added environmental concentrations at continental and regional scale ( $PEC_{\text{con, add}}$  and  $PEC_{\text{reg, add}}$ ). Therefore  $C_{\text{continental}}$  is considered as the calculated  $PEC_{\text{con, add}}$ , and  $C_{\text{regional}}$  is calculated as the difference between  $PEC_{\text{reg, add}}$  and  $PEC_{\text{con, add}}$ .

The results are presented in the **Tables 3.168-3.176**.

#### *Current situation*

It can be concluded that for all scenarios investigated the added regional/continental concentrations calculated on the basis of the emissions from the NiCd batteries life cycle only (indicated in bold) are very small. Due to the rather high Cd background concentrations for some environmental compartments (soil, sediment, surface water) the resulting  $PEC_{\text{regional}}$  and  $PEC_{\text{continental}}$  for these compartments are comparable to the overall regional/continental PECs (see **Table 3.157**).

Table 3.168 Contribution of NiCd batteries (fraction 0.1) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 24.4%; land-filling 75.6%). Scenario 10 mg kg<sup>-1</sup> dry wt

Input continental (anthropogenic):				
amount released to air		313 kg year <sup>-1</sup>		
amount released to surface water		106 kg year <sup>-1</sup>		
amount released to agricultural soil		50 (sludge from STP landfill)		
amount released to natural soil		0		
amount released to industrial soil		0		
Input regional (anthropogenic):				
amount released to air		63 kg year <sup>-1</sup>		
amount released to surface water		45 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		6 (sludge from STP landfill)		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
Results		C_continental concentration	background <sup>(2)</sup>	C_regional
Concentration in air	ng m <sup>-3</sup>	3.8 · 10 <sup>-13</sup>	0	6.8 · 10 <sup>-12</sup>
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0001	0.266	0.00137
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00006	0.266	0.0011
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00006	0.266	0.0011
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
Concentration in surface water	µg L <sup>-1</sup>	1.5 · 10 <sup>-5</sup>	0.05	0.00024
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0007	0.77	0.0122
PEC values		PEC continental		PEC regional
PEC air	ng m <sup>-3</sup>	3.8 · 10 <sup>-13</sup>		7.8 · 10 <sup>-12</sup>
PEC agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.05		0.050
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.77		0.78

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

Table 3.169 Contribution of NiCd batteries (fraction 0.5) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 24.4%, land-filling 75.6%). Scenario 10 mg kg<sup>-1</sup> dry wt

Input continental (anthropogenic)				
amount released to air		1,477 kg year <sup>-1</sup>		
amount released to surface water		408 kg year <sup>-1</sup>		
amount released to agricultural soil		250 (sludge from STP landfill)		
amount released to natural soil		0		
amount released to industrial soil		0		
Input regional (anthropogenic)				
amount released to air		193 kg year <sup>-1</sup>		
amount released to surface water		78 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		28 (sludge from STP landfill)		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
Results		C_continental concentration	background <sup>(2)</sup>	C_regional
Concentration in air	ng m <sup>-3</sup>	1.81 · 10 <sup>-12</sup>	0	2.1 · 10 <sup>-11</sup>
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00046	0.266	0.005
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00028	0.266	0.003
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00028	0.266	0.003
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
Concentration in surface water	µg L <sup>-1</sup>	6.5 · 10 <sup>-5</sup>	0.05	0.0006
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0032	0.77	0.03
PEC values		PEC continental		PEC regional
PEC air	ng m <sup>-3</sup>	1.81 · 10 <sup>-12</sup>		2.3 · 10 <sup>-11</sup>
PEC agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.27
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.27
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.27
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.05		0.051
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.773		0.80

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

Table 3.170 Contribution of NiCd batteries (fraction 0.1) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 100%, land-filling 0%). Scenario 10 mg kg<sup>-1</sup> dry wt

Input continental (anthropogenic)				
amount released to air		1,284 kg year <sup>-1</sup>		
amount released to surface water		160 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		0 (sludge from STP is land-filled)		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
Input regional (anthropogenic)				
amount released to air		171 kg year <sup>-1</sup>		
amount released to surface water		50 kg year <sup>-1</sup>		
amount released to agricultural soil		0		
amount released to natural soil		0		
amount released to industrial soil		0		
Results		C_continental concentration	background <sup>(2)</sup>	C_regional
Concentration in air	ng m <sup>-3</sup>	1.57 · 10 <sup>-12</sup>	0	1.84 · 10 <sup>-11</sup>
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00024	0.266	0.0028
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00025	0.266	0.0029
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00025	0.266	0.0029
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
Concentration in surface water	µg L <sup>-1</sup>	0.00004	0.05	0.0004
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.002	0.77	0.02
PEC values		PEC continental		PEC regional
PEC air	ng m <sup>-3</sup>	1.57 · 10 <sup>-12</sup>		2 · 10 <sup>-11</sup>
PEC agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.269
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.269
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.269
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.050		0.050
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.772		0.79

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

Table 3.171 Contribution of NiCd batteries (fraction 0.5) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (incineration 100%, land-filling 0%). Scenario 10 mg kg<sup>-1</sup> dry wt

Input continental (anthropogenic):				
amount released to air		6,330 kg year <sup>-1</sup>		
amount released to surface water		679 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		0 (sludge from WWTP is land-filled)		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
Input regional (anthropogenic):				
amount released to air		730 kg year <sup>-1</sup>		
amount released to surface water		108 kg year <sup>-1</sup>		
amount released to agricultural soil		0		
amount released to natural soil		0		
amount released to industrial soil		0		
Results:		C_continental concentration	background <sup>(2)</sup>	C_regional
Concentration in air	ng m <sup>-3</sup>	7.8 · 10 <sup>-12</sup>	0	7.9 · 10 <sup>-11</sup>
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0012	0.266	0.012
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0012	0.266	0.012
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0012	0.266	0.012
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
Concentration in surface water	µg L <sup>-1</sup>	0.00019	0.05	0.0015
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0096	0.77	0.074
PEC values		PEC continental		PEC regional
PEC air	ng m <sup>-3</sup>	7.8 · 10 <sup>-12</sup>		8.7 · 10 <sup>-11</sup>
PEC agricultural soil	mg kg <sup>-1</sup> <sub>wwt</sub>	0.27		0.28
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.27		0.28
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.27		0.28
K <sub>p</sub> sediment/suspended matter = 130 10 <sup>3</sup> L kg <sup>-1</sup>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.05		0.052
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.78		0.85

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

Table 3.172 Contribution of NiCd batteries (fraction 0.1) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (land-filling 100%, incineration 0%). Scenario 10 mg kg<sup>-1</sup> dry wt

<b>Input continental (anthropogenic):</b>				
amount released to air		22 kg year <sup>-1</sup>		
amount released to surface water		80 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		54 (sludge from STP landfill)		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
<b>Input regional (anthropogenic):</b>				
amount released to air		31 kg year <sup>-1</sup>		
amount released to surface water		43 kg year <sup>-1</sup>		
amount released to agricultural soil		6 kg year <sup>-1</sup> (sludge from STP (landfill))		
amount released to natural soil		0		
amount released to industrial soil		0		
<b>Results:</b>		<b>C_continental concentration</b>	<b>background<sup>(2)</sup></b>	<b>C_regional</b>
Concentration in air	ng m <sup>-3</sup>	2.7 · 10 <sup>-14</sup>	0	3.3 · 10 <sup>-12</sup>
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	5 · 10 <sup>-5</sup>	0.266	0.00098
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	4.2 · 10 <sup>-6</sup>	0.266	0.00052
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	4.2 · 10 <sup>-6</sup>	0.266	0.00052
<b>K<sub>p</sub> sediment/suspended matter = 130 10<sup>3</sup> L kg<sup>-1</sup></b>				
Concentration in surface water	µg L <sup>-1</sup>	6.4 · 10 <sup>-6</sup>	0.05	0.00019
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00032	0.77	0.0093
<b>PEC values</b>		<b>PEC continental</b>		<b>PEC regional</b>
PEC air	ng m <sup>-3</sup>	2.7 · 10 <sup>-14</sup>		3.3 · 10 <sup>-12</sup>
PEC agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
<b>K<sub>p</sub> sediment/suspended matter = 130 10<sup>3</sup> L kg<sup>-1</sup></b>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.050		0.05
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.770		0.78

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

Table 3.173 Contribution of NiCd batteries (fraction 0.5) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (land-filling 100%, incineration 0%). Scenario 10 mg kg<sup>-1</sup> dry wt

<b>Input continental (anthropogenic):</b>				
amount released to air		22 kg year <sup>-1</sup>		
amount released to surface water		268 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		272 (sludge from STP landfill)		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
<b>Input regional (anthropogenic):</b>				
amount released to air		31 kg year <sup>-1</sup>		
amount released to surface water		62 kg year <sup>-1</sup>		
amount released to agricultural soil		30kg year <sup>-1</sup> (sludge from STP (landfill))		
amount released to natural soil		0		
amount released to industrial soil		0		
<b>Results:</b>		<b>C_continental concentration</b>	<b>background<sup>(2)</sup></b>	<b>C_regional</b>
Concentration in air	ng m <sup>-3</sup>	2.7 · 10 <sup>-14</sup>	0	3.3 · 10 <sup>-12</sup>
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00023	0.266	0.0028
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	4.2 · 10 <sup>-6</sup>	0.266	5.2 · 10 <sup>-4</sup>
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	4.2 · 10 <sup>-6</sup>	0.266	5.2 · 10 <sup>-4</sup>
<b>K<sub>p</sub> sediment/suspended matter = 130 10<sup>3</sup> L kg<sup>-1</sup></b>				
Concentration in surface water	µg L <sup>-1</sup>	2.43 · 10 <sup>-5</sup>	0.05	3.11 · 10 <sup>-4</sup>
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0012	0.77	0.0156
<b>PEC values</b>		<b>PEC continental</b>		<b>PEC regional</b>
PEC air	ng m <sup>-3</sup>	2.7 · 10 <sup>-14</sup>		3.3 · 10 <sup>-12</sup>
PEC agricultural soil	mg kg <sup>-1</sup> <sub>wwt</sub>	0.266		0.296
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.266		0.267
<b>K<sub>p</sub> sediment/suspended matter = 130 10<sup>3</sup> L kg<sup>-1</sup></b>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.05		0.05
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.77		0.79

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

*Future situation (incineration only)*

The overall effect of a future possible increase in the total cadmium content of the MSW up to  $24 \text{ mg kg}^{-1}$  dry wt. is represented in **Table 3.174**.

Table 3.174 Contribution of all MSW waste to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (Future scenario 100% incineration). Scenario  $24 \text{ mg kg}^{-1}$  dry wt

Input continental (anthropogenic):				
amount released to air		12,638 kg year <sup>-1</sup>		
amount released to surface water		3,140.6 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		0		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
Input regional (anthropogenic):				
amount released to air		1,433 kg year <sup>-1</sup>		
amount released to surface water		381.5 kg year <sup>-1</sup>		
amount released to agricultural soil		0		
amount released to natural soil		0		
amount released to industrial soil		0		
Results:		C_continental concentration	background <sup>(2)</sup>	C_regional
Concentration in air	ng m <sup>-3</sup>	$1.55 \cdot 10^{-11}$	0	$1.55 \cdot 10^{-10}$
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0023	0.266	0.023
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0024	0.266	0.024
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0024	0.266	0.024
K <sub>p</sub> sediment/suspended matter = $130 \cdot 10^3 \text{ L kg}^{-1}$				
Concentration in surface water	µg L <sup>-1</sup>	0.00047	0.05	0.0034
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.023	0.77	0.17
PEC values		PEC continental		PEC regional
PEC air	ng m <sup>-3</sup>	$1.55 \cdot 10^{-11}$		$1.7 \cdot 10^{-10}$
PEC agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.268		0.29
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.268		0.29
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.268		0.29
K <sub>p</sub> sediment/suspended matter = $130 \cdot 10^3 \text{ L kg}^{-1}$				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.050		0.054
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.79		0.97

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

It can be concluded that the effect of an increase in MSW cadmium content up to  $24 \text{ mg kg}^{-1}$  dry wt. will have only a minor influence on the currently derived PECs regional for air, water and soil. Therefore there is no need to revise the current PEC reg, water and the PEC reg, air in order to derive the PEC values for the future situation (see Section 3.1.3.2). The specific future contribution of NiCd batteries to the overall PEC is given in **Tables 3.175-3.176** and is overall low.

Table 3.175 Contribution of NiCd batteries (fraction 0.32) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (Future scenario 100% incineration). Scenario  $13.2 \text{ mg kg}^{-1}$  dry wt

Input continental (anthropogenic):				
amount released to air		4,059 kg year <sup>-1</sup>		
amount released to surface water		584 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		0		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
Input regional (anthropogenic):				
amount released to air		480kg year <sup>-1</sup>		
amount released to surface water		98 kg year <sup>-1</sup>		
amount released to agricultural soil		0		
amount released to natural soil		0		
amount released to industrial soil		0		
Results:		C_continental concentration	background <sup>(2)</sup>	C_regional
Concentration in air	ng m <sup>-3</sup>	$4.97 \cdot 10^{-12}$	0	$5.2 \cdot 10^{-11}$
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00074	0.266	0.0077
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00077	0.266	0.0081
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.00077	0.266	0.0081
K <sub>p</sub> sediment/suspended matter = $130 \cdot 10^3 \text{ L kg}^{-1}$				
Concentration in surface water	µg L <sup>-1</sup>	0.00013	0.05	0.001
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0065	0.77	0.053
PEC values		PEC continental		PEC regional
PEC air	ng m <sup>-3</sup>	$4.97 \cdot 10^{-12}$		$5.7 \cdot 10^{-11}$
PEC agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.267		0.274
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.267		0.275
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.267		0.275
K <sub>p</sub> sediment/suspended matter = $130 \cdot 10^3 \text{ L kg}^{-1}$				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.050		0.051
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.777		0.83

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

Table 3.176 Contribution of NiCd batteries (fraction 0.63) to the overall Cd emission values, total concentration and total PEC values for the regional and continental environment (Future scenario 100% incineration). Scenario 24 mg kg<sup>-1</sup> dry wt

<b>Input continental (anthropogenic):</b>				
amount released to air		7,970 kg year <sup>-1</sup>		
amount released to surface water		1,990 kg year <sup>-1</sup>		
amount released to agricultural soil <sup>(1)</sup>		0		
amount released to natural soil <sup>(1)</sup>		0		
amount released to industrial soil <sup>(1)</sup>		0		
<b>Input regional (anthropogenic):</b>				
amount released to air		914 kg year <sup>-1</sup>		
amount released to surface water		254 kg year <sup>-1</sup>		
amount released to agricultural soil		0		
amount released to natural soil		0		
amount released to industrial soil		0		
<b>Results</b>				
		<b>C_continental Concentration</b>	<b>Background<sup>(2)</sup></b>	<b>C_regional</b>
Concentration in air	ng m <sup>-3</sup>	9.77 · 10 <sup>-12</sup>	0	9.86 · 10 <sup>-11</sup>
Concentration in agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0015	0.266	0.015
Concentration in natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0015	0.266	0.015
Concentration in industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.0015	0.266	0.015
<b>K<sub>p</sub> sediment/suspended matter = 130 10<sup>3</sup> L kg<sup>-1</sup></b>				
Concentration in surface water	µg L <sup>-1</sup>	0.00030	0.05	0.0022
Concentration in sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.015	0.77	0.11
<b>PEC values</b>		<b>PEC continental</b>		<b>PEC regional</b>
PEC air	ng m <sup>-3</sup>	9.77 · 10 <sup>-12</sup>		1.1 · 10 <sup>-10</sup>
PEC agricultural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.268		0.28
PEC natural soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.268		0.28
PEC industrial soil	mg kg <sub>wwt</sub> <sup>-1</sup>	0.268		0.28
<b>K<sub>p</sub> sediment/suspended matter = 130 10<sup>3</sup> L kg<sup>-1</sup></b>				
PEC surface water (dissolved fraction)	µg L <sup>-1</sup>	0.050		0.053
PEC sediment	mg kg <sub>wwt</sub> <sup>-1</sup>	0.79		0.90

1) Not including atmospheric deposition;

2) Natural or ambient background Cd, Section 3.1.3.4.3.

### 3.1.3.4.2 An alternative model predicting regional and continental concentrations in agricultural soils

#### Model description

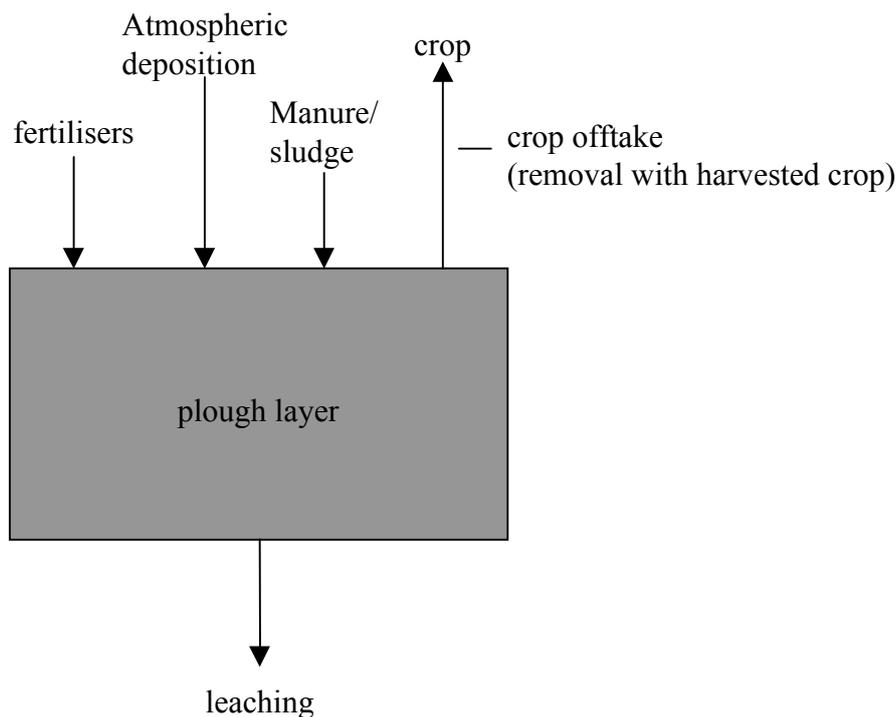
The predicted environmental Cd concentration in soil ( $PEC_{\text{soil}}$ ) is a critical parameter in the risk assessment of Cd. The Cd exposure to the general population is predominantly controlled by dietary intake of Cd (see the human health part of this Risk Assessment Report, in separate document) and, hence, by Cd in crops used for food production. Food Cd concentrations are related to soil Cd and increasing trends in soil Cd may result in increasing trends in dietary intake. It is known that Cd availability is not greatly reduced upon ageing in soil and, therefore, a reduced Cd input in soil does not warrant reduced crop Cd concentrations if soil Cd input still exceeds the Cd losses from the soil (Smolders et al., 1999 and references therein). Whereas Cd in air and in the aquatic compartments have reduced since the late 70's in Europe, soil Cd concentrations may still increase with time (see the human health part of this Risk Assessment Report, in separate document). The relationship between Cd input in the agricultural environment and the resulting Cd concentrations in soil is discussed in this section.

A wealth of information exists on Cd balances in agricultural soils and this information will be used in an alternative soil Cd model. The alternative model is based on the Cd mass balance in the plough layer. The mass balance model calculates trends in soil Cd concentrations from the annual input-output balance and the existing Cd in soil. Cadmium mass balances in agricultural soils have been described before (Tjell and Christensen, 1992, Jensen and Bro-Rasmussen, 1992, Moolenaar and Lexmond, 1998, Hellstrand and Landner, 1998, Kiene, 1999) and are reproduced here with small modifications and updated information. The Cd mass balance offers distinct advantages over the EUSES 1.0 model for predicting soil Cd since the former (i) includes the main pathways of cadmium to and from agricultural soils and (ii) uses local Cd input rates that are measured and (iii) predicts future soil Cd concentrations at any time after  $t=0$  in contrast with the EUSES predictions which are steady state concentrations that may only be reached after several decades. No distinction will be made between regional or continental scales, and the balances will be constructed for a number of conditions that are relevant in European agriculture.

The Cd mass balance is presented graphically in **Figure 3.12**. The Cd input in the agricultural soils mainly originates from the atmospheric deposition, from the fertilisation with phosphate fertilisers and from the application of manure or sludge. The main Cd fluxes out of the plough layer are leaching losses and removal of Cd with the harvested crop (= crop offtake). The input of Cd through manure or sludge application recycles some of the Cd that was previously removed from soil by crop offtake (see below).

It can be discussed that the Cd mass balance should be made on the whole rooting zone (i.e. 1 m) rather than on the plough layer. Losses of Cd by leaching out of the plough layer may indeed not be a reduction of risk for crop uptake as Cd may be retained in deeper horizons where it is still available for root uptake. However, because information on soil properties of deeper horizons is often lacking (e.g. total Cd, pore water concentrations, net water flux out of the rooting zone, rooting depth) it was preferred to focus on the plough layer only.

Fig. 3.12 The Cd input-output balance in agricultural soils



The Cd concentration in the topsoil at year  $i$  ( $Cd_{soil,i}$ ,  $mg\ kg_{dw}^{-1}$ ) is calculated from the net Cd balance (input-output,  $g\ ha^{-1}\ y^{-1}$ ) in year  $i-1$  and the soil Cd concentration in year  $i-1$  as

$$Cd_{soil,i} = Cd_{soil,i-1} + (\text{input-output}) / (1,000 \cdot W_{soil})$$

in which  $W_{soil}$  represents the soil weight of the plough layer ( $kg_{dw}\ ha^{-1}$ ). In all calculations presented below,  $W_{soil}$  is assumed to be  $3 \cdot 10^6\ kg_{dw}$  (i.e., 0.23 m ploughing depth and  $1,300\ kg_{dw}\ m^{-3}$  bulk density). All data are calculated on dry soil weight basis. No data were found for Cd losses by erosion and it is furthermore assumed that these Cd losses are marginal. This model does not assume that a fraction of the wet deposition is lost to the aquatic environment (see assumption in the EUSES 1.0 model). Input and output of Cd are discussed in detail below before predicting future trends in soil Cd.

### Input of Cd in agricultural soil

#### *Fertilisers*

Phosphate fertilisers contain appreciable levels of Cd. The phosphate rock is the source of Cd and only a limited fraction of Cd is lost to the by-products during manufacture of high analysis fertiliser. As a result, the final Cd content in fertilisers, expressed on a unit P basis, is not very different from that in the rock phosphate, and the Cd:P ratio in the rock phosphate determines the fertiliser Cd content (McLaughlin et al., 1996). The Cd:P concentration ratio in rock phosphate varies from 1 to 640  $mg\ Cd/kgP$ . Typical low Cd rock phosphates ( $<100\ mg\ Cd/kgP$ ) are those from Florida and Russia (Kola). Many rock phosphates from Africa (Morocco, Togo) contain average to high Cd levels ( $100-350\ mg\ Cd/kgP$ ). More details on Cd levels in rock phosphates can be found in the compilation made by McLaughlin et al. (1996). The fertiliser industry has developed a process to remove cadmium from the phosphoric acid, which is used in the production of many phosphate fertilisers. However, this process has not been incorporated at industrial scale (IFA, 1998).

Based on data from 1990, the annual Cd input from phosphate fertilisers in the EEC countries was estimated to be 275 tonnes (Landner et al., 1996). This number was obtained from phosphate fertiliser consumption data and Cd concentration in these fertilisers ranging between 128 and 176 mg Cd/kgP in different European countries. Current annual Cd input from phosphate fertiliser is somewhat reduced because of lower fertiliser consumption and because the Cd content in fertiliser is restricted (231 tonnes  $y^{-1}$ , **Table 3.156** and **3.178**). Between 1990 and 1995, annual consumption of phosphate fertilisers in West Europe has reduced from 4.5 million tonnes  $P_2O_5$  to 3.6 million tonnes  $P_2O_5$  (Statistics of the International Fertiliser Industry Association, Paris). During the last decade, several countries adopted limits of Cd content in fertilisers (see **Table 3.177**). **Table 3.178** lists input of Cd to agricultural soils from phosphate fertilisers in Europe. Most of the data are based on the OECD questionnaire (Pearse, 1996). The total Cd load in those EU-16 countries that responded to the 1995 questionnaire is about half of the value that was estimated based on the 1990 data (details not shown). The 1990 data are given for those EU countries that did not respond to the OECD questionnaire.

The annual Cd flux to agricultural soils from phosphate application varies from  $< 0.1g\ ha^{-1}$  (Finland) to  $4.5g\ ha^{-1}$  (The Netherlands). Most of the data are calculated from total P consumption per country, the Cd concentrations in fertilisers and the total arable surface in that country. Since these fluxes are country averages, they do not reflect the variance that exists between cropping systems. The highest Cd flux (The Netherlands) is a local value for an experimental arable farm using only mineral fertilisers (Moolenaar and Lexmond, 1998). The high flux of  $3.2\ g\ Cd\ ha^{-1}y^{-1}$  in France is based on data from the late 1980's. The present use of phosphate rock fertiliser in agriculture is further declining in Europe mainly due to the high production of manure and compost.

Table 3.177 Maximum permissible and currently applied Cd concentrations P fertilisers in European countries (sources: International Fertiliser Industry Association, pers. comm.; Hutton et al., 2001 and references therein); value of Germany is based on a personal communication for the Umweltbundesamt (2002)

Country	Limit (mg Cd/kgP)	From	Currently applied (mg Cd/kgP)
Austria	170 (max 20 g Cd $ha^{-1}2y^{-1}$ on arable land, max 10 g Cd $ha^{-1}2y^{-1}$ on grassland)	1994	57
Belgium	210(voluntary)	1994	75
Denmark	110	1995	34
Finland	50	1992	2.5
Germany	90 (voluntary)	1984	80
Norway	100	1992	5.3
Sweden	100, above 5 mg $kg^{-1}$ P, an environmental fee is raised of 30 SEK per g Cd	1994	< 20
UK			34

Other fertilisers than P fertilisers contain low and negligible Cd concentrations with the exception of trace element fertilisers (McLaughlin et al., 1996). The general impact of these fertilisers on total Cd input in agricultural soils is most likely low. Lime may contain elevated Cd levels where it is a by-product of industrial processing. KEMI (1996) reports Cd levels in Danish lime around 1 mg Cd/kg. An annual lime application of 300 kg is then equivalent to  $0.3\ g\ Cd\ ha^{-1}$ . In Sweden, lime applications are estimated to import  $0.02\ g\ ha^{-1}y^{-1}$  (Hellstrand and Landner, 1998).

Table 3.178 Annual Cd input into agricultural soils from phosphate fertilisers in European countries

Country	Cd input		Source*
	tonne	g ha <sup>-1</sup>	
Austria	2.9	1.1	1
Austria		0.8	7
Belgium	1.5	0.59-1.40	7
Denmark	0.707	0.79-1.44	7
France	92	3.2	2
Finland	0.2	<0.1	1
Finland		0.02-0.1	2
Finland	0.052	0.03	5
Finland		0.025	7
Germany	20.4	1.7	1
Germany <sup>¶</sup>	22.1	1.28	6
Greece	10	2.8	2
Ireland	9	1.8	2
Ireland	7.4	1.67	7
Italy	44	3.0	2
The Netherlands	3	1.5	1
The Netherlands		4.5	3
Norway	0.072	0.12-0.21	7
Portugal	5	1.4	2
Spain	30	1.5	2
Sweden	1.1	0.5	1
Sweden		0.8	2
Sweden		0.20	4
United Kingdom	11.3	0.9	1
United Kingdom		1.0-2.1	7
EEC (1990)	231	2.5	2

\* Source;

- 1) Pearse, 1996, data based on the OECD questionnaire (1995), conversion to Cd flux (g ha<sup>-1</sup> y<sup>-1</sup>) made by Landner et al., 1995;
- 2) Landner et al., 1996, data from 1990;
- 3) Moolenaar and Lexmond, 1998;
- 4) Hellstrand and Landner, 1998;
- 5) Finnish Environment Institute, 1997;
- 6) Kiene, 1999;
- 7) Hutton et al., 2001.

<sup>¶</sup> The current average Cd content in P fertilisers might also be 35 mg Cd/kg P<sub>2</sub>O<sub>5</sub> or 79 mg Cd/kg P (personal communication). At an application rate of 407,000 tonnes P fertiliser per year, this makes a Cd input of 32 tonnes Cd/year.

### *Manure, compost and sludge*

The Cd input into agricultural soil by application of animal manure recycles some of the Cd that was previously taken up by crops. Therefore, Cd input from manure is only a net input into agricultural soil at a continental scale if there is a net import of animal feed crops. No data were found on the net total Cd import in Europe by this pathway. In Sweden, it was estimated that a total of 155 kg Cd is imported annually through animal feeds to farms with animal production. This corresponds to a Cd influx of  $0.05 \text{ g Cd ha}^{-1} \text{ y}^{-1}$  at the national level (Hellstrand and Landner, 1998). Moolenaar and Lexmond (1998) estimated the average net Cd influx from imported animal feed (feed concentrates) as  $0.05 \text{ g Cd ha}^{-1} \text{ y}^{-1}$  for a mixed farming system in The Netherlands. Kiene (1999) calculated the total Cd input via slurry and dung (gross input, no net input) to be 13 tonnes  $\text{y}^{-1}$  in Germany, equivalent to  $0.76 \text{ g Cd ha}^{-1} \text{ y}^{-1}$ . Since these values are much lower than the total Cd load from P fertilisers, it is unlikely that manure application is an important net source of Cd in agriculture at the European level. A similar reasoning is made for compost.

**Table 3.18** shows the Cd input into agricultural soils from manure application. The country average fluxes range from  $0.4\text{-}2.1 \text{ g Cd ha}^{-1} \text{ y}^{-1}$ . In The Netherlands, the Cd input from application of manure and compost is higher than that from the use of mineral fertilisers. This reflects the importance of the intensive livestock industry in that country (Pearse, 1996).

It should be noted that the Cd:P ratio in manure is lower than that in most mineral fertilisers. Moolenaar and Lexmond (1998) report Cd:P ratios of 18 mg Cd/kgP in poultry manure and 47 mg Cd/kgP in cattle manure. Manure samples from Belgium were found to contain 70 mg Cd/kgP (cattle) or 43 mg Cd/kgP (pig, Landner et al., 1996). Therefore, lower Cd input values are found in these farming systems where P from mineral fertiliser is (partly) replaced by P from manure. Local excesses in areas of intensive livestock industry have resulted in almost zero P-fertiliser consumption in some areas (e.g. Flanders, Belgium). In Sweden, more than 50% of total P fertilisation was applied as manure-P in 1994-1995 (Hellstrand and Landner, 1998).

The application of sludge is an important source of Cd where it is applied. In the European countries listed in **Table 3.179**, sewage sludge Cd load is estimated to be lower than fertiliser Cd load (exception: Belgium, **Table 3.179**). The country average fluxes of Cd from sewage sludge application are below  $0.2 \text{ g ha}^{-1} \text{ y}^{-1}$  for those countries for which data were found. However, it must be stressed that these fluxes are country averages (i.e. total load divided by the area of arable land for each country) and are not reflecting the much higher flux where it is applied. These fluxes vary widely and depend on local restrictions on the use of sludge in agriculture. Legislation in EU-16 countries is either based on maximal Cd concentrations in sludge (i.e. 1.2-10 mg Cd/kg) or maximum Cd fluxes (e.g. 3-15  $\text{g ha}^{-1} \text{ y}^{-1}$ ). Some countries restrict a cumulative load (OECD, 1994). Total Cd input from sludge in the EU-16 is estimated to be at least 11.6 tonnes  $\text{y}^{-1}$  (see **Table 3.156**).

Table 3.179 Annual Cd input into agricultural soils from manure, sludge, lime and compost in European countries. All flux data are country averages, i.e. total load divided by area of arable land and, hence, do not reflect the flux where it is applied

Country	Manure and compost		Sludge		Lime	Source
	tonne	g ha <sup>-1</sup>	tonne	g ha <sup>-1</sup>	g ha <sup>-1</sup>	
Austria	1.3		0.1	0.04		1, 3
Austria		0.95				2
Belgium		1.7	> 6			1, 3
Belgium		0.78-2.66		< 0.01		5
Denmark			0.12	0.06		3
Denmark				1.45	0.4	5
Finland	0.2		0.07	0.02-0.05		3
Finland		0.322			0.035	5
Germany			1.27			3
Germany			2.4			1
Germany <sup>¶</sup>	14.1	0.82	3.2	0.19		4
The Netherlands	4.2	2.1	0.4	0.2		1, 3
Norway					0.02	5
Sweden	0.6-0.7	0.05 <sup>(5)</sup>	0.1			1
Sweden			0.13			3
UK		0.4	2.3		0.375-0.503	1

\* Source;

- 1) Pearse, 1996, data based on the OECD questionnaire (1995), conversion to Cd flux (g ha<sup>-1</sup> y<sup>-1</sup>) made by Landner et al., 1996;
- 2) Dachler and Kermaeyr, 1997;
- 3) Source: report from the commission to the council and the European Parliament on the implementation of community waste legislation Directive 86/278/EEC on sewage sludge for the period 1995-1997, data from 1997;
- 4) Kiene (1999);
- 5) Hutton et al. (2001).

### Atmospheric deposition

The atmospheric deposition has been a major source of Cd in European agricultural soils in the past. As a result of increased emission control, atmospheric Cd deposition notably decreased over the last decades (see also Section 3.1.3.4.3). Therefore, only more recent data (> 1985) are included in this section. Total atmospheric deposition includes wet and dry deposition. It can be

<sup>¶</sup> In Germany, the total production of municipal STP sludge is at the moment approximately 3 million tonnes y<sup>-1</sup> (in dry weight). The following table indicates the fate of the sludge (rates are from year 1996). The source for the data is Umweltbundesamt (2001).

Use in agriculture	44.1%
Use for landscaping	11.8%
Composting	10%
Incineration	19.5%
Deposition into landfills	11.4%
Other	3.2%

argued that the dry Cd deposition is not completely a net Cd input into soil on a regional or larger scale. Dry deposition contains Cd that was previously removed from other locations. Total deposition in rural areas is, however, dominated by wet deposition (CCRX, 1991).

**Table 3.180** shows the measured atmospheric Cd deposition in rural areas of different EU-16 countries. The deposition values range between 0.15 and 4 g ha<sup>-1</sup> y<sup>-1</sup>, depending on country and on sampling method. The deposition values generally decrease from North- to Central Europe. No deposition data for southern European countries were found. The EU-16 average is calculated based on total atmospheric emission data at EU-16 scale (see **Table 3.154**) and an area of 3.56 10<sup>6</sup> km<sup>2</sup>. The calculated EU-16 average is 0.4 g ha<sup>-1</sup> y<sup>-1</sup> and is lower than most measured data (e.g. Dutch averages, about 1 g ha<sup>-1</sup> y<sup>-1</sup>). It is unknown if the net deposition is overestimated (even wet-only deposition data can include Cd that is resuspended from soil) or if the estimated total Cd emission is underestimated.

Table 3.180 Atmospheric Cd deposition in rural areas of European countries (measured, Eu-16 average is calculated)

Country	Cd deposition g ha <sup>-1</sup> y <sup>-1</sup>	Comments	Source
Austria	2.6 <sup>1</sup>	Lower Austria (1987)	BFL, 1997
Austria	0.4-0.6 <sup>2</sup>	original reference from 1994	BFL, 1997
Austria	2.1	National mean (wet+dry deposition)	Hutton et al., 2001
Belgium	3.6 <sup>3</sup>	1 rural site at Belgian coast; 1995-1997	VMM, 1999
Belgium	1.1 <sup>5</sup>		Landner et al., 1995
Denmark	1.5 <sup>3</sup>		Jensen and Bro-Rasmussen, 1992
Denmark	1.1 <sup>5</sup>		Landner et al., 1995
Denmark	0.41	bulk deposition (wet deposition)	Hutton et al., 2001
Finland	0.2-0.4 <sup>1</sup>	original reference from 1995	Landner et al., 1995
Finland	0.09-0.35	gradually from north to south Finland	Hutton et al., 2001
France	2 <sup>4</sup>	southern France, 1985-1986	Jensen and Bro-Rasmussen, 1992
Germany	1.4-4.0	field measurements ("wet only" and "bulk")	Bachmann et al., 1998
Germany	4	wet only measurements	Kiene, 1999
The Netherlands	1.2 <sup>4</sup>	average of 14 sampling points in 1992	CCRX, 1994
The Netherlands	0.9 <sup>5</sup>		Landner et al., 1995
Norway	0.2-1.2	north -south, 1985-1986	Jensen and Bro-Rasmussen, 1992
Norway	0.37	average value for Norway	Hutton et al., 2001
Sweden	0.6-1.1 <sup>2</sup>	two districts in Sweden, original reference from 1994	Eriksson et al., 1996
Sweden	0.15-0.6 <sup>4</sup>	north -south, 1996	Hellstrand and Landner, 1998
Sweden	0.4-1.5 <sup>5</sup>		Landner et al., 1995

Table 3.180 continued overleaf

Table 3.180 continued Atmospheric Cd deposition in rural areas of European countries (measured, Eu-16 average is calculated)

Country	Cd deposition g ha <sup>-1</sup> y <sup>-1</sup>	Comments	Source
UK	2 <sup>5</sup>		Landner et al., 1995
UK	1.8	median value of 29 rural sites	Hutton et al., 2001
EU-16-average predicted	0.4	126 tonnes y <sup>-1</sup> deposited over 3.56 10 <sup>6</sup> km <sup>2</sup>	This study

- 1) Methodology unknown;
- 2) Deposition calculated from Cd in moss;
- 3) Total deposition;
- 4) Wet deposition;
- 5) Based on OECD questionnaire (Pearse, 1996) with recalculations made in Landner et al., 1995.

### Output of Cd from agricultural soils

#### *Leaching*

The Cd losses by leaching out of the plough layer are difficult to quantify in agricultural soils. The estimated losses of Cd from the plough layer are generally smaller than 1% per year (Landner et al., 1995). Therefore, downward movement of Cd is only detectable in long-term observations.

Detailed Cd leaching studies at the field scale have been performed for a number of polluted soils (e.g. Streck and Richter, 1997 and references therein). No such studies or model predictions were found for agricultural soils at an ambient Cd concentration. Therefore, Cd losses by leaching are estimated here based on a simplified model that is commonly used in Cd mass balance studies. The annual leaching losses  $L$  (g Cd ha<sup>-1</sup>y<sup>-1</sup>) is estimated as the Cd concentrations in pore water multiplied by the annual net water flux (also called the precipitation excess), formally:

$$L = [Cd]_l 10F$$

in which  $[Cd]_l$  represents the Cd concentration in the liquid ( $\mu\text{g L}^{-1}$ ) and  $F$  is the annual precipitation excess (m). A typical value for  $F$  in temperate regions is  $0.2 \text{ m y}^{-1}$ . The concentration of Cd in pore water is calculated from the solid-liquid distribution coefficient  $K_D$  (L/kg) and the soil Cd concentration (see Section 3.1.3.1.4).

Despite a high correlation between  $K_D$  and soil properties (see **Table 3.88**, Section 3.1.3.1.4), large systematic variations in predicted  $K_D$  values exist among the different studies. As an examples, for a typical arable soil of the temperate regions with pH 6.5 and 2% OM (1.2%C), predicted  $K_D$  values range between 90 and 1,560 L kg<sup>-1</sup> depending on the regression equations. Effectively, the uncertainty in the  $K_D$  results in an equal uncertainty in the predicted annual Cd losses per unit of excess precipitation.

**Table 3.181** shows the predicted Cd leaching from an agricultural soil at an ambient Cd concentration for different soil properties. This table shows that the predicted Cd leaching strongly depends on the soil pH and on the type of regression equation. As will be shown below, this uncertainty will imply that it is impossible to predict if Cd will accumulate in soil or not in low Cd input cropping systems. Therefore, we feel that more accurately estimating average Cd losses by leaching is critical for predicting future trends in average soil Cd in Europe.

There is little experimental evidence that could be used to validate the model that estimates Cd leaching losses. The predicted annual Cd losses from the plough layer ( $0.3\text{-}26 \text{ g ha}^{-1} \text{ y}^{-1}$ ) are generally higher than those estimated in most other soil Cd balances (typically  $< 2 \text{ g ha}^{-1} \text{ y}^{-1}$ , Tjell and Christensen, 1992, Jensen and Bro-Rasmussen, 1992, Moolenaar and Lexmond, 1998, Hellstrand and Landner, 1998). Nicholson et al., (1996) estimated Cd leaching from the unlimed long-term park grass soils of Rothamsted (UK) using the Cd mass balance. The increase of Cd in the 0-22.5 cm horizon during 1913-1983 was compared with the Cd input by atmospheric deposition (estimated) and by phosphate fertilisers (based on analysis). After accounting for a small (measured) Cd loss by crop offtake, the leaching losses were found to vary between  $0.7\text{-}3.1 \text{ g ha}^{-1} \text{ y}^{-1}$  (untreated) and  $2.4\text{-}4.9 \text{ g ha}^{-1} \text{ y}^{-1}$  (P-treated). The authors estimated a range for the atmospheric Cd input from the average and maximum net annual increase of Cd in 4 different untreated plots of the Rothamsted long-term trials (Jones et al., 1987). Obviously, even the maximum net Cd accumulation in these plots (i.e.  $5.4 \text{ g ha}^{-1} \text{ y}^{-1}$ ) is likely lower than the atmospheric Cd input because of Cd losses from these plots. Therefore, the highest estimated Cd leaching from the park grass plots (i.e.  $3.1\text{-}4.9 \text{ g ha}^{-1} \text{ y}^{-1}$ ) may still be conservative values. Using our model, we calculated the average annual Cd losses from the P treated plots from the soil properties (soil pH values as given in Nicholson et al., 1994), 0.2 m annual water flux out of the topsoil and the  $K_D$  estimated with the model of Römken and Salomons, 1998. Our model predicted  $7.1 \text{ g ha}^{-1} \text{ y}^{-1}$  for the P treated plots, i.e. not too much higher than the  $4.9 \text{ g ha}^{-1} \text{ y}^{-1}$  estimated by Nicholson et al., 1996.

Table 3.181 The annual Cd leaching from the plough layer (L, in  $\text{g ha}^{-1}\text{y}^{-1}$ ). The Cd leaching is calculated for a soil with  $0.3 \text{ mg kg}^{-1}$  total Cd (background concentration) and an annual net water flux out of the plough layer of 0.2 m. The different models used for estimating the  $K_D$  of Cd in soil are referred to in Table 3.88

Soil pH	%OM	$K_D$ model	L $\text{g ha}^{-1} \text{ y}^{-1}$
6.5	2	Christensen, 1989	2.0
6.5	4		1.4
5.5	2		6.6
6.5	2	Lee et al., 1996	1.6
6.5	4		0.8
5.5	2		5.3
6.5	2	Gerritse and Van Driel, 1984	2.8
6.5	4		1.4
5.5	2		10.8
6.5	2	Römken and Salomons, 1998	2.0
6.5	4		2.0
5.5	2		7.2
6.5	2	McBride et al., 1997	0.4
6.5	4		0.3
5.5	2		1.2

Table 3.181 continued overleaf

Table 3.181 continued The annual Cd leaching from the plough layer (L, in  $\text{g ha}^{-1}\text{y}^{-1}$ ). The Cd leaching is calculated for a soil with  $0.3 \text{ mg kg}^{-1}$  total Cd (background concentration) and an annual net water flux out of the plough layer of 0.2 m. The different models used for estimating the  $K_D$  of Cd in soil are referred to in Table 3.88

Soil pH	%OM	KD model	L $\text{g ha}^{-1} \text{y}^{-1}$
6.5	2	Smolders et al. (in situ data, unpublished)	0.9
6.5	4		0.9
5.5	2		4.0
6.5	2	Smolders et al. (adsorption data, unpublished)	6.6
6.5	4		3.4
5.5	2		26

### Crop offtake

Crop offtake of Cd is the amount of Cd that is removed from the soil with the harvested part of the plant. The crop offtake of Cd is generally small in agricultural conditions and does not largely influence the soil Cd balance. The crop offtake in three different crop rotation systems in agricultural districts of Sweden varied from  $0.17$  to  $0.62 \text{ g Cd ha}^{-1} \text{y}^{-1}$  (averages for each rotation, Eriksson et al., 1996). The crops included in the rotations were carrots, potatoes, barley, oil seed, oat and winter wheat. Detailed farm-gate and field-scale Cd balances were calculated for arable, dairy and mixed farming systems at two locations in The Netherlands (Moolenaar and Lexmond, 1998). On the arable farm, crop offtake varied from  $0.6$ - $0.9 \text{ g Cd ha}^{-1} \text{y}^{-1}$  (averages for a rotation including potato, sugar beets, chicory and onion, winter wheat and spring barley). Crop offtake in grassland was  $1.4 \text{ g Cd ha}^{-1} \text{y}^{-1}$  but most of this returns to the soil as manure. The farm-gate balance of the mixed-farming system showed that the net Cd loss with milk and meat/animal was less than  $0.01 \text{ g Cd ha}^{-1} \text{y}^{-1}$ . The crop offtake can also be calculated from typical yields and crop Cd concentrations. **Table 3.182** shows such estimates for wheat grain and potatoes in several European countries. It can be deduced from the table that harvesting wheat grain removes, on average,  $0.4 \text{ g ha}^{-1}$ . A potato yield removes around  $1.2 \text{ g Cd ha}^{-1}$ .

Table 3.182 The Cd content in selected agricultural crops and the estimated annual crop offtake

Crop	Crop Cd <sup>†</sup> $\mu\text{g kg}^{-1}$	Comment	Typical yield (tonnes)	Crop offtake $\text{g ha}^{-1}$
wheat grain	38 (M)	UK <sup>2</sup> , n=393	7.7	0.29
	58 (M)	France <sup>3</sup> , n=16	6.5	0.38
	70 (M)	The Netherlands <sup>4</sup> , n=84	8.8	0.62
	40-69 (M)	Sweden <sup>1</sup> , n=354, averages of three data sets	6.0	0.24-0.41
	56 (M)	Germany <sup>5</sup> , n=886	6.9	0.39
potato tuber	51 (M)	Sweden <sup>1</sup> , n=69	30	1.53
	30 (M)	The Netherlands <sup>4</sup> , n=94	35	1.05

† Mean;

m Median;

Source;

1) Eriksson et al., 1996;

2) Chaudri et al., 1995;

3) Mench et al., 1997;

4) Wiersma et al., 1986;

5) Weigert et al., 1984.

For modelling purposes, crop offtake is assumed proportional to soil Cd and, hence, future crop offtake values are changed proportionally to the change in soil Cd. No changes in crop offtake are assumed with long-term changes in soil properties (e.g. soil pH).

#### Future trends in soil Cd: the regional $PEC_{soil}$ in 8 different scenarios

The Cd mass balance in the plough layer will be calculated for a number of scenarios representative of European agriculture. These scenarios are indicative for average conditions.

Three different input scenarios are combined with a low or high output scenario each. The difference in output scenario is mainly based on a different soil pH, either pH 6.8 (low output) or pH 5.8 (high output). Leaching losses are calculated with the  $K_D$  model of Römken and Salomons (1998) and assuming 0.2 m annual water flux out of the plough layer and 2% organic matter. The soil Cd concentration at  $t=0$  is derived from measured Cd concentrations in areas well away from point sources (see **Table 3.190**). The Cd content in soil at  $t=0$  refers to natural Cd (from geological origin) and some Cd that was added in the past (fertiliser Cd and Cd from atmospheric deposition).

The low input scenarios 1 and 2 represent agricultural conditions of northern Europe (Sweden, Finland and Denmark) and Cd input/offtake and soil Cd data were selected to correspond with preceding tables. Scenario 3 and 4 represent central European agricultural conditions (e.g. UK, France, The Netherlands, Germany) using average Cd fluxes from P fertilisers and atmospheric deposition in these countries. The offtake values were selected from Moolenaar and Lexmond, 1998 (either mixed farming or arable farming) and a typical soil Cd concentration was selected for these countries. Scenario 5 and 6 represents high input farming systems, which may be found in e.g. wheat/corn rotations. Applications of P in these systems are typically 30 kg P ha<sup>-1</sup> (i.e. data of France, Italy and Germany, Harris, 1998) and it is assumed that the P fertiliser contains 150 mg Cd/kg P. The atmospheric deposition (3 g Cd ha<sup>-1</sup> y<sup>-1</sup>) represents a high value for European rural areas (see above). The offtake is low and represents farming systems with high Cd recycling (i.e. corn used for roughage). A worst case scenario 7 is included: this scenario may represent land use in some Mediterranean agricultural areas where very low output prevails. The Mediterranean biogeographical region comprises up to 9% of the Pan-European area (Roekaerts, 2002). This region can be characterised by a limited excess drainage (0.05m/year rather than 0.2 m/year; note default value of TGD is 0.175 m/year) and a large  $K_d$  value (calcareous soils which prevail in Mediterranean areas, pH 7.5). The scenario is considered as worst case because the very low output is coupled with high input as described above. High input of fertiliser is unusual for these areas because of lower crop yields (unless combined with irrigation, for which the low excess drainage may not be realistic). Data of Cd deposition in these areas are not available, and a realistic worst case assumption of 3 g/ha/year was made. The scenario 8 is an attempt to represent an average for the whole of Europe. Average Cd inputs are derived from the tables given above and the EU-16 average Cd deposition is based on the net emission at the regional scale (see **Table 3.180**). The average Cd input from fertiliser may be based on the 1990 data and, as discussed above, this value may overestimate current input of Cd from fertilisers. The average Cd output is difficult to estimate. The leaching losses are based on a soil pH of 6.5 and the crop offtake is an average for scenarios 1-6.

The soil Cd is predicted to increase in 6 scenarios (between 2.8 and 46%) and decrease in two scenarios (11 and 19%) after 60 years of exposure to current inputs. At the EU scale (average), soil Cd is predicted to increase by 6% after 60 years. This increase is lower than the historical increasing trends in soil Cd in Europe (see the human health part of this Risk Assessment Report, in separate document). The (realistic) worst case of scenario (5) predicts soil Cd concentration =

0.411 mg Cd/kg<sub>dw</sub>. This is equivalent to 0.363 mg Cd/kg<sub>ww</sub> (standard environment characteristics, TGD) and is used as the PEC<sub>regional,soil</sub>.

The soil Cd concentration at t=0 has a major impact on the PEC<sub>soil</sub>. This is obviously related to the fact that the amount of background Cd in soil is several folds higher than the annual Cd addition. For example, the 90<sup>th</sup> percentile of the Cd concentrations in cultivated soils in France is 0.8 mg kg<sup>-1</sup> (Baize, 1999; see **Table 3.190**). This concentration would increase to 0.875 mg Cd/kg<sub>dw</sub> after 60 years, assuming a high input/low output scenario as in scenario 5. However, we do not prefer to use upper percentiles (=local situation) as a realistic worst case for PEC<sub>regional</sub> since the risk scenarios in soil (see Section 3.3) are mainly important for human food chain contamination (regional/continental) and food items are not grown in one location in this scenario (see the human health part of this Risk Assessment Report, in separate document). The upper percentiles of background Cd in soil are certainly more relevant for local exposure to Cd but the PEC<sub>local,soil</sub> should then be contrasted to PNEC values derived for these scenarios (e.g. human diets dominated by home-grown food, see the human health part of this Risk Assessment Report, in separate document). The PEC<sub>local,soil</sub> values obviously span a wider range than the PEC<sub>regional,soil</sub> values in **Table 3.183**. It can be shown that the risk characterisation of diffuse Cd emissions in agricultural scenarios (fertiliser Cd, atmospheric deposition) is controlled by the regional and continental assessment and not by local risk assessment, even if the local Cd background is 3-4 fold larger than assumed in **Table 3.183**. Moreover, soils with high natural background Cd are usually soils that have large clay content and have a high pH, both factors known to reduce risk of Cd for foodchain contamination (see the human health part of this Risk Assessment Report, in separate document) or secondary poisoning (see Section 3.2.7) and which are the critical pathways of Cd in soil.

In the context of the continued review, under the Fertilisers Directive (76/116/EEC), of risks posed to human health and the environment by cadmium in fertilisers, Member States were encouraged to perform national risk assessments during summer/autumn 2000. To ensure conformity, a suggested template of procedures had been established. Eight Member States (Austria, Belgium, Denmark, Finland, Greece, Ireland, Sweden and the United Kingdom) and Norway submitted risk assessments. These were analysed and summarised in a consultants report to the Commission (Hutton et al.) in January 2001.

Compared to the accumulation calculations performed within this report, a longer time horizon, 100 years, was chosen by most Member States. The time period (60 or 100 years) only weakly affects the PEC<sub>soil</sub>. As an example, the EU average PEC<sub>soil</sub> (60 years) = 0.318 mg Cd/kg dw whereas the PEC<sub>soil</sub> (100 years) = 0.329 mg Cd/kg d.w. Different algorithms for K<sub>D</sub> were chosen based on national soil properties. Also, a majority of the MS modelled scenarios with different cadmium concentration in fertilisers, e.g. “low”, national average” and “high/EU average”. Finally, many MS chose to use different input values for cadmium via fertilisers in order to assess the importance of crop rotation or regional agriculture practices.

Predictions of PEC<sub>soil</sub> after 60 or 100 years, performed by Austria, Belgium, Denmark, Finland, Norway, Sweden and the UK are given as an illustration in **Table 3.22**. Ireland presented a risk assessment using default input parameters, while the input and output values in the Greek risk assessment are difficult to comprehend. Therefore the results of these assessments are not integrated in **Table 3.183**.

Despite the differences in input values, the consultant found the following consistent trends in the various assessments, based on current fertiliser input levels<sup>46</sup>:

- for low fertiliser cadmium concentrations (between 2.5 to 40 mg Cd/kg P), cadmium in soil tends to accumulate relatively slowly, or decreases after 100 years of application due to net removal rates (leaching, crop uptake) exceeding inputs
- for fertilisers with Cd concentrations of 60 mg kg<sup>-1</sup> P and above, accumulation in agricultural soils over 100 years is more pronounced (between 17 and 43% increase after 100 years).

The future soil Cd content might be slightly overpredicted by some countries because they included animal manure as a net input in soil. Cadmium input from manure is, however, only a net input at the country level if there is a net import of minerals added to animal feed. The Cd input in soil from animal feed is low compared to the input from P-fertilisers (see **Table 3.183**). The soil Cd content in some Belgian regions is predicted to increase by more than a factor two over 60 years. These values are based on Cd deposition data near former industrial sites (atmospheric deposition 36 g ha<sup>-1</sup> y<sup>-1</sup>) where resuspension is a possible source of atmospheric Cd.

Low Cd input values through fertiliser addition are currently applied in northern European countries (Sweden, Finland and Denmark). As seen from **Table 3.177**, these countries introduced maximum permissible Cd concentrations in the mid 1990's. The calculations represent the present day situation, where risk reduction measures strongly influence the Cd input by fertilisers, and not a worst case scenario.

Some countries have predicted steady state soil Cd concentrations which are significantly above those calculated by the alternative model for the 6 regions (e.g. Austria: soil Cd at steady state = 1.13 mg Cd/kg dw). But steady state concentrations are only reached after very long periods (e.g. about 930 years, recalculated for Austrian data) during which soil properties (pH) land use (crop offtake) may change and that undoubtedly affect the soil Cd balance. In other words, the assumption of constant parameter values in predicting soil Cd concentrations in the very far future is highly questionable.

It is difficult to judge if the Cd balance in European soils is at a steady state or not. Current European Cd inputs in agricultural soil (2-3 g ha<sup>-1</sup> y<sup>-1</sup>) have strongly reduced from historical inputs (e.g. 7-9 g ha<sup>-1</sup> y<sup>-1</sup> in Denmark between 1923-1980, Tjell and Christensen, 1985; at least 8-10 g ha<sup>-1</sup> y<sup>-1</sup> in UK, P treated park grass soils 1913-1983, Nicholson et al., 1996). In the low input scenarios, predicted trends are extremely sensitive to changes in soil pH. Lowering the soil pH increases predicted Cd leaching and results in a predicted downward trend of soil Cd. No other soil Cd balance has predicted a reduction in soil Cd.

It can be concluded that the current Cd input in European agricultural soils is reduced from historical input and that the European soil Cd concentration is predicted to change by between a 19% decrease to a 46% increase in 60 years. However, there is always uncertainty in the input-output data and it now appears that estimating Cd leaching losses is critical for drawing firm conclusions. An average steady state obviously does not preclude that a strong increase in soil Cd is found in local areas. The steady state in soil Cd may not be reached in agricultural

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<sup>46</sup> MS have also made predictions for fertiliser Cd concentrations that are larger than currently applied values to evaluate the effect of new regulations on future trends in soil Cd. For example, Denmark predicted that future soil Cd may increase by 53%-74% in 100 years if fertiliser Cd contains 140 mg Cd/kg P (60 mg Cd/kg P205) and which is fourfold above the current concentrations in Denmark.

systems that have characteristics as given in scenario 5, 6 and 7. These systems have a high Cd input from fertilisers, even where fertiliser Cd is below the legal limits of e.g. Germany and Belgium.

Predicting future trends in crop Cd is even more difficult than predicting future trends in soil Cd. It is very likely, for example, that soil acidification may have more effect on crop Cd concentrations than the slow changes in soil Cd. Trends in crop Cd concentrations are not included in this report because annual variations in crop Cd can be higher than changes over long periods of time. Andersson and Bingefors (1985) found an increase of a factor two in grain Cd content (winter wheat) between 1918 and 1980, while the annual variations in the grain Cd content were up to a factor five. Large annual variations in crop Cd are also observed by Kjellstrom et al. (1975) (see the human health part of this Risk Assessment Report, in separate document). Soil Cd typically explains a minor part of the variance in crop Cd. As an example: Swedish field data show that soil Cd only explains 3-19% of the variability of crop Cd concentrations (Eriksson et al., 1996).

Table 3.183 The predicted environmental concentration of Cd in agricultural soil ( $PEC_{soil}$ , -plough layer only) after 60 years of exposure to current Cd influx in agricultural soils. Seven scenarios are selected that may be representative for European agriculture. Predictions are made using the Cd mass balance approach described in the text. The full description of the scenarios is given in the text

scenario	Cd input ( $g\ ha^{-1}\ y^{-1}$ )				Cd output ( $g\ ha^{-1}\ y^{-1}$ ) at t=0			net Cd balance	Cd soil at t=0	$PEC_{soil}$ after 60 years
	P fertiliser	Atmospheric deposition	Animal feed	Total	Crop offtake	Leaching	Total	$g\ ha^{-1}\ y^{-1}$	$mg\ kg^{-1}_{dw}$	
1. low input-low output	1.1	0.6	0.05	1.75	0.3	1.1	1.4	+0.35	0.250	0.257
2. low input-high output	1.1	0.6	0.05	1.75	0.5	4.1	4.6	-2.85	0.250	0.203
3. average input-low output	2.0	2.0	0.1	4.1	0.66	1.6	2.26	+1.84	0.350	0.385
4. average input-high output	2.0	2.0	0.1	4.1	0.8	5.7	6.5	—4	0.350	0.310
5. high input-low output	4.5	3.0	-	7.5	0.3	1.3	1.6	+5.9	0.300	0.411
6. high input-high output	4.5	3.0	-	7.5	0.3	4.9	5.2	+2.3	0.300	0.339
7. high input-very low output (worst case Mediterranean)	4.5	3.0	-	7.5	0.3	0.1	0.4	+7.4	0.300	0.439
8. EU average	2.5	0.4 <sup>(1)</sup>	0.05	2.95	0.5	2.0	2.5	+0.45	0.300	0.318

Table 3.183 continued overleaf

Table 3.183 continued The predicted environmental concentration of Cd in agricultural soil (PEC<sub>soil</sub>, -plough layer only) after 60 years of exposure to current Cd influx in agricultural soils. Seven scenarios are selected that may be representative for European agriculture. Predictions are made using the Cd mass balance approach described in the text. The full description of the scenarios is given in the text

Predicted environmental concentrations in agricultural soils as calculated <sup>(3)</sup> in the Risk assessments on Cd in fertilisers performed by EU Member States and Norway (Hutton et al., 2001) at current Cd application rates through fertilisers (Table 3.177)			
	Current Cd concentration in the soil	PEC <sub>soil</sub> after 60 years (mg kg <sup>-1</sup> <sub>dw</sub> )	PEC <sub>soil</sub> after 100 years (mg kg <sup>-1</sup> <sub>dw</sub> )
UK	0.23	-	0.27
Austria	0.242	-	0.345
Belgium	0.22-0.35	0.114-0.772 <sup>(2)</sup>	-
Denmark	0.144-0.249	-	0.076-0.273
Finland	0.21	-	0.145-0.228
Sweden	0.23 (wheat + potatoes) 0.33 (carrots)	-	0.20-0.30 (wheat + potatoes) <sup>(4)</sup> 0.30-0.35 (carrots)
Norway	0.24	-	0.19-0.21

- 1) 126 tonnes y<sup>-1</sup> deposited over 3.56 10<sup>6</sup> km<sup>2</sup> = 0.4 g ha<sup>-1</sup> y<sup>-1</sup>;
- 2) Based on Cd deposition data near former industrial sites (atmospheric deposition 36 g ha<sup>-1</sup> y<sup>-1</sup>) where resuspension is a possible source of atmospheric Cd;
- 3) Calculations are based on net Cd inputs from different sources (P-fertilisers, atmospheric deposition, manure, sludge application and/or liming). Cadmium output is based on Cd offtake by several crops and leaching estimated by different K<sub>D</sub> models;
- 4) Calculations based on the algorithm of McBride et al. (1997).

### 3.1.3.4.3 Measured regional data in the environment

#### Aquatic systems

Cadmium enters rivers and lakes because of both natural and anthropogenic factors. Weathering and erosion processes may wash Cd from geological sources into rivers. Industrial and municipal effluents are discharged into rivers and lakes. There is direct deposition of atmospheric Cd onto surface waters as well as run-off of Cd-bearing water from the soil and from landfills. Acidification of soil and water may increase the mobilisation of Cd in the environment which would otherwise remain adsorbed to rock and soil particles (Pearse, 1996). Measured Cd concentrations in freshwaters and in suspended matter are presented in **Tables 3.184, 3.185 and 3.186**. Measured Cd concentrations in freshwater sediments are presented in **Table 3.187**.

Most of the data presented in these tables originate from national or regional monitoring programs. The following data treatment was applied to derive statistics (e.g. 90<sup>th</sup> percentiles) from the data in the following consecutive steps:

- Data are sorted per country as a surrogate for region
- When measurements were reported as being smaller than the detection limit (DL), a value of half the DL was assigned to this measurement.
- Outliers: a statistical approach was used for defining outliers in an attempt to exclude the contribution of local emissions from diffuse emissions. The uncertainty related to either including or excluding outliers will be taken forward to the risk characterisation where the effect of outlier analysis on the risk factors will be compared<sup>47</sup>. In this section, however, percentiles only refer to the database obtained after outlier exclusion. Outliers are selected based on the TGD (EC, 2003) using the equation:  $\log(X_i) > \log(P75) + K(\log(P75) - \log(P25))$  where  $X_i$  is the concentration above which a measured value may be considered an outlier,  $P_i$  is the value of the  $i^{\text{th}}$  percentile of the statistic and  $K$  is a scaling factor. This filtering of data with a scaling factor  $K = 1.5$  is used in most statistical packages, but the factor can be subject dependent. A value of 1.5 was chosen in this report. Outliers are detected by calculating the P75 and P25 statistics on the entire dataset, i.e. not per sampling site. Outlier calculation per sampling site detects measurement errors.
- Derivation of statistics: the revised TGD (EC, 2003) recommends calculating the  $PEC_{\text{regional}}$  as the mean of 90<sup>th</sup> percentiles within a region. The 90<sup>th</sup> percentiles refer to observations at one sampling site. Almost all data referred to below do not give data organised per sampling site but rather list data without reference to a site. In order of preference we calculated the statistics as:  $x^{\text{th}}$  percentile = mean of  $x^{\text{th}}$  percentiles within the region; if this was not possible, then  $x^{\text{th}}$  percentile =  $x^{\text{th}}$  percentile of the data within the dataset. The P90 value is calculated from the rank in the observed frequency distribution and not from the rank in a curve fitted to the frequency distribution. This means that the P90 is not affected by the exact values of data at lower percentiles
- Data are presented as dissolved (D) concentrations. If the original data refer to total concentrations, then dissolved concentrations are estimated (ED) assuming that the dissolved Cd concentration in freshwater is 33% of the total Cd concentration in water (see Section 3.1.2.3.1: dissolved fraction =  $1/((1+K_p \cdot C_{\text{susp}} \cdot 10^{-6}))$  with  $K_p = 130 \cdot 10^3 \text{ L kg}^{-1}$ ,  $C_{\text{susp}} = 15 \text{ mg L}^{-1}$ ; TGD, 1996). In Swedish oligotrophic lakes, about 60-100% of the Cd is dissolved (< 2.4 nm) at pH 4.5-6.0 and about 10-60% at pH 6-7 (Parkman et al., 1998).

<sup>47</sup> However, the methodology proposed by the rapporteur i.e. exclusion of outliers that are detected by statistical approach only was not endorsed by MSs (see ECB document ‘mi\_302+303\_tc0404\_env’).

Fractionation is unknown (U) for the large Scandinavian database of Skjelkvåle et al. (1999). For all these data, the dissolved fraction is set at 100%. As will be shown in the risk characterisation, this conservative assumption does not affect the conclusion for regional risk.

Priority is given to the most recent data for risk characterisation. All data below are drawn from the original databases and secondary information about regional averages (or 90P values) are not used if the background information (i.e. detection or reporting limit<sup>48</sup>) is missing. The data of surface water are classified in reliability classes (RI1: most reliable, RI4, least reliable) to aid the risk characterisation. The detection limit (DL) is most critical. As the PNEC<sub>water</sub> is  $0.19 \mu\text{g L}^{-1}$  (see Section 3.2), we propose that a dataset with  $\text{DL} \geq 0.1 \mu\text{g L}^{-1}$  (dissolved) is less reliable within the risk characterisation.

- RI 1: the detection limit is  $< 0.1 \mu\text{g L}^{-1}$  (dissolved), the Cd fractionation is known as dissolved or estimated dissolved and water hardness data are known. This allows the risk characterisation to be corrected for water hardness.
- RI 2: the detection limit is  $< 0.1 \mu\text{g L}^{-1}$  (dissolved), the Cd fractionation is known as dissolved or estimated dissolved; hardness is unknown and no correction for hardness can be made.
- RI 3: the detection limit is  $< 0.1 \mu\text{g L}^{-1}$  (dissolved), the Cd fractionation is known as dissolved, estimated dissolved or is assumed as dissolved when no information regarding the Cd fractionation was given.
- RI 4: the detection limit  $\geq 0.1 \mu\text{g L}^{-1}$  (dissolved) and data are considered on a case-by-case basis because the detection limit is too large.

In what follows the datasets of various European countries are described and discussed. Several databases contain series with different detection limits and a specific data analysis was performed, discussed below, to allow classification in the above-mentioned reliability classes. Data are presented in **Tables 3.184, 3.186 and 3.187**. The underlined values are taken forward to the risk characterisation and are summarised in **Table 3.185** and **Table 3.188** in which the average of 90<sup>th</sup> percentiles are calculated per region. .

- Belgium

Flanders region: Monitoring data of total cadmium were obtained from the Flemish Environment Agency (VMM; <http://www.vmm.be>). For the purpose of this risk assessment, data for the years 2000-2002 are used. After analysis of the dataset and exclusion of the outliers, the dataset contained 3,591 measurements. The DL ranges from 0.1 to  $1.2 \mu\text{g L}^{-1}$ . Only 6% of the data were above the detection limit. This means that the 90<sup>th</sup> percentile of that dataset,  $0.5 \mu\text{g L}^{-1}$  (total) i.e.  $0.17 \mu\text{g L}^{-1}$  (estimated dissolved) is unreliable.

Additionally, a qualitative description of the data-set was provided by VMM (pers. com., 2004). The monitoring network in Flanders contains a large number of sampling locations distributed over various types of surface waters in Flanders (834 sampling points in 2002). Total cadmium levels have been analysed and the data show that most higher cadmium levels are concentrated in the Kempen (i.e. the results of Dommel, Molve Neet and the Scheppelijke Neet are conspicuous). In 1997, 24% of the measurements were above the detection limit (mainly 0,2 and  $1 \mu\text{g L}^{-1}$ ). In 2002, 13% of the results were above the detection limit (between 0,1 and  $1,2 \mu\text{g L}^{-1}$ ). Calculation of the average of 90<sup>th</sup> percentiles on the datasets of 1997 and 2002 separately and without any data exclusion and by setting data lower than detection limit at half the detection limit, yields a

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<sup>48</sup> The reporting limit (RL) is the lowest reported Cd concentration if no detection limit is indicated.

90<sup>th</sup> percentile (total cadmium) of  $1.0 \mu\text{g L}^{-1}$  in 1997 as well as in 2002 (VMM, pers. com., 2005). Given however that these P90's are within the range of the DL, these cannot be considered as reliable for the risk characterisation.

The monitoring data for the Walloon region were generated and reported by the Scientific Institute for Public Services (ISSeP). The dataset contains 690 values for the dissolved Cd content and 39 for the total Cd content of Walloon surface waters. The DL is reported to range from 0.1 to  $0.3 \mu\text{g L}^{-1}$  for the dissolved Cd content and is equal to  $1 \mu\text{g L}^{-1}$  for the total Cd concentration. The reporting limit exceeds the critical value of this report, however the P90-value is still useful as it exceeds the critical reporting limits (notice that all values below the reporting limit have been set to half the reporting limit). After excluding the outliers following the procedure mentioned above a dataset of 659 values remained ranging from 0.05 to  $1.53 \mu\text{g L}^{-1}$ . Statistics were calculated once for the entire dataset.

Recently more (detailed) data for the Walloon region (years 2000, 2002 and 2004) were submitted via Industry's commentary file (ICdA, 2005) but could not be taken into account in this assessment<sup>49</sup>

- Denmark

For Denmark, data concerning Cd concentrations in surface waters were found in a survey of the national lakes for the Nordic Council of Ministers by Skjelkvåle et al. (1999). Measurements were performed in the year 1995 with the ICP-MS method.  $0.03 \mu\text{g L}^{-1}$  was reported as the DL. The method was subjected to quality control. The statistics of the report for Denmark are based on 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Cd in Danish lakes. For this reason, Skjelkvåle et al. (1999) only reported the 50<sup>th</sup> percentile. The maximum measured concentration is  $0.266 \mu\text{g L}^{-1}$ , the lowest reported value is below the DL.

- Finland

A first dataset was found in the survey of the national lakes for the Nordic Council of Ministers by Skjelkvåle et al. (1999). Measurements were performed in the year 1995 with the ICP-MS method.  $0.03 \mu\text{g L}^{-1}$  was reported as the DL. The method was subjected to quality control. 464 lakes were selected at random keeping in mind basic requirements concerning size and location. The data can be considered to represent the entire country.

A second dataset was obtained from the cooperation project "Ecogeochemical mapping of Eastern Barents region 1999-2000" (Salminen et al., 2004). The dataset reports the dissolved cadmium content of 339 measurements. The lowest reported value is  $0.005 \mu\text{g L}^{-1}$ , the highest  $0.48 \mu\text{g L}^{-1}$ . No DL is indicated.

- France

A number of monitoring data (52 in total), representative for the Rhône-mediterranean basin, were gathered from the "Réseau des Données sur l'eau du Bassin Rhône-Méditerranée-Corse" (RNB-eauRMC). This dataset for the region of the Rhône-Méditerranée for the year 2001 contains no actual measured data for Cadmium. All data are reported as smaller than the DL of  $0.5 \mu\text{g L}^{-1}$ .

Data for the Seine were gathered from the Réseau National de Données sur l'Eau (RNDE) and can be consulted on the web at <http://www.rnde.tm.fr/>. The dataset contains 9 values for the years 1998 to 2000. No DL is indicated and values range from 0.025 to  $0.073 \mu\text{g L}^{-1}$ .

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<sup>49</sup> Data were submitted in August 2005 and thus well beyond the agreed deadline for new data submission to be incorporated within the RAR following the CSTEE opinion.

Data for the Rhine-Meuse basin are reported by the Office International de l'Eau (1999) for the years 1995 to 1999. Data were obtained from 104 measurements. No information regarding the method of detection or DL is reported.

The datasets for France were designated RI 4. The reporting limits are unknown or exceed  $0.1 \mu\text{g L}^{-1}$  or the dataset is not considered representative for a region.

- Germany

The dataset from the Elbe for the year 2000 originates from the Wassergütestelle Elbe (Hamburg). It reports the total Cd concentrations and consists of 114 measurements. The DL is reported as  $0.05 \mu\text{g L}^{-1}$  and values range from  $0.05$  to  $0.7 \mu\text{g L}^{-1}$  for total Cd concentrations. 111 values are reported as higher than the DL. Statistics were calculated once for the entire dataset.

A large dataset was obtained from the "Hessisches Landesamt für Umwelt und Geologie" (HLUG), containing recent information (2001) on cadmium concentrations in a large number of rivers in Germany (26 in total). The data can be presumed to represent the entire country. The dataset consists of 531 measurements. The fractionation of the measured cadmium is not indicated. The lowest reported values range from  $0.1$  to  $0.5 \mu\text{g L}^{-1}$ , the highest is  $64.2 \mu\text{g L}^{-1}$ . One measuring site was excluded, however, according to the aforementioned selection procedure. This resulted in a dataset of 520 values with a range of  $0.1$ - $0.98 \mu\text{g L}^{-1}$ . No DL is reported. Statistics were calculated by averaging over the different measuring sites, following the TGD, revised 2002 procedure. The reliability of the database is, overall, low because the fractionation is unknown, the detection limit is unknown and the majority of the data within a site are reported as a constant value (e.g.  $0.5 \mu\text{g L}^{-1}$ ), suggesting that this is the reporting limit. Because of lack of information on DL's, it was considered unreliable to divide the lowest values by 2. This database will not be taken forward to the Risk Characterisation because of all these uncertainties.

A third dataset for the year 1998 was obtained from the "Joint Water Commission of the Federal Länder (LAWA), Federal institute of Hydrology, Berlin. This dataset contains 2,614 measurements of 89 rivers. Data for different measurement points are available for some of these rivers. The 90<sup>th</sup> percentiles for some of the major rivers are given here. If 90<sup>th</sup> percentiles of different measuring points for a river are available, only the average of these 90<sup>th</sup> percentiles is indicated. Cadmium concentrations are reported for the total cadmium concentration and the DL ranges from  $0.05$  to  $0.5 \mu\text{g L}^{-1}$ .

In addition, data concerning the Cd content of German surface waters were extracted from the COMMPS database (Combined Monitoring-based and Modelling-based Priority Setting scheme) of the European Commission (European Commission, 1999). This smaller dataset contains 33 values for the year 1996. Measurements were performed for the dissolved cadmium content and range from  $0.02$  to  $0.21 \mu\text{g L}^{-1}$ . No DL is reported. Statistics were calculated once for the entire dataset.

- Greece

Data concerning the Cd content of Greek surface waters were extracted from the COMMPS database (Combined Monitoring-based and Modeling-based Priority Setting scheme) of the European Commission (European Commission, 1999). This dataset contains 39 values for the year 1998. Data refer to total concentrations (Dr. Lekkas, personal communication) and no DL is given. The reported values range from  $0.06$  to  $1.89 \mu\text{g L}^{-1}$ . Statistics were calculated once for the

entire dataset. For reference: Estrela et al. (2000) report an average value for the Axios river of  $0.25 \mu\text{g L}^{-1}$ . No information regarding the original dataset, method of detection or DL is given.

- Italy

Data concerning the Cd content of Italian surface waters were extracted from the COMMPS database (Combined Monitoring-based and Modelling-based Priority Setting scheme) of the European Commission (European Commission, 1999). This dataset contains 6 values for the year 1996. The fractionation of the measured Cd content is not indicated and no DL is given. The reported values range from  $0.5$  to  $2 \mu\text{g L}^{-1}$ . No information is available about the location of sampling. Statistics were calculated once for the entire dataset.

Because of the small amount of data for the year 1996, data for the year 1995 from the same database are also given. Notice the large difference in measured values between the 2 years. Questions can be raised regarding the representative ness of this dataset for the entire country. Statistics were calculated once for the entire dataset.

For reference: Breder (1988) reported dissolved Cd concentrations in Italian rivers to range from  $0.004$  to  $0.113 \mu\text{g L}^{-1}$  in the years 1980 – 1982. Furthermore, Breder (1988) reports values in the Po river to range from  $0.028$  to  $0.19 \mu\text{g L}^{-1}$  in the year 1983 with an average of  $0.065 \mu\text{g L}^{-1}$  and the Cd content of Italian lakes to range from  $0.004$  to  $0.013 \mu\text{g L}^{-1}$ . Jensen and Bro-Rasmussen (1992) report the average Cd content in the Tiber as  $0.015 \mu\text{g L}^{-1}$  and in the Arno  $0.1 \mu\text{g L}^{-1}$ . Because of the large difference between the dataset and the literature date, the dataset should not be taken forward to the risk analysis (RI 4).

- The Netherlands

Monitoring data for the Netherlands were gathered by the Rijkswaterstaat (RWS; executive organisation of the Dutch Ministry of Transport, Public Works and Water Management). The dataset presented here contains 333 values for the measured total Cd content of Dutch surface waters for the year 2002. Data are obtained from the “Waterstat” database on the internet to be found on <http://www.actuelewaterdata.nl/>. The data can be presumed to represent the entire country (data from 27 sampling sites). The DL is reported as  $0.05 \mu\text{g L}^{-1}$ . Statistics were calculated by averaging the 90<sup>th</sup> percentiles of measurements at each sampling point, following the TGD, revised 2002 procedure.

A second dataset for regional waters was obtained, containing 1692 data from 242 sampling points. Total Cd concentrations are reported. The reporting limit varies from  $0.01$  to  $0.3 \mu\text{g L}^{-1}$  total Cd depending on the regional water management authority. Data were screened according to the aforementioned selection procedures (i.e. excluding data from regional water management authorities with RI 4 and excluding outlier data). This resulted in a dataset of 1492 values from 228 sampling points, with total Cd concentrations ranging from  $0.005$  to  $0.56 \mu\text{g L}^{-1}$  (RL  $0.01$ - $0.24 \mu\text{g L}^{-1}$ ). Including outlier data, total Cd concentrations range from  $0.005$  to  $21 \mu\text{g L}^{-1}$ . Statistics were calculated by averaging the 90<sup>th</sup> percentiles of measurements at each sampling point, following the TGD, revised 2002 procedure. The analysis by the responsible Dutch Water Authorities for these waters yielded a P90 of  $0.73 \mu\text{g L}^{-1}$  (total) or  $0.24 \mu\text{g L}^{-1}$  (estimated dissolved) which is about 3-fold above the P90 value calculated here and which was mainly related to the either or not including data with large detection limits. The MSR has returned this data analysis to the responsible Dutch Water Authorities but no further comments were received.

An additional dataset on total Cd content of Dutch surface waters for the year 1997 can be extracted from the COMMPS database (Combined Monitoring-based and Modeling-based

Priority Setting scheme) of the European Commission (European Commission, 1999). However, in the presence of more recent datasets, NL proposed to base the risk characterisation on the latter and preferred not to use the older COMMPS dataset to this aim (COM302+303\_env\_NL4, 19.11.04).

For reference:

Crommentuijn et al. (1997a) report a background concentration for the 90<sup>th</sup> percentile of dissolved Cd in the Netherlands of 0.08  $\mu\text{g L}^{-1}$ .

Ros and Slooff (1990) report values for the dissolved Cd concentration of 0.18 - 0.026 and 0.34-0.059  $\mu\text{g L}^{-1}$  for the Rhine (near Lobith) respectively the Meuse (near Eysden) in the years 1983 to 1986.

The “Coördinatie-Commissie voor de metingen van Radioactiviteit en Xenobiotische stoffen” (CCRX, 1994) reports the following 90<sup>th</sup> percentiles for the Cd content in the year 1992: 0.1, 0.8, 0.38, 0.2, 0.15, 0.09 and 0.2  $\mu\text{g L}^{-1}$  for the Rhine (near Lobith), the Meuse (near Eysden), the Westerscheldt Schaar van Ouden Doel, the Nieuwe Waterweg Maassluis, the Nieuwe Waterweg Haringvlietsluizen, the Netherlands IJ23 and the Netherlands NZK KM2 respectively. The fractionation of the measured Cd is not given.

Pearse (1996) reports the following 90<sup>th</sup> percentiles for the Cd content of the year 1993: 0.1 and 0.6  $\mu\text{g L}^{-1}$  for the Rhine (near Lobith) and the Meuse (near Eysden) respectively. The fractionation of the measured Cd is not reported.

- Norway

A first dataset was found in the survey of the national lakes for the Nordic Council of Ministers by Skjelkvåle et al. (1999). Measurements were performed in the year 1995 with the ICP-MS method. 0.02  $\mu\text{g L}^{-1}$  was reported as the DL. The method was subjected to quality control. 985 lakes were selected at random keeping in mind basic requirements concerning size and location. The data can be considered to represent the entire country.

- Portugal

Data for Portugal were found in the Portuguese Database for Water (the National Information System for Water, to be found on the web at <http://snirh.inag.pt>). Values are presented here for the total Cd content of Portuguese surface waters in the year 2002. Detection limits vary per region from 0.1 to 5  $\mu\text{g L}^{-1}$  total Cd or from 0.03 to 1.7  $\mu\text{g L}^{-1}$  estimated dissolved Cd. In the whole dataset, 84% of the measurements are smaller than the DL, but for some of the surface waters more than 90% of the data are below the DL. As such, the DL strongly determines the statistics derived from this dataset. The dataset for Portugal, although very extensive, will not be fully included in the risk characterisation, because the detection limits exceed 0.1  $\mu\text{g L}^{-1}$ . Statistics were calculated by averaging over the different regions, following the TGD, revised 2002 procedure.

- Spain

A dataset was found for one region of Spain: Andalusia. Data originate from the “Consejería de medio ambiente en Andalusia” and were reported on the web by the Spanish Ministry of Environment. (<http://www.mma.es>). The database consists of 330 measurements of the cadmium concentrations of Spanish surface waters for the year 1994. The fractionation of the measured Cd is not indicated. The DL was 0.3  $\mu\text{g L}^{-1}$ . Reported concentrations range from < 0.3 to 68  $\mu\text{g L}^{-1}$  with 39% of the dataset being smaller than the DL. High values are encountered because of a historical contamination of the Guadalquivir. The results can, therefore, not be considered to

represent ambient Cd concentrations of Spanish waters. Statistics were calculated once for the entire dataset but the data are not taken forward to the risk characterisation in this report because of the influence of data with historical contamination.

Recent data for Spain were submitted (Ministerio de medio ambiente, 2005) but could not be taken into account in this assessment<sup>50</sup>.

Additional data were extracted from the COMMPS database (Combined Monitoring-based and Modeling-based Priority Setting scheme) of the European Commission (European Commission, 1999). This dataset contains 11 values for the year 1996. The fractionation of the measured Cd content is not indicated and no DL is given, but the reporting limit, as well all the values in the dataset, equal  $0.1 \mu\text{g L}^{-1}$ . Therefore, the COMMPS dataset for Spain will not be included in the risk characterisation (RI 4). Statistics were calculated once for the entire dataset.

Notice the large difference between the 2 datasets. Keeping in mind the overall measured concentrations in Europe, one is inclined to rely stronger on the dataset from the COMMPS database.

For reference: Jensen and Bro-Rasmussen (1992) report the Cd concentrations of the Ebro as  $0.12 \mu\text{g L}^{-1}$ . No additional information is provided.

- Sweden

Data were gathered by the Swedish University of Agricultural Sciences and can be consulted on the web at <http://info1.ma.slu.se/>. Data are presented for the year 2000 for lakes and for the years 1995 – 2001 for rivers. DLs vary but all cover the very low range of encountered values. Reported values range from  $0.002$  to  $2.03 \mu\text{g L}^{-1}$  for rivers and from  $0.001$  to  $4.46 \mu\text{g L}^{-1}$  for lakes. Statistics were calculated for the 2 datasets separately by averaging over the different regions, following the TGD, revised 2002 procedure.

A second dataset was found in the survey of the national lakes for the Nordic Council of Ministers by Skjelkvåle et al. (1999). Measurements were performed in the year 1995 with the ICP-MS method.  $0.003 \mu\text{g L}^{-1}$  was reported as the DL. The method was subjected to quality control. 820 lakes were selected at random keeping in mind basic requirements concerning size and location.

- The United Kingdom

Data for the Cd content of British surface waters were gathered by the U.K Environmental Change Network (ECN) and can be found on the web at <http://www.ecn.ac.uk/index.html>. Data are presented for the year 1995 and consist of 10 measurements. The fractionation of the measured Cd is not indicated. The DL is reported as  $0.02 \mu\text{g L}^{-1}$ . Reported values range from  $< 0.02$  to  $0.46 \mu\text{g L}^{-1}$  with 30% of the values reported as smaller than the DL. Statistics were calculated once for the entire dataset.

Data were also extracted from the COMMPS database (Combined Monitoring-based and Modeling-based Priority Setting scheme) of the European Commission (European Commission, 1999). This dataset contains 1,363 values for the year 1996. Measurements were performed on the dissolved Cd content and the lowest reported values range from  $0.02$  to  $0.2 \mu\text{g L}^{-1}$ . No DL was indicated. Measured concentrations range from  $0.02 \mu\text{g L}^{-1}$  to  $346 \mu\text{g L}^{-1}$ . After excluding the

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<sup>50</sup> Data were submitted in May 2005 and thus well beyond the agreed deadline for new data submission to be incorporated within the RAR following the CSTEE opinion.

outliers a dataset was obtained with 1244 values ranging from 0.02 to 1.38  $\mu\text{g L}^{-1}$ . Statistics were calculated once for the entire dataset.

A 3<sup>rd</sup> database (WIMS) was received from the Environment Agency and contains 7108 Cd measurements in freshwater for the year 2003. Measurements were performed on the dissolved Cd content. The detection limit varies from 0.01 to 1  $\mu\text{g L}^{-1}$ . Sampling points with DL  $> 0.1 \mu\text{g L}^{-1}$  and sampling points with only one measurement were rejected. This resulted in a dataset of 6,905 values from 728 sampling points, with dissolved Cd concentrations ranging from 0.005 to 158  $\mu\text{g L}^{-1}$ . Of these values, 5,388 are reported as ' $< 0.1 \mu\text{g L}^{-1}$ '. Because of the high number of measurements found under the DL, an outlier analysis on the full dataset was not useful because it resulted in a limit value at the DL. Therefore, it is proposed here to make an outlier analysis on the sub-dataset of measurements found above the DL. It should be noted that this results in a very conservative outlier analysis and only 20 P90 values of the 729 were rejected. Statistics were calculated by averaging the 90<sup>th</sup> percentiles of measurements at each sampling point, following the TGD, revised 2002 procedure.

Table 3.184 Measured or estimated dissolved Cd concentrations in surface water. Underlined data are used for risk characterisation

Location (source/database)	Cd fractionation <sup>1</sup>	Sampling period	n	Reporting limits [ $\mu\text{g L}^{-1}$ ]	90 <sup>th</sup> percentile [ $\mu\text{g L}^{-1}$ ]	50 <sup>th</sup> percentile [ $\mu\text{g L}^{-1}$ ]	10 <sup>th</sup> percentile [ $\mu\text{g L}^{-1}$ ]	Statistics <sup>2</sup>	RI
<b>Belgium</b>									
Flanders (VMM)	ED	2000-2002	3591	0.03 - 0.4	(0.17: unreliable, only 6% of data>DL)	-	-	*	4
Wallon (ISSeP)	D	1999-2000	681	0.1 – 0.3	0.66	0.10	0.05	**	4
<b>Denmark</b>									
Denmark (Skjelkvåle et al., 1999)	U	1995	19	0.03	-	0.05	-	***	-
<b>Finland</b>									
Finland (Skjelkvåle et al., 1999)	U	1995	464	0.030	0.03	<0.03	<0.03	***	2
Eastern Barents Region (Salminen et al., 2004)	D	1999-2000	339	0.005	0.085	0.020	0.005	**	2
<b>France</b>									
Rhône-Méditerranée (RNB-eauRMC)	U	2001	52	0.5	0.25	0.25	0.25	**	4
Seine (RNDE)	D	1998 -2000	9	0.025	0.06	0.03	0.03	**	4
Rhine-Meuse (Office International de l'eau)	U	1995-1999	104	-	0.85	-	0.05	***	4

Table 3.184 continued overleaf

Table 3.184 continued Measured or estimated dissolved Cd concentrations in surface water. Underlined data are used for risk characterisation

Location (source/database)	Cd fractionation <sup>1</sup>	Sampling period	n	Reporting limits [ $\mu\text{g L}^{-1}$ ]	90 <sup>th</sup> percentile [ $\mu\text{g L}^{-1}$ ]	50 <sup>th</sup> percentile [ $\mu\text{g L}^{-1}$ ]	10 <sup>th</sup> percentile [ $\mu\text{g L}^{-1}$ ]	Statistics <sup>2</sup>	RI
Germany									
Elbe (Wassergütestelle Elbe)	ED	2000	114	0.02	0.12	0.07	0.07	**	2
Germany (HLUG)	U	2001	520	0.1 - 0.5	0.46	0.45	0.44	*	4
Danube (LAWA)	ED	1998	52	0.03 - 0.07	0.03	-	-	*	2
Mosel (LAWA)	ED	1998	26	0.02 - 0.03	0.03	-	-	*	2
Oder (LAWA)	ED	1998	52	0.07	0.10	-	-	*	2
Rhein (LAWA)	ED	1998	194	0.02 - 0.07	0.03	-	-	*	2
Ruhr (LAWA)	ED	1998	22	0.07	0.11	-	-	*	2
Saar (LAWA)	ED	1998	76	0.03	0.03	-	-	*	2
Weser (LAWA)	ED	1998	67	0.02 - 0.13	0.09	-	-	*	4
Germany (COMMPS)	D	1996	33	0.02	0.11	0.05	0.02	**	2

Table 3.184 continued overleaf

Table 3.184 continued Measured or estimated dissolved Cd concentrations in surface water. Underlined data are used for risk characterisation

Location (source/database)	Cd fractionation <sup>1</sup>	Sampling period	n	Reporting limits [µg L <sup>-1</sup> ]	90 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	50 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	10 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	Statistics <sup>2</sup>	RI
Greece									
Greece (COMMPS)	ED	1998	39	0.02	0.18	0.08	0.03	**	3
Italy									
Italy (COMMPS)	U	1996	6	0.5	1.74	0.75	0.52	**	4
Italy (COMMPS)	U	1995	7	0.5	11.42	2.86	0.56	**	4
The Netherlands									
The Netherlands (RWS)	ED	2002	333 (27 sampling sites)	0.02	0.07	0.03	-	*	2
The Netherlands (regionale wateren)	ED	2002	1492 (228 sampling sites)	0.003-0.08	0.06	-	-	*	2
Norway									
Norway (Skjelkvåle et al., 1999)	U	1995	985	0.02	0.055	<0.02	<0.02	***	2

Table 3.184 continued overleaf

Table 3.184 continued Measured or estimated dissolved Cd concentrations in surface water. Underlined data are used for risk characterisation

Location (source/database)	Cd fractionation <sup>1</sup>	Sampling period	n	Reporting limits [µg L <sup>-1</sup> ]	90 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	50 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	10 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	Statistics <sup>2</sup>	RI
Portugal									
Arade (SNIRH)	ED	2002	6	0.33	-	0.17	-	**	4
Ave/ Leca (SNIRH)	ED	2002	22	0.33	0.17	0.17	0.17	**	4
Cavado/rib Costeiras (SNIRH)	ED	2002	39	0.33	0.17	0.17	0.17	**	4
Douro (SNIRH)	ED	2002	219	0.17 - 0.33	0.17	0.17	0.08	**	4
Guadiana (SNIRH)	ED	2002	35	1.7	0.83	0.83	0.83	**	4
Lima/ Neiva (SNIRH)	ED	2002	24	0.33	0.17	0.17	0.17	**	4
Lis/rib. Costa (SNIRH)	ED	2002	92	0.17	0.43	0.08	0.08	**	4
Minho/ Ancora (SNIRH)	ED	2002	41	0.33	0.17	0.17	0.17	**	4
Mira (SNIRH)	ED	2002	4	1.7	-	0.83	-	**	4

Table 3.184 continued overleaf

Table 3.184 continued Measured or estimated dissolved Cd concentrations in surface water. Underlined data are used for risk characterisation

Location (source/database)	Cd fractionation <sup>1</sup>	Sampling period	n	Reporting limits [µg L <sup>-1</sup> ]	90 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	50 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	10 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	Statistics <sup>2</sup>	RI
<b>Portugal</b>									
Mondego (SNIRH)	ED	2002	193	0.17	0.21	0.08	0.08	**	4
Rib. Algarve (SNIRH)	ED	2002	8	0.33	0.17	0.17	0.17	**	4
rib. Oeste (SNIRH)	ED	2002	57	0.03	0.02	0.02	0.02	**	3
Sado (SNIRH)	ED	2002	27	1.7	0.83	0.83	0.83	**	4
Tejo (SNIRH)	ED	2002	280	0.03 -1.7	0.83	0.83	0.02	**	4
Vouga/ rib. Costeiras (SNIRH)	ED	2002	127	0.17	0.28	0.08	0.08	**	4
<b>Spain</b>									
Andalusia (MMA)	U	1994	330	0.3	7	1	0.1	**	4
Spain (COMMPS)	U	1997	11	0.1	0.1	0.1	0.1	**	4

Table 3.184 continued overleaf

Table 3.184 continued Measured or estimated dissolved Cd concentrations in surface water. Underlined data are used for risk characterisation

Location (source/database)	Cd fractionation <sup>1</sup>	Sampling period	n	Reporting limits [µg L <sup>-1</sup> ]	90 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	50 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	10 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	Statistics <sup>2</sup>	RI
<b>Sweden</b>									
Sweden - rivers (SLU)	U	1995-2001	6,975	0.002	0.052	0.023	0.007	*	1
Sweden - lakes (SLU)	U	2000	1,204	0.001	0.027	0.011	0.006	*	1
Sweden (Skjelkvåle et al., 1999)	ED	1995	820	0.003	0.052	0.01	0.003	***	2
<b>The United Kingdom</b>									
The UK (ECN)	U	1995	10	0.02	0.31	0.10	0.01	**	3
The UK (COMMPS)	D	1996	1,244	0.02 – 0.2	0.43	0.17	0.10	**	4
The UK (WIMS)	D	2003	6,905 (728 sampling sites)	0.01-0.1	0.15	0.10	0.08	*	2

1) Cd fractionation: D: dissolved Cd; ED: estimated dissolved Cd. If total concentrations are measured, dissolved concentrations are estimated to be 33% of the total Cd concentration (see Section 3.1.3.1.1); U: unknown Cd (presumed as 100% dissolved);

2) Statistics;

\* The statistics (=percentiles) are averages of corresponding values of the different sampling sites per region (TGD - EC, 2003);

\*\* The statistics are the percentiles of the entire dataset due to a lack of geographically-referenced data;

\*\*\* Statistics are reported by the author of the respective dataset.

Reported average Cd concentrations in European surface waters range from 0.03  $\mu\text{g L}^{-1}$  (Sweden) to 0.14  $\mu\text{g L}^{-1}$  (U.K.; **Table 3.185**). Notice that reported Cd concentrations increase as the uncertainty (RI) increases. We propose to use the data of RI 3 as a trade off between data richness and quality. Countries from northern, western and southern Europe are included and as such a general view of the ambient Cd concentration in European surface waters is obtained. The dataset for the Seine (France; n=9, P90= 0.06  $\mu\text{g L}^{-1}$ ) is not included as it comprises a very limited area and, as such, does not represent the entire region. If included, the effect on the resulting statistics would be minimal.

The average of the average 90<sup>th</sup> percentiles per region is 0.12  $\mu\text{g L}^{-1}$  and is a first approximation of a  $\text{PEC}_{\text{regional}}$ . This value is slightly above the 90<sup>th</sup> percentile obtained in the EU-wide systematic survey of FOREGS study (0.10  $\mu\text{g L}^{-1}$ , see below). The statistics of the datasets with RI 4 are not summarised as the uncertainty regarding these data is too large.

It is most likely that all surface waters contain some Cd that is emitted by man. Natural background Cd in surface water can therefore only be estimated indirectly. Scandinavian rivers and lakes probably contain minor quantities of Cd added by man since atmospheric Cd deposition data are lowest in the Scandinavian countries (see **Table 3.180**). The median Cd concentration in Scandinavian lakes is 0.01  $\mu\text{g Cd/L}$  (Skjellkvåle et al., 1999). This value may not be representative for natural Cd in other regions since weathering of natural Cd from minerals may certainly vary between regions. Surface sediments in EU lakes contain 3.6-30-fold higher Cd concentrations than deeper sediments (see below: sediment data). These enrichment factors could be combined with actual Cd concentrations in the lakes to calculate pre-industrial Cd concentrations. An overall view of Cd concentrations in European aquatic systems is provided by the FOREGS Geochemical Baseline Program (FGBP). This program has been initiated to provide high quality environmental geochemical baseline data for Europe. The data presented here are based on samples of stream water collected throughout Europe. High quality and consistency of the obtained data are ensured by using standardised sampling methods and by treating and analysing all samples in the same laboratories. The FGBP is authorised by the directors of the Geological Surveys within FOREGS (Forum of European Geological Surveys) and can be found on the web at <http://www.eurogeosurveys.org/foregs/>. The cadmium concentration was measured using the ICP-MS method with a DL of 0.002  $\mu\text{g L}^{-1}$ . 807 samples were taken randomly throughout Europe to obtain an overall view of the Cd concentration. The survey yielded a median concentration of 0.01  $\mu\text{g L}^{-1}$  and a 90<sup>th</sup> percentile of 0.10  $\mu\text{g L}^{-1}$ .

We propose a (high) estimate of 0.05  $\mu\text{g L}^{-1}$  as a general natural background Cd in freshwater (dissolved fraction). This value is used as the natural background concentration in the calculation of  $\text{PEC}_{\text{continental}_{\text{water}}}$ . A high estimate of the natural background can be considered as a conservative choice because it is added to the calculated concentrations. The choice of this background is, however, not very relevant for local risk characterisation since the PNEC is about 4-fold higher than the natural background. The risk characterisation at regional scale is performed with measured data.

Table 3.185 Measured Cd concentrations in surface water classified per reliability index (RI) taken forward to the risk characterisation. The statistics (90<sup>th</sup> percentile and average) are the averages of corresponding values of the regional data from Table 3.184 which meet the criteria of reliability'. Datasets with RI=4 were discussed on a case-by-case basis above. Datasets with RI>1 include also data of classes with lower RI index (i.e. cumulative number of data)

RI'	Region	n	90 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	Average [µg L <sup>-1</sup> ]
1	Sweden	8,179	0.0395	0.03
2	Finland	803	0.057	-
	Germany	608	0.07	-
	Norway	985	0.055	-
	Sweden	8,999	0.044	0.03
	The Netherlands	1,825	0.07	0.04
	Greece	39	0.18	0.12
3	Finland	803	0.06	-
	Germany	608	0.07	-
	Greece	39	0.18	0.12
	The Netherlands	1,825	0.07	0.04
	Norway	985	0.06	-
	Sweden	8,999	0.04	0.03
	UK (ECN)	10	0.31	0.14
	UK (WIMS)	6,905	0.15	
4	Belgium	4,272	-	-
	Finland	803	-	-
	France	165	-	-
	Germany	1,295	-	-
	Italy	13	-	-
	The Netherlands	405	-	-
	Norway	985	-	-
	Portugal	1,174	-	-
	Spain	11	-	-
	Sweden	3,353	-	-
	UK(COMMPS)	1,244	-	-

RI 1 DL<0.1 µg L<sup>-1</sup>, Cd fractionation: D or ED (D: dissolved Cd; ED: estimated dissolved Cd) and water hardness known;

RI 2 DL<0.1 µg L<sup>-1</sup>, Cd fractionation: D or ED;

RI 3 DL<0.1 µg L<sup>-1</sup>, Cd fractionation: D, ED or U (Unknown=assumed dissolved);

RI 4 All data;

N Number of values in the dataset.

An important fraction of total Cd in freshwater is adsorbed on suspended matter. The Cd concentrations in suspended matter typically range between 1 and 10 mg kg<sup>-1</sup><sub>dw</sub> (see

**Table 3.186).** Higher values are typically recorded in the river Maas that carries Zn ore particles. The dissolved fraction Cd ranges 10-40% in the rivers Rhine, Meuse and Schelde (Ros and Slooff, 1990), about 50% in the rivers Rhine and Arno (Breder, 1988) and 30-40% in Tiber and Elbe (Breder 1988). In lake Constance and Zurich, the percentage dissolved Cd is 80 and 84% respectively. High dissolved fractions are found in acid waters, in which total concentrations are also elevated.

The Cd concentrations in EU freshwater generally decrease since the end of the 1970s. Breder (1988) noticed the largest drop in dissolved Cd concentration in the lower course of the Rhine between 1977 and 1984. Ros and Slooff (1990) demonstrated that Cd concentrations in great Dutch rivers (total and dissolved and on suspended matter) decreased 4-fold from 1983 to 1986. Since 1990, the decrease in Cd is generally less pronounced (Milieucompendium, 2001; see also **Annex J**). The total Cd concentration in the Schelde at the border Belgium-Netherlands decreased from 3.5  $\mu\text{g L}^{-1}$  in 1975 to about 0.4  $\mu\text{g L}^{-1}$  in 1988 (no further trend).

Seasonal changes in Cd concentrations occur in lakes. Borg (1987) investigated 59 forest lakes in northern Sweden. The Cd concentrations are 2.4 fold higher in winter than in than in summer. During summer, there is higher production of phytoplankton and the higher input of particulate matter from the watershed. Therefore, more metal becomes particle bound and settles to the lake sediment.

A negative correlation between Cd concentrations and pH is observed in Swedish rivers and in lakes. Cadmium concentrations in Swedish surface waters increase from north to south along with acidification and air-born Cd. Different fractions of Cd in five soft water forest lakes with differing pH (average 4.85-6.61) in southern Sweden were measured. Most of the Cd in water was in dialysable form, especially in the more acidic lakes. This Cd form increases with decreasing pH, resulting in increased total Cd levels (Parkman et al., 1998).

Table 3.186 Measured cadmium concentrations in suspended matter

Location	Concentration (mg kg <sup>-1</sup> dw)	Moment	Year	Source
Germany Danube, Jochenstein	0.41 0.32-0.50	average (n=2) min-max	1998	LAWA database <sup>1</sup>
Germany Danube	0.82	average of 90 <sup>th</sup> percentiles	1998	LAWA database <sup>1, 2</sup>
Germany Elbe, Grauerort	1.81 0.73-5.10	average (n=12) min-max	1998	LAWA database <sup>1</sup>
Germany Elbe	7.11	average of 90 percentiles	1998	LAWA database <sup>1, 2</sup>
Germany Mosel, Koblenz	0.94 0.43-1.34	average (n=13) min-max	1998	LAWA database <sup>1</sup>
Germany Mosel	1.09	average of 90 percentiles	1998	LAWA database <sup>1, 2</sup>
Germany Rhine, Koblenz	0.76 0.39-1.18	average (n=26) min-max	1998	LAWA database <sup>1</sup>
Germany Rhine	0.94	average of 90 percentiles	1998	LAWA database <sup>1, 2</sup>
Germany Weser, Bremen	3.60 1.60-5.00	average (n=14) min-max	1998	LAWA database <sup>1</sup>
Germany Weser	3.65	average of 90 <sup>th</sup> percentiles	1998	LAWA database <sup>1, 2</sup>
France: basin Artoie, Picardie	11.83	average (n=10)	1995-1999	Office International de l'Eau, 1999
France: basin Rhin-Meuse	1.33	average (n=10)	1995-1999	Office International de l'Eau, 1999
France: basin Seine, Normandie	2.56	average (n=10)	1995-1999	Office International de l'Eau, 1999
France: basin Loire, Bretagne	3.73	average (n=10)	1995-1999	Office International de l'Eau, 1999
France: basin Rhône-Méditerranée-Corse	1.09	average (n=10)	1995-1999	Office International de l'Eau, 1999
The Netherlands: Rhine Lobith	6.3 2.3	n.a.	1983 1986	Ros and Slooff, 1990

Table 3.186 continued overleaf

Table 3.186 continued Measured cadmium concentrations in suspended matter

Location	Concentration (mg kg-1dw)	Moment	Year	Source
The Netherlands: Rhine Lobith	3.0	n.a.	1988	CCRX, 1991
	3.5		1989	
	3.0		1990	
The Netherlands Rhine Lobith	4	90 <sup>th</sup> percentile	1992	CCRX, 1994
The Netherlands Maas Eysden	34			
The Netherlands Westerschelde Schaar van Ouden Doel	1			
The Netherlands Nieuwe Waterweg Maassluis	7.5			
The Netherlands Nieuwe Waterweg Haringvlietsluizen	6.5			
The Netherlands IJ 23	2			
The Netherlands NZK KM2	2.2			
The Netherlands: Rhine	7.5	90 <sup>th</sup> percentile	2000	Milieucompendium, 2001
The Netherlands: Maas	19.1	90 <sup>th</sup> percentile	2000	Milieucompendium, 2001
The Netherlands: Schelde	8.1	90 <sup>th</sup> percentile	2000	Milieucompendium, 2001
The Netherlands: Rijkswateren	8.5	90 <sup>th</sup> percentile	2000	Milieucompendium, 2001
The Netherlands: IJsselmeer	1.9	90 <sup>th</sup> percentile	2000	Milieucompendium, 2001
The Netherlands: Maas Eysden	29	n.a.	1983	Ros and Slooff, 1990
	11		1986	
The Netherlands: Maas Eysden	133	n.a.	1988	CCRX, 1991
	19		1989	
	32		1990	
The Netherlands: Schelde Schaar van Ouden Doel	17	n.a.	1983	Ros and Slooff, 1990
	9		1986	

n.a. Information not available;

1) Source: Joint Water Commission of the Federal Länder (LAWA), Federal Institute of Hydrology, Berlin;

2) The LAWA database contains 2614 measurements of 89 rivers. Data for different measurement points are available for some of these rivers. The 90<sup>th</sup> percentiles for some of the major rivers are indicated as an example in this table. If 90<sup>th</sup> percentiles of different measurement points for a river are available, only the average of these 90<sup>th</sup> percentiles is indicated.

## Sediment

The datasets of various European countries are described and discussed below. Data are presented in **Table 3.187**. Older (literature) data are summarised in **Table 3.188**. The averages of percentiles per region are summarised in **Table 3.189**. It should be noted that these measured data in the sediment refer to total cadmium concentrations and are thus not corrected for bioavailability.

A statistical approach was used for defining outliers in an attempt to exclude the contribution of local emission sources from diffuse emission sources. The uncertainty related to either including or excluding outliers will be taken forward to the risk characterisation where the effect of outlier analysis on the risk factors will be compared. In this section, however, percentiles only refer to the database obtained after outlier exclusion. Outliers are selected based on the TGD (EC, 2003) using the equation:  $\log(X_i) > \log(P75) + K(\log(P75) - \log(P25))$  where  $X_i$  is the concentration above which a measured value may be considered an outlier,  $P_i$  is the value of the  $i^{\text{th}}$  percentile of the statistic and  $K$  is a scaling factor. This filtering of data with a scaling factor  $K = 1.5$  is used in most statistical packages, but the factor can be subject dependent. A value of 1.5 was chosen in this report. Outliers are detected by calculating the P75 and P25 statistics on the entire dataset, i.e. not per sampling site. Outlier calculation per sampling site detects measurement errors.

- Belgium

Monitoring data of cadmium concentrations in Flemish sediments (Belgium) were obtained from the Flemish Environment Agency (VMM). Data can also be consulted at the website (<http://www.vmm.be>). After exclusion of the outliers (8), the dataset contained 512 values of the year 2001. Data range from 0.02 to 7.4 mg kg<sup>-1</sup><sub>dw</sub>. Data were aggregated to obtain the statistics presented below as not enough data were available to calculate site-specific statistics.

Additional data were extracted from the COMMPS database. 20 values for the year 1995 yield the statistics presented below. The values range from 1.48 to 31.33 mg kg<sup>-1</sup><sub>dw</sub>. Samples were taken in rivers burdened by a high historical pollution load, however, and the data are therefore not taken forward in this report.

For reference: Plasman and Verreet (1992) report Cd concentrations in the sediment of the Dijle river to range from 0.1 to 3 mg kg<sup>-1</sup><sub>dw</sub>.

- France

Data were obtained of the Cd concentration of the sediment for the year 2001 from the Réseau National de Données sur l'Eau (RNDE) and can be consulted on the web at <http://www.rnde.tm.fr/>. Data were selected for 2 regions: Artois-Picardie (n = 126) and Rhône-Méditerranée (n = 66). For Artois-Picardie it was possible to calculate river-specific statistics. For the Rhône-Méditerranée only the main rivers and tributaries were included in the database. For the latter region, all individual data were used to calculate region-specific statistics.

Additional data were found in the COMMPS database and consist of 123 values for the year 1996 (after excluding the outliers). The measured Cd concentration ranges from 1 to 20 mg kg<sup>-1</sup><sub>dw</sub>.

For reference, averaged data per basin reported by the Office International de l'Eau are included in the table. In addition Breder (1988) reports values of 2 mountain lakes of Dauphiné to range from 0.15 to 2.5 mg kg<sup>-1</sup><sub>dw</sub>, which are not incorporated in the risk assessment, however.

- The Netherlands

Monitoring data for the Netherlands were gathered by the Rijkswaterstaat (RWS; executive organisation of the Dutch Ministry of Transport, Public Works and Water Management). The dataset presented here contains 12 values of 12 different points for the measured Cd concentration of sediments for the year 2000. Data are obtained from the “Waterstat” database to be found on <http://www.actuelewaterdata.nl/>. The reported values range from 0.05 to 4.89 mg kg<sup>-1</sup><sub>dw</sub>.

Data for the year 1997 were found in the COMMPS database. It contains 6 values with a range of 0.63 to 4.68 mg kg<sup>-1</sup><sub>dw</sub> (after excluding one outlier).

For reference: Breder (1988) reports a Cd concentration in the sediment of the IJsselmeer of 3 mg kg<sup>-1</sup><sub>dw</sub> and in the Ketelmeer of 34 mg kg<sup>-1</sup><sub>dw</sub>. Crommentuijn et al. (1997a) report a background Cd concentration of Dutch sediments of 0.8 mg kg<sup>-1</sup><sub>dw</sub>. Pearse (1996) reports Cd concentrations in Maas sediments to range from < 0.6 to 15 mg kg<sup>-1</sup><sub>dw</sub> for the year 1994.

- Spain

One dataset of 9 values was found for Spain in the COMMPS database. Values represent Cd concentration in the sediment for the year 1997 and range from 0.1 to 17.2 mg kg<sup>-1</sup><sub>dw</sub>. The highest measurement was rejected however, considered as being an outlier, resulting in a dataset of 8 values with a range of 0.1-0.52 mg kg<sup>-1</sup><sub>dw</sub>.

- Sweden

Data for the Cd concentration of Swedish sediments was gathered by the Swedish University of Agricultural Sciences (SLU) and can be consulted on the web at <http://info1.ma.slu.se/>. Data for the years 1998-2000 are presented here. The dataset consists of a total of 297 values measured in 99 distinct locations. As such, it can be considered to represent the entire country. Values range from 0.12 to 7.64 mg kg<sup>-1</sup><sub>dw</sub>.

For reference: Pearse (1996) reports Cd concentrations in pre-industrial sediments of lake bed deposits to range from 0.3 to 0.6 mg kg<sup>-1</sup><sub>dw</sub>. Jensen and Bro-Rasmussen (1992) report for northern Sweden background Cd concentrations in lake sediments of 0.1 to 0.4 mg kg<sup>-1</sup><sub>dw</sub> and Cd concentrations in the upper cm of the lake sediments to range from 0.1 to 2 mg kg<sup>-1</sup><sub>dw</sub>. Parkman et al. (1998) reports Cd concentrations in the surface sediment of forest lakes in south-west Sweden to range from 1 to 6 mg kg<sup>-1</sup><sub>dw</sub> in the year 1977 and in central and northern Sweden to range from 0.4 to 2.4 mg kg<sup>-1</sup><sub>dw</sub> in the year 1979.

Table 3.187 Measured Cd concentrations in sediments. Underlined data are used for risk characterisation. All values are expressed as total Cd concentrations and thus not corrected for bioavailability

Location (source)	Sampling period	n	Range [mg kg <sup>-1</sup> <sub>dw</sub> ]	90 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	50 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	10 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	Average [mg kg <sup>-1</sup> <sub>dw</sub> ]	Statistics <sup>1</sup>
Belgium								
Flanders (VMM)	2001	512	0.02 – 7.4	1.59	0.27	0.03	0.68	**
Belgium (COMMPS)	1995	20	1.48 – 31.33	14.83	7.89	2.88	8.58	**
France								
AA-delta (Artois-Picardie) (RNDE)	2001	13	0.1 - 6.1	4.66	1	0.54	1.78	**
Boulonnais (Artois-Picardie) (RNDE)	2001	4	0.2 - 0.4	0.34	0.2	0.2	0.25	**
Bresle (Artois-Picardie) (RNDE)	2001	2	0.2 – 0.5	0.47	0.35	0.23	0.35	**
Canche (Artois-Picardie) (RNDE)	2001	7	0.1 – 1.1	0.68	0.2	0.1	0.34	**
Deule (Artois-Picardie) (RNDE)	2001	14	0.8 – 7.8	7.74	2.9	0.86	3.91	**
Lys (Artois-Picardie) (RNDE)	2001	13	0.2 – 0.9	0.9	0.5	0.2	0.55	**
Samber (Artois-Picardie) (RNDE)	2001	13	0.3 – 1.2	0.8	0.4	0.3	0.53	**
Scarpe (Artois-Picardie) (RNDE)	2001	15	0.4 – 9.7	3.84	1.8	0.42	2.4	**

Table 3.187 continued overleaf

Table 3.187 continued Measured Cd concentrations in sediments. Underlined data are used for risk characterisation. All values are expressed as total Cd concentrations and thus not corrected for bioavailability

Location (source)	Sampling period	n	Range [mg kg <sup>-1</sup> <sub>dw</sub> ]	90 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	50 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	10 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	Average [mg kg <sup>-1</sup> <sub>dw</sub> ]	Statistics <sup>1</sup>
France								
Scheldt (Artois-Picardie) (RNDE)	2001	20	0.2 – 12	1.41	0.35	0.29	1.15	**
Somme (Artois-Picardie) (RNDE)	2001	23	0.2 – 4.3	1.32	0.4	0.2	0.71	**
Yser (Artois-Picardie) (RNDE)	2001	2	0.3 – 0.4	0.39	0.35	0.31	0.35	**
Artois-Picardie (RNDE)	2001	126	0.1 - 12	2.05	0.77	0.35	1.12	**
Rhône-Méditerranée (RNDE)	2001	66	0.01 – 4.2	0.93	0.12	0.01	0.37	**
France (COMMPS)	1996	123	1 - 20	5.6	2	1	2.91	**
Rhine-Meuse (Office International de l'eau)	1995-1999	135	-	-	-	-	1.23	**
Seine, Normandie (Office International de l'eau)	1995-1996	260	-	-	-	-	2.16	**
Loire, Bretagne (Office International de l'eau)	1995-1996	97	-	-	-	-	8.32	**
Adour, Garonne (Office International de l'eau)	1995-1996	365	-	-	-	-	2.38	**
Rhone-Méditerranée-Corse (Office International de l'eau)	1995-1996	431	-	-	-	-	1.55	**

Table 3.187 continued overleaf

Table 3.187 continued Measured Cd concentrations in sediments. Underlined data are used for risk characterisation. All values are expressed as total Cd concentrations and thus not corrected for bioavailability

Location (source)	Sampling period	n	Range [mg kg <sup>-1</sup> <sub>dw</sub> ]	90 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	50 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	10 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	Average [mg kg <sup>-1</sup> <sub>dw</sub> ]	Statistics <sup>1</sup>
The Netherlands								
The Netherlands (RWS)	2000	12	0.05 – 4.89	3.75	1.49	0.08	1.92	**
The Netherlands (COMMPS)	1997	6	0.63 – 4.68	3.63	1.74	0.83	2.07	**
Spain								
Spain (COMMPS)	1997	8	0.1 – 6.13	2.20	0.34	0.18	1.05	**
Sweden								
Sweden (SLU)	1998-2000	297	0.12 – 7.64	2.97	1.07	0.3848	1.4168956	**

1) Statistics;

\*\* The statistics are the X<sup>th</sup> percentile of the entire dataset.

Table 3.188 Literature data on the Cd concentrations in European sediments. All values are expressed as total Cd concentrations and thus not corrected for bioavailability

Location	Concentration [mg kg <sup>-1</sup> <sub>dw</sub> ]	Moment	Year	Source
Germany: 12 lakes in southern Bavaria	0.4-5.9	max		Breder, 1988
Germany: 12 lakes in southern Bavaria	0.1-0.95	min		Breder, 1988
Lower and middle Rhine <sup>(*)</sup>	12.8, 16.1, 5.1		1972, 1979, 1985	Jensen and Bro-Rasmussen, 1992
European rivers: the lower Rhine	11.8	max		KEMI, 1997
Upper Rhine <sup>(*)</sup>	5.3, 3.1, 2.1		1972, 1979, 1985	Jensen and Bro-Rasmussen, 1992
Elbe <sup>(*)</sup>	17, 11.8		1972, 1985	Jensen and Bro-Rasmussen, 1992
Danube <sup>(*)</sup>	19.8, 2.1		1972, 1985	Jensen and Bro-Rasmussen, 1992
Weser <sup>(*)</sup>	13.6, 2.6		1972, 1985	Jensen and Bro-Rasmussen, 1992
Ems <sup>(*)</sup>	10.4, 1.7		1972, 1985	Jensen and Bro-Rasmussen, 1992
Main <sup>(*)</sup>	12, 3.9		1972, 1985	Jensen and Bro-Rasmussen, 1992
Neckar <sup>(*)</sup>	37.3, 11.9, 2.4		1972, 1979, 1985	Jensen and Bro-Rasmussen, 1992
N-Italy: lake Como	1.1			Breder, 1998
N-Italy: lake Maggiore	0.25-2.5			Breder, 1998
Italy: rivers, natural background	0.2-0.3			Breder, 1998
Italy: rivers, surface sediment	0.6-1.8			Breder, 1998
Lake Zürich, background	0.2			Breder, 1988
Lake Zürich, surface	6			Breder, 1988

The ambient Cd concentration in surface sediments away from point sources ranges between 0.1-34 mg Cd/kg<sub>dw</sub> with most values in the 1-10 mg Cd/kg<sub>dw</sub> range (0.38-3.8 mg Cd/kg<sub>ww</sub>). All data from **Table 3.187** are taken forward to the risk characterisation and are summarised in **Table 3.189**. Countries from northern, western and southern Europe are included and as such a general view of the ambient Cd concentration in European sediments is obtained. The total average Cd concentration of European sediments is 1.32 mg Cd/kg<sub>dw</sub>. 10% of the sediments contain Cd concentrations exceeding 2.66 mg kg<sup>-1</sup><sub>dw</sub>.

Table 3.189 Measured Cd concentrations in sediments taken forward to the risk characterisation. The statistics (90<sup>th</sup> percentile and average) are the averages of corresponding values of the regional data from Table 3.187. All values are expressed as total Cd concentrations and thus not corrected for bioavailability

PEC regional	n	90 <sup>th</sup> percentile [mg kg <sup>-1</sup> <sub>dw</sub> ]	Average [mg kg <sup>-1</sup> <sub>dw</sub> ]
Flanders	512	1.59	0.68
France	315	2.86	1.47
The Netherlands	18	3.69	2.00
Spain	8	2.20	1.05
Sweden	297	2.97	1.42

The average of 90<sup>th</sup> percentiles of measured Cd concentrations in various countries is 2.66 mg kg<sup>-1</sup><sub>dw</sub>. This value represents a realistic worst case for the EU ambient Cd concentrations in sediment (natural Cd + historical Cd) and is used as the PEC<sub>regional</sub> in the risk characterisation. The modelled PEC values for sediment are calculated from regional emission to sediments and a background concentration that is typical for EU (i.e. no realistic worst case). That typical ambient background concentration away from point sources is derived here as the median of the averages reported in **Table 3.189** and **Table 3.188** to encompass more countries. The resultant typical ambient background sediment Cd concentration is 2 mg Cd/kg<sub>dw</sub> (= 0.77 mg Cd/kg<sub>ww</sub>). This value is used in **Table 3.157** to calculate modelled PEC values.

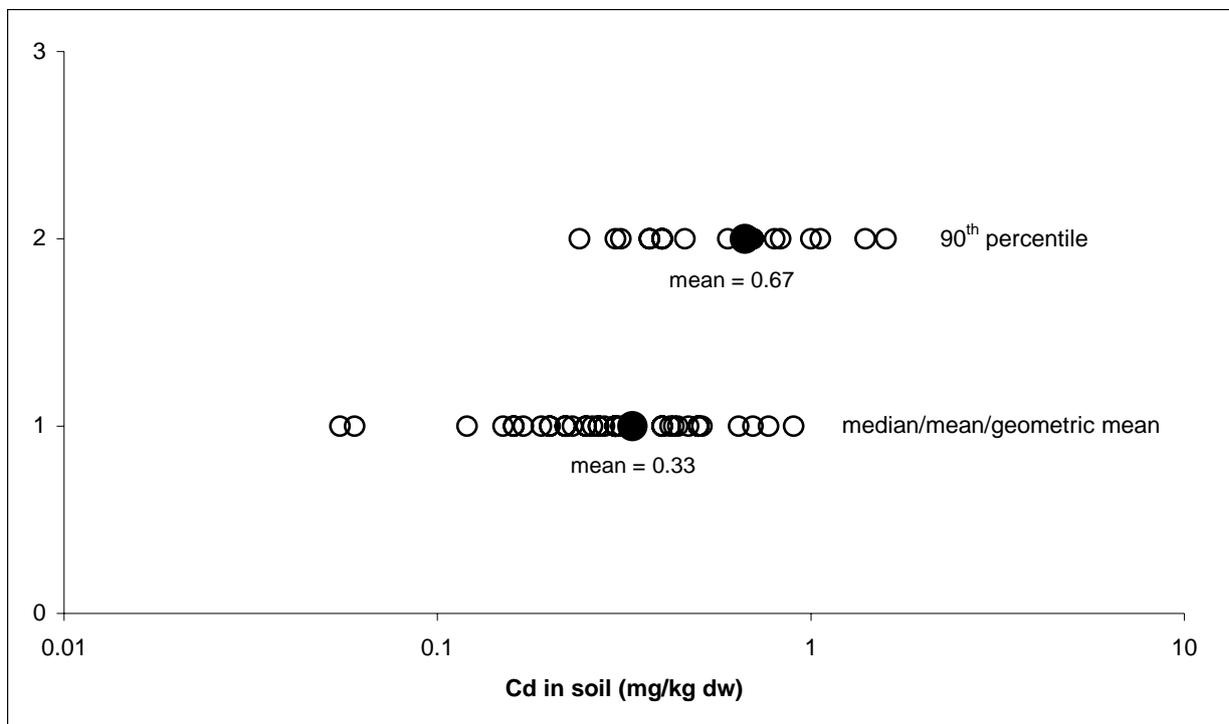
The Cd concentrations in the deeper layers of sediments in lakes range between 0.1-0.8 mg kg<sup>-1</sup><sub>dw</sub> (0.04-0.3 mg Cd/kg<sub>ww</sub>). These concentrations may be representative for natural background. In lakes in SW Sweden concentrations in pre-industrial sediment layers, below 20 cm depth, are 0.3-0.6 mg kg<sup>-1</sup><sub>dw</sub> and 0.1-0.4 in middle and northern Sweden (Johansson, 1989 cited in KEMI, 1997). A generalised background concentration of 0.4 mg kg<sup>-1</sup><sub>dw</sub> was therefore proposed for Swedish lake sediments (Pearse, 1996). Surface sediments (0 - 20 cm) are enriched with Cd compared to deeper layers. Results from Swedish lakes show a gradient significantly decreasing from south to north and an enrichment factor of about 7, referring to the background in southern areas of Sweden. The enrichment factor in Lake Zurich is 30 (Breder, 1988). Concentrations in river sediments show a 3-6 fold enrichment compared with background concentrations in Italian rivers (Breder, 1988). However, in many non-polluted lakes of northern Europe a decrease in Cd concentration of surface sediments is found compared to concentrations in deeper sediment layers deposited during less acidic conditions. Borg et al. (1989) found Cd in the sediment to decrease at pH below 5. Decreasing pH values in the sediment pore water may also cause leakage of Cd from the sediments to the water phase. In acid forest lakes, Johansson (1980) found lower Cd concentrations in surface sediments (0-1cm) compared to in subsurface layers (1-3cm). Furthermore he found that the fixation of Cd to sediment decreased at pH < 5, increasing the residence time for Cd in the water phase.

In general, Cd concentrations of surface sediments show downward trends. Breder (1988) demonstrated for the river Rhine a decrease from 1977 to 1983 from 38.6 mg kg<sup>-1</sup><sub>dw</sub> to 21.9 mg kg<sup>-1</sup><sub>dw</sub> at the most contaminated site. At other locations of the river Rhine, a 2- to 5-fold decrease was recorded.

### Terrestrial compartment

Measured Cd concentrations in soil are presented in **Table 3.190**. Little data were found for southern European countries<sup>51</sup>. The soil Cd concentrations in areas away from point sources range between 0.05 and 14 mg kg<sup>-1</sup><sub>dw</sub> and most concentrations are found in the 0.1-1.8 mg kg<sup>-1</sup><sub>dw</sub> range. **Figure 3.13** illustrates the concentration ranges that are listed in the **Table 3.190**.

Figure 3.13 Measured concentrations of Cd in soils in Europe. Points are averages, medians or geometric means (of min-max) or 90<sup>th</sup> percentiles of all European surveys listed in Table 3.190. Full points are the means of corresponding ranges. Observations near point sources and industrial activities are excluded and only the most recent data are included when data were reported for various periods



The data from **Table 3.190** can be subdivided in different regions as a tool for the risk characterisation. Regional ambient Cd concentrations can be derived for the different countries/regions according to two different methodologies:

- method 1: ambient Cd concentration = 90<sup>th</sup> percentile of all data from a single country/region (TGD, 1996);
- method 2: ambient Cd concentration = average of the 90<sup>th</sup> percentiles that have been derived for the different sites within the region of interest (TGD, revised 2002)

<sup>51</sup> For Spain measured data (LÓPEZ ARIAS, M. & GRAU CORBÍ, J.M., 2004) were submitted in May 2005 and thus well beyond the agreed deadline for new data submission to be incorporated within the RAR following the CSTEE opinion.

However, it is difficult to combine the data of all soils within a country because of the large differences between soils (e.g. sandy versus clay soils). Ideally, averages of 90<sup>th</sup> percentiles should be calculated per soil type within a country or region.

An attempt was made to average the 90<sup>th</sup> percentiles of German sand, löss and clay soils. The data were identified (wherever possible), selected and compiled from the data set “Hintergrundwerte für anorganische und organische Stoffe in Böden” (LABO, 1998). In this selection only the data related to the for this risk assessment most relevant ‘soil-use’ and ‘soil-exposure’ categories i.e. the data of the so-called ‘Type 0’ (“ohne Gebietsdifferenzierung”) and ‘Type II’ (“verdichtete Raume”) are included:

- average P90 for sandy soils:  $0.56 \text{ mg kg}^{-1}_{\text{dw}}$
- average P90 for löss (loamy) soils:  $0.67 \text{ mg kg}^{-1}_{\text{dw}}$
- average P90 for clay soils:  $0.89 \text{ mg kg}^{-1}_{\text{dw}}$

All data from **Table 3.191** are taken forward to the risk characterisation as is presented in **Table 3.251**. Reported P90 values are averaged per country as a surrogate for region. No attempt was made to differ between soil classes. 10% of the soils contain Cd concentrations exceeding  $0.86 \text{ mg kg}^{-1}$ . Recent data for Spain are reported (Ministerio de medio ambiente, 2005) but could not be taken into account in this assessment.

A typical average Cd concentration (ambient Cd concentration) in soils located away from point sources is  $0.30 \text{ mg kg}^{-1}_{\text{dw}}$  ( $0.26 \text{ mg kg}^{-1}_{\text{ww}}$ ). This concentration is close to the average soil Cd concentrations of the different surveys. This concentration is used as the ambient background concentration that is included in the  $\text{PEC}_{\text{soil}}$ . The Cd concentration in the soil depends on the parent material of the soil, the localisation and the land use. Districts associated with Cambrian bedrock, have enhanced Cd concentrations in the soils. Shales and sandstone are important components of the Cambrian formation and have generally high Cd concentrations. Marine clays in western Sweden and the coarser textured sediments in the middle of Sweden generally have lower-than-average contents (KEMI, 1998). Little information is available to estimate the natural background of Cd. The archived soil collection of Rothamsted shows that soil Cd has increased about 0.1-0.2 mg Cd/kg between about 1850 and 1980 (Jones et al., 1987, see **Table 3.190**). A more detailed analysis of this trend is described in Section 4 (see the human health part of this Risk Assessment Report, in separate document).

Influence of atmospheric deposition in areas around industrial point sources is well demonstrated in the Shipman area in the UK. Shipman was the centre of Zn mining from the middle of the 17<sup>th</sup> until the middle of the 19<sup>th</sup> century. Very high Cd concentrations have been found in these soils. Atmospheric deposition is the dominant source of cadmium in forest soils (Pearse, 1996). In Sweden, concentrations of Cd in the mor layer (the top layer of podzolic soils, 5-8 cm thick, rich in organic matter) of forest soils increased threefold since the pre-industrial era (Pearse, 1996). The mor layer absorbs heavy metals very effectively, and metal concentrations reflect the historical deposition over many decades (Pearse, 1996). The enrichment factor decreases to the north, but even in the northern-most part of Sweden the soil content is somewhat affected by long-range atmospheric transport and deposition of Cd. The concentrations showed a large-scale pattern with the highest values in the south of Sweden and decreasing concentrations towards the north. Regional average Cd concentrations in the mor layer ranged from  $1 \text{ mg kg}^{-1}_{\text{dw}}$  in the south to  $0.4 \text{ mg kg}^{-1}_{\text{dw}}$  in the north. About  $2 \text{ mg kg}^{-1}$  has been measured in surface layers (0-20 cm) of peatlands (Hellstrand and Landner, 1998). Locally enhanced Cd concentrations in forest soils are attributed to larger point sources, such as the Rönnskär smelters. The concentrations in the mor layer are  $> 5 \text{ mg kg}^{-1}$ , within a distance of 15 km from the Rönnskär smelter (Hellstrand and

Landner, 1998). There are indications of enriched concentrations also in the B-horizon of the soils (15-25 cm below surface), in southern Sweden (Hellstrand and Landner, 1998). Recent data indicate that Cd concentrations in the mor layer of Swedish forest soils are presently decreasing in most areas. In northern Sweden, decreasing concentrations in the mor layer are probably a result of the decreasing atmospheric deposition. In southern Sweden, acidification has caused increased leakage rates of Cd from soil surface layers which, together with decreased deposition, result in net outflow of Cd from the mor layers. This indicates that Cd is leaching from surface soils to deeper soil layers, and finally to the runoff water (Hellstrand and Landner, 1998).

Table 3.190 Measured total cadmium concentrations in soils

Location	Concentration (mg kg <sup>-1</sup> dw)	Moment	Year	Source
<b>Natural soils</b>				
Sweden: concentration in forest mor layer	0.35	5 <sup>th</sup> percentiles		Pearse, 1996
	0.64	50 <sup>th</sup> percentiles		
	1.27	95 <sup>th</sup> percentiles		
Netherlands: natural areas	0.05 - 1.8			Ros and Slooff, 1990
Germany: Niedersachsen (country area)				LABO, 1994
sandy soils	0.16	median (n=3379)		
	0.24	90 <sup>th</sup> percentile		
loamy soils	0.19	median (n=1833)		
	0.30	90 <sup>th</sup> percentile		
Germany: forest soil on sand	< 0.3	Median (n=164)		Hindel et al., 1997; LABO, 1998
	0.7	90 <sup>th</sup> percentile		
Germany: forest soil on sandloam	< 0.3	Median (n=20)		Hindel et al., 1997; LABO, 1998
	0.4	90 <sup>th</sup> percentile		
<b>Agricultural soils</b>				
Sweden: background concentration in agricultural soil	0.15			SEPA, 1987
Swedish agricultural soil	0.26	average		Pearse, 1996
	0.22	median		
	0.11-0.49	5 -95 <sup>th</sup> percentiles		
Finland: normal agricultural topsoil	0.06	average		KEMI, 1997
Finland agricultural soil	0.2	average		Pearse, 1996

Table 3.190 continue overleaf

Table 3.190 continued Measured total cadmium concentrations in soils

Location	Concentration (mg kg <sup>-1</sup> dw)	Moment	Year	Source
Agricultural soils				
Denmark: arable soil	0.22 0.25	median average (n=44)	1966	Tjell and Hovmand, 1978
UK: Rothamsted agricultural soils	0.51-0.77 0.33-0.43 0.27-0.42 0.37-0.47	averages	1846-1980 1881-1983 1882-1982 1870-1983	Jones et al., 1987
soils under permanent grassland	0.19-0.27		1876-1984	
The Netherlands: agricultural soils	< 0.1 - 1.6			Pearse, 1996
The Netherlands: agricultural soils	0.30 - 0.87			Ros and Slooff, 1990
The Netherlands: arable soils	0.5 0.4 0.04-14	average (n=708) median min-max		Wiersma et al., 1986
Belgium: agricultural soils in Flanders			1994-1995	De Temmerman et al., 2000
sandy soil	0.25 0.37	median (n=222) 90 <sup>th</sup> percentile		
sandy loam soil	0.3 0.4	median (n=270) 90 <sup>th</sup> percentile		
loam soil	0.32 0.46	median (n=120) 90 <sup>th</sup> percentile		
clay soil	0.27 0.31	median (n=19) 90 <sup>th</sup> percentile		

Table 3.190 continue overleaf

Table 3.190 continued Measured total cadmium concentrations in soils

Location	Concentration (mg kg <sup>-1</sup> dw)	Moment	Year	Source
Agricultural soils				
France: plough layer of agricultural soils	0.01	min	1995-1999	Baize, 1999
	0.30	median		
	0.39	average (n=10634)		
	0.69	90 <sup>th</sup> percentile		
France: cultivated soils	0.02	min	1995-1999	Baize, 1999
	0.25	median		
	0.41	average (n=1063)		
	0.80	90 <sup>th</sup> percentile		
France: all soils (surface and deep soils, agricultural and forest)	< 0.02	min	1995-1999	Baize, 1999
	0.16	average (n=768)		
	0.46	median		
	1.06	90 <sup>th</sup> percentile		
Germany: agricultural soil on sand	< 0.3	median		Hindel et al., 1997; LABO, 1998
	0.6	90 <sup>th</sup> percentile		
Germany: agricultural soil on loam	< 0.3	median		Hindel et al., 1997; LABO, 1998
	0.7	90 <sup>th</sup> percentile		
Germany: agricultural soil on sandloam	< 0.3	median		Hindel et al., 1997; LABO, 1998
	0.7	90 <sup>th</sup> percentile		
Germany: agricultural soils (Südoldenburg)	0.31	median (n=269)		Leinweber, 1996
	1.59	90 <sup>th</sup> percentile		

Table 3.190 continue overleaf

Table 3.190 continued Measured total cadmium concentrations in soils

Location	Concentration (mg kg <sup>-1</sup> dw)	Moment	Year	Source
<b>Soils near point sources</b>				
UK: Shipman (n=329)	97 2 - 360	average range		Jensen and Bro-Rasmussen, 1992
Germany: Hamburg region	1.2 < 0.1-27.8	average min-max		Lux et al., 1988
The Netherlands: organic matter layer of forest soils and borders of highway	1.13-4.91			CCRX, 1994
The Netherlands; subsoil of forest soils and borders of highway	< 0.35			
<b>Unknown land use</b>				
Sweden	0.22 0.03-2.3	average min-max		Jensen and Bro-Rasmussen, 1992
N-Sweden: top soils	0.17-0.28	averages		KEMI, 1998
S-Sweden: top soils	0.23-0.31	averages		KEMI, 1998
Middle of-Sweden: top soils	0.22-0.28	averages		KEMI, 1998
Sweden (north, south and middle), top soils	0.26 0.40	average 90 <sup>th</sup> percentile		KEMI, 1998
Denmark	0.17 0.11-0.32	average min-max		Jensen and Bro-Rasmussen, 1992
The Netherlands	0.4	average		Jensen and Bro-Rasmussen, 1992
The Netherlands: background concentrations	0.01 - 0.3			Ros and Slooff, 1990

Table 3.190 continue overleaf

Table 3.190 continued Measured total cadmium concentrations in soils

Location	Concentration (mg kg <sup>-1</sup> dw)	Moment	Year	Source
Unknown land use				
The Netherlands: calculated background conc. for a standard soil with 10% OM and 25% clay.	0.8			Crommentuijn et al., 1997a
The Netherlands: Kempen (0 - 25 cm)	0.3 - 2.7			Ros and Slooff, 1990
The Netherlands: Kempen (0 - 2 cm)	0.2 - 100			Ros and Slooff, 1990
The Netherlands: clay soils	0.5	average (n=248)		Van Driel and Smilde (1982)
sandy soils	0.3	average (n=63)		
Belgium	0.28	average		Jensen and Bro-Rasmussen, 1992
Belgium: background concentration in Flanders	0.5	average (n=470)		Cornelis et al., 1993
	0.4-1.0	25-75 <sup>th</sup> percentile		
	1.0	90 <sup>th</sup> percentile		
France	0.2	average		Jensen and Bro-Rasmussen, 1992
UK	0.5	average		Jensen and Bro-Rasmussen, 1992
UK (England and Wales)	0.2, 0.7, 1.4	10,50,90 <sup>th</sup> percentiles		McGrath and Loveland, 1992.
UK	0.49	mean	2000	Black et al., 2002
	0.3	median		
	11.2	max		
UK	0.44	mean		Ross et al. (draft)
	0.29	median		
	2.39	max		
Germany	0.3	average		Jensen and Bro-Rasmussen, 1992

Table 3.190 continue overleaf

Table 3.190 continued Measured total cadmium concentrations in soils

Location	Concentration (mg kg <sup>-1</sup> dw)	Moment	Year	Source
Unknown land use				
Germany	0.44	average		Crössman and Wüstermann, 1992
Germany: Hessen	0.12 0.1-2.4	average min-max		Jensen and Bro-Rasmussen, 1992
Sweden, top soil (0-20 cm)	0.23 0.37	average (n=3067) 90 <sup>th</sup> percentile		Eriksson et al., 1997
The Netherlands: top soil, all land uses (n=4094)	0.3 0.83	50 <sup>th</sup> percentile 90 <sup>th</sup> percentile	1993-1998	Brus et al., 2002

Table 3.191 Measured Cd concentrations in soils taken forward to the risk characterisation. The statistics (90<sup>th</sup> percentile) are the averages of corresponding values of the regional data from Table 3.190

Location	90 <sup>th</sup> percentile [ $\mu\text{g kg}^{-1}$ ]
Belgium	0.51
France	0.85
Germany	0.65
Sweden	0.39
The Netherlands	0.83
The United Kingdom	1.40

### Atmospheric compartment

Important sources of Cd in the atmosphere are natural sources, industrial point sources and the combustion of fuel and coal. Atmospheric Cd concentrations measured in various sites in the EU, are shown in **Table 3.192**.

The air Cd concentrations in remote areas are about  $0.1 \text{ ng m}^{-3}$ . Such values are found in northern Norway in 1978 and in southern Norway in 1985 (Jensen and Bro-Rasmussen, 1992). Recent levels in European rural areas vary from  $0.1$  to  $0.5 \text{ ng m}^{-3}$ , averaging  $0.5 \text{ ng m}^{-3}$  in Germany and the Netherlands. The natural background of Cd in air (pre-industrial background) is most likely lower than the ranges now found in rural areas. The estimated emission of Cd due to natural processes is  $15 \text{ tonnes y}^{-1}$  (sea spray, Mount Etna, forest fires, RL, 1990) whereas the current anthropogenic emissions are  $126 \text{ tonnes y}^{-1}$ . Therefore, natural background of Cd in air is probably 10 fold lower than the  $0.1$ - $0.5 \text{ ng m}^{-3}$  range of rural areas. Because air Cd concentrations below  $0.1 \text{ ng m}^{-3}$  are hardly detectable and have no meaning in terms of risk, we choose to select a zero Cd concentration as the natural background.

Dutch measurements in 1982/83 demonstrate a decrease in the concentrations from south to north caused by Belgian emissions. A Norwegian study demonstrated, that the long-range Cd transport from Western Europe has decreased from 1978/79 to 1985, whereas transport from eastern Europe has not changed. In Germany, the mean concentration of Cd in the air decreased between 1979 and 1994 from  $0.97 \text{ ng m}^{-3}$  to  $0.22 \text{ ng m}^{-3}$  (Bieber, 1995) because of a decreasing content of total dust as well as a decreasing Cd content in dust. In The Netherlands, average concentrations ranged from  $0.7 - 2 \text{ ng m}^{-3}$  (Ros and Slooff, 1990). The Cd concentrations decreased from south to north. Since 1990, the average Cd concentration in The Netherlands decreased from  $0.5$  to  $0.2 \text{ ng m}^{-3}$  in 2000 (Milieucompendium, 2001). In general, no large differences are measured between industrial areas and rural area, but higher values are recorded around metal-processing industries. The air Cd in Belgium is generally higher than in other countries. This may reflect resuspension of historic polluted particles although it is possible that the detection limit is higher than  $1 \text{ ng m}^{-3}$  (no data were reported below  $10 \text{ ng m}^{-3}$ ). More details on recent time trends in air Cd are given in Section 4 (see the human health part of this Risk Assessment Report, in separate document).

More recent measured cadmium concentrations in air for the Belgian region, Flanders, can be found in VMM (2004). Air monitoring data of remote/rural areas for EU-countries for more recent years (till 2003) are reported in EMEP (2004).

Table 3.192 Measured cadmium concentrations in air

Location	Cd concentration (ng m <sup>-3</sup> )	Moment	Year	Source
Sweden background concentrations	0.1			SEPA, 1987
N-Norway	0.1		1978	Jensen and Bro-Rasmussen, 1992
S-Norway	0.3		1978/1979	Jensen and Bro-Rasmussen, 1992
S-Norway	0.1		1985	Jensen and Bro-Rasmussen, 1992
The Netherlands: Witteveen	5			Hutton, 1982
The Netherlands: background concentrations	3-6			Ros and Slooff, 1990
The Netherlands: Rekken: background area	1, 4, 11	50,75,98 <sup>th</sup> percentiles		Ros and Slooff, 1990
The Netherlands: 17 locations	1 - 11	average	1981-1983	Ros and Slooff, 1990
The Netherlands: 17 locations	1 - 10	50 <sup>th</sup> percentile	1981-1983	Ros and Slooff, 1990
The Netherlands: 17 locations	4 - 21	95 <sup>th</sup> percentile	1981-1983	Ros and Slooff, 1990
The Netherlands: 17 locations	5 - 59	98 <sup>th</sup> percentile	1981-1983	Ros and Slooff, 1990
The Netherlands: 17 locations	10 - 73	max	1981-1983	Ros and Slooff, 1990
The Netherlands: 5 locations	0.71 - 1.27	min	1982-1983	Ros and Slooff, 1990
The Netherlands: 5 locations	2.9 - 11.6	max	1982-1983	Ros and Slooff, 1990
The Netherlands	0.5		1982-83	Jensen and Bro-Rasmussen, 1992
The Netherlands: 4 locations	1.1	average	1982-1983	CCRX, 1994
	0.71		1992	
	1.3		1982-1983	
	0.71		1992	
	1.7		1982-1983	
	0.53		1992	
	0.35		1992	

Table 3.192 continued overleaf

Table 3.192 continued Measured cadmium concentrations in air

Location	Cd concentration (ng m <sup>-3</sup> )	Moment	Year	Source
Belgium: Botrange	4 - 6	average	1972 - 77	Hutton, 1982
Belgium, 1984/88	< 10			Jensen and Bro-Rasmussen, 1992
Belgium: rural areas	10		1985-1995	VMM, 1997
Western Germany (5 sampling sites)	0.97 0.22		1979 1994	Bieber, 1995
Germany, Corviglia	2.1			Hutton, 1982
Germany	1 - 0.4		1979-1987	Jensen and Bro-Rasmussen, 1992
The Netherlands	0.5-0.2	n.a.	1990-2000	Milieucompendium, 2001
UK: 7 rural sites	1 - 2.7	average		Hutton, 1982
UK, Wales	0.4 - 0.1		1984-1987	Jensen and Bro-Rasmussen, 1992
France, Corsica	0.66		1986	Jensen and Bro-Rasmussen, 1992
Mediterranean Sea	0.36		1984	Jensen and Bro-Rasmussen, 1992
Central Europe: rural areas	0.1 - 0.8		late 1980s	KEMI, 1997
EU: annual, rural	0.1-4			OECD, 1994
EU: rural annual mean	< 1 - 5			KEMI, 1997
<b>Near point sources</b>				
Belgium: area around non-ferro plants	10, 27, 50		1992-1993	Ecolas, 1995
Belgium: area around non-ferro plants	10, 57, 120		1993-1994	Ecolas, 1995
Belgium: urban areas	10-20		1985-1995	VMM, 1997
Belgium: non-ferro industrial areas	10-100		1985-1995	VMM, 1997
Belgium: ferro industrial areas	10-20		1985-1995	VMM, 1997
Belgium: other industrial areas	10-20		1985-1995	VMM, 1997

Table 3.192 continued overleaf

Table 3.192 continued Measured cadmium concentrations in air

Location	Cd concentration (ng m <sup>-3</sup> )	Moment	Year	Source
Near point sources				
at the edge of a lead smelter in Belgium	60	max		OECD, 1994
at the edge of a lead smelter in Germany	29			
EU: annual, urban areas	2-150			OECD, 1994
EU: urban annual mean	5 - 15			KEMI, 1997
EU: industrial annual mean	15 -50			KEMI, 1997

### 3.1.3.4.4 Comparison of measured and calculated data

**Table 3.193** summarises the typical regional Cd concentration in surface water, sediments, soils and air and shows regional and continental PEC's in these various compartments.

Both calculated regional and continental PEC's of freshwater are found in the typical range of measured Cd concentrations. The calculated regional PEC is close to the 90<sup>th</sup> percentile of Cd concentration in the dissolved fraction.

The modelled regional PEC's of the sediment are about 8 fold higher than the average Cd concentrations although the continental PEC is still in the typical range. Regional and continental PEC's are calculated for 'steady state' conditions with EUSES for the sediment. Steady state conditions in the environment can only be achieved after a very long period, presumably several centuries (see Section 3.1.3.4.1). Regional sediment Cd concentrations may exceed actual ambient concentrations because the indirect input via runoff from soil with steady state Cd concentrations is much larger than the actual input via runoff. The regional steady state soil Cd concentrations (EUSES predictions) were 4-5 fold above ambient soil Cd concentrations (see Section 3.1.3.4.1). Regional PEC's can also be above the typical Cd concentrations because of the assumption that only 1% of the total EU sediment volume collects Cd from 10% of the EU Cd releases into surface water.

The PEC's of soil, calculated with the alternative model, is close to the measured Cd concentrations. This correspondence is related to the fact that the model II predicts on average only 14% change in soil Cd in 60 years with current Cd emissions.

Air Cd is remarkably well predicted. Typical Cd concentrations in air are, however, only valid for rural areas.

**Table 3.193** Typical measured regional Cd concentrations in the environment (away from point sources and remote areas = ambient Cd concentrations) and the regional and continental predicted environmental concentrations (PEC's). The measured concentrations and natural background are derived from compilations given in **Tables 3.184-3.192** as discussed in the previous section. PEC's are derived from **Table 3.157**.

Table 3.193 Typical measured regional Cd concentrations in the environment (away from point sources and remote areas = ambient Cd concentrations) and the regional and continental predicted environmental concentrations (PEC's). The measured concentrations and natural background are derived from compilations given in Tables 3.184-3.192 as discussed in the previous section. PEC's are derived from Table 3.157

Compartment	Measured Cd		Natural background	PECcontinental	PECregional
	Typical range	Average concentration (90 <sup>th</sup> percentile)			
freshwater $\mu\text{g L}^{-1}$ (dissolved fraction)	0.02-0.27	0.12 <sup>§</sup>	<0.05	0.06	0.11
aq. sediment $\text{mg kg}^{-1}_{\text{ww}}$	0.38-3.8	0.51 (1.01)	0.04-0.3	1.25	3.88
aq. sediment $\text{mg kg}^{-1}_{\text{dw}}$	1-10	1.3 (2.6)	0.1-0.8	3.2	10
soil $\text{mg kg}^{-1}_{\text{ww}}$	0.1-1.6	0.26	unknown	0.28-0.44	0.36
soil $\text{mg kg}^{-1}_{\text{dw}}$	0.11-1.81	0.29		0.32-0.50	0.41
air $\text{ng Cd m}^{-3}$	0.1-0.5	~0.5	~0	0.15	0.55

<sup>§</sup> Average of regionally averaged P90 values.

## 3.2 EFFECTS ASSESSMENT

### 3.2.1 Methods and definitions

#### 3.2.1.1 Data quality

A wealth of information is available on the ecotoxicity of Cd. The data quality of that information varies between source documents. Not all source documents provide complete background information of the toxicity test. A Reliability Index (RI, score 1-4) was given to each test result based on a number of quality criteria. These criteria are described in the introduction of the sections on the terrestrial and aquatic compartments. In this way, the risk assessments can be made for various levels of data quality.

Not all data that were incorporated in the tables, have been used in the effect assessment (e.g. derivation of the Predicted No Effect Concentrations – PNEC's). A first selection was made based on the RI values of the test results. Secondly, some test results were not taken into account to avoid overrepresentation of similar data. As an example, some tests provide data at different exposure times. In these conditions, only the data at the highest exposure time were selected. If various endpoints are derived from one test (i.e. reproduction, growth and mortality), only the most sensitive endpoint was included. Similar toxicity tests are reported in different source documents (i.e. using the same organism, endpoint, soil or water and test conditions). For these cases, the lowest value is selected or a geometric mean value is calculated. All data selected for the effects assessment (PNEC calculation and summarising graphs and tables) are underlined in the tables presenting toxicity data.

#### 3.2.1.2 Definitions of critical concentrations

A number of critical concentrations are derived from the dose response relationship of each test result. Based on guidelines of the TGD (TGD 1996, part II, p. 327), these concentrations are defined as:

No Observed Effect Concentration - NOEC. In order of preference, the NOEC is derived as:

- *Category 1*: the NOEC is the highest tested concentration at which the endpoint is not significantly different from the control treatment at the 5% level of significance, or at which the endpoint shows  $\leq 10\%$  significant adverse effect.
- *Category 2*: if the test shows a significant toxic effect at the lowest concentration tested, the NOEC is defined as LOEC/2 if the inhibition is  $\leq 20\%$ .
- The statistical analysis in the source document is used to identify NOEC's of category 1 and 2.
- *Category 3*: if no statistics are provided in the source document, the NOEC is determined as the highest concentration at which inhibition is  $\leq 10\%$ .
- *Category 4*: if no statistics are provided in the source document and there is more than 10% inhibition at the lowest tested concentration, the NOEC is determined as half the highest concentration at which the inhibition is  $> 10\%$  but  $\leq 20\%$ .

There has to be a concentration-effect relationship to derive a NOEC, i.e. no NOEC is defined if the test does not show a toxic effect up to the highest concentration tested. If the % inhibition is > 20% at the lowest tested concentration, no NOEC can be derived.

*Category 5:* the NOEC is defined as the EC<sub>10</sub>, the concentration at which 10% inhibition is found, as given in the source document. This value is often found by intra- or extrapolation.

Lowest Observed Effect Concentration (LOEC), the lowest tested concentration at which > 10% inhibition is found. The toxic effect must be statistically significant at the 5% level. The statistical analysis in the source document is used to find that concentration. If no statistics are provided in the source document but if there is a dose-effect relationship, the LOEC value is derived as the lowest concentration at which the inhibition is > 20% but ≤ 30%. In some exceptional cases, an insignificant toxic effect (or, when no statistics are provided, ≤ 20% inhibition) can be found at concentrations higher than the LOEC as defined above. In these cases, LOEC's are re-defined as the lowest concentration at which and above which significant toxicity (or, when no statistics were provided, > 20% inhibition) is found.

Along with the LOEC value, the % effect (inhibition) relative to the control is given. If the LOEC is found at the lowest concentration tested, this is given in the table (LT). Along the same lines, NOEC values found at the highest concentration tested (HT) are indicated. NOEC or LOEC data have not been included if they were found by extrapolation outside the test range, i.e. below the lowest or above the highest Cd application rate.

The EC<sub>x≥50</sub> (LC<sub>x≥50</sub>) is the concentration at which at least 50% inhibition (mortality) is found. This value is calculated from the response curve given in the source document or is defined as the concentration at which the toxicity is 50% or more. The % effect is indicated in the tables.

The definitions of NOEC and LOEC are essential for a consistent approach. Some information is, however, lost using these definitions. Insensitive tests are not included in the effect assessment if the test failed to detect any toxic effect (no NOEC can be defined). Sensitive tests do not affect the derivation of the PNEC if the test showed 20% or more inhibition at the lowest concentration tested (no NOEC can be derived).

## **3.2.2 Aquatic compartment**

### **3.2.2.1 General**

#### **3.2.2.1.1 Data quality: definitions of Reliability Indices (RI's)**

A reliability index (RI) is given for each test based on a number of criteria. These criteria are given below and the IUCLID file contains the information which criteria were not met by each test.

- RI 1: standard test (OECD approved tests) and performed according to the standard procedures.
- RI 2: no standard test but complete background information is given, i.e. the following information is present:
  - a) water hardness (either measured or calculated from Ca and Mg concentrations)

- b) pH
  - c) the background Cd concentration in the test medium for all data  $< 1 \mu\text{g L}^{-1}$
  - d) measured Cd concentrations or indications that nominal concentrations are close to measured concentrations
  - e) information that actual Cd concentrations were maintained during the test
  - f) statistical analysis of the dose-response relationship
  - g) no varying metal contamination along with increasing Cd application
  - h) the control must be tested along with at least two Cd concentrations above the control
  - i) information about the origin of the test organisms
  - j) information on the test concentration range
- RI 3: no standard test and one or more of the following information from the above-mentioned list is missing as background information: b), d), e), f), i), or j). All other information from that list is present.
  - RI 4: no standard test and one or more of the following information from the above-mentioned list is missing as background information: a), c), g) or h).

The requirement c) is critical since some tests have reported toxic effects below  $1 \mu\text{g L}^{-1}$  nominal Cd concentrations. Background Cd concentrations in filtered water typically range between  $0.05$  and  $0.2 \mu\text{g L}^{-1}$  and the lack of reporting the background concentration may underestimate the Cd concentration at which the first toxic effects are found. Some tests were included that did not show Cd toxicity up to the highest Cd concentration tested. These tests cannot be used for risk assessment (no NOEC can be found) and were considered unreliable (RI4) but were quoted in the tables for illustration.

### 3.2.2.1.2 Source of data and its limitations for risk assessment

A wealth of information is available on the toxicity of Cd to aquatic organisms. In this section, a compilation is made of different studies, which provide data of Cd toxicity to different species. Most of the tests were performed in laboratory conditions where Cd was added to the solution as soluble  $\text{Cd}^{2+}$  salts. Four tests on the toxicity of the CdO powder were found. The tests were performed using the filtrate of a dispersion of CdO powder. These tests are the OECD 203 fish acute toxicity test (Janssen Pharmaceutica, 1993b), the OECD 202 acute immobilisation test with *Daphnia* sp. (Janssen Pharmaceutica, 1993d) and the OECD 201 algae growth inhibition test (Janssen Pharmaceutica, 1993f, Lisec 1998b). The test results were reported as measured concentrations in the filtrates. It is most likely that Cd in the soluble fraction of the dispersion has the same speciation as that in a corresponding solution where Cd is added as soluble  $\text{Cd}^{2+}$  salts. Therefore, the toxicity tests using the filtrates of the CdO dispersion are treated equally as tests performed using soluble  $\text{Cd}^{2+}$  salts.

The CdO powder is only slightly soluble in water. The solubility decreases with increasing solution pH.

It is assumed that the dissolved fraction of a CdO dispersion represents the toxic Cd compound. The dissolved fraction of CdO has most likely the same speciation as the soluble  $\text{Cd}^{2+}$  salts

dissolved in the same medium. It is therefore assumed that the toxicity of CdO can be assessed based on studies with Cd<sup>2+</sup> salts, providing that the assessments are based on the dissolved fractions. Both the effect and exposure assessments of CdO in the aquatic environment are being made based on soluble fraction, as far as possible.

Cadmium toxicity in the aquatic environment can as well be overestimated or underestimated based on the laboratory data for various reasons. The major factors limiting a proper risk assessment are the unknown Cd speciation in environmental samples, the joint toxic actions of different pollutants, the process of long-term acclimation of organisms/populations to Cd and the general lack of information about the most toxic pathways of the higher trophic levels. A short discussion of these factors is given below.

### Speciation

Cadmium can be present in an aquatic environment as inorganic species, including the free metal ion Cd<sup>2+</sup>, as soluble complexes or sorbed on suspended particles. The free metal ion is considered as the most toxic species. Evidence for this concept was found in studies where metal speciation was altered by varying Cl<sup>-</sup> concentration, affecting the concentration of CdCl<sub>n</sub><sup>2-n</sup> species (Sunda et al., 1978) or where synthetic chelates were added to the test solution (Allen et al., 1980). Other evidence on limited Cd toxicity of Cd complexed by dissolved organic matter is illustrated by the data of Giesy et al. (1977) discussed in Section 3.2.2.3. The toxicity of cadmium sorbed on suspended particles is far less than that of soluble Cd (see e.g. Van Leeuwen et al., 1985 discussed in Section 3.2.2.2). Soluble Cd is traditionally distinguished from insoluble forms by membrane (0.45 µm) filtration. Soluble cadmium in freshwater can be lower than 10% of total cadmium as discussed in the exposure section. Certainly, membrane filtered water samples should be used in risk analysis when concentrations are compared with toxic concentrations given in this compilation.

Data on Cd speciation in the soluble fraction of freshwater samples are limited. Complexation of Cd<sup>2+</sup> by *inorganic ligands* is not pronounced in freshwater systems. Concentrations of inorganic ligands such as Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> are generally below 0.001 M in freshwaters (Stumm and Morgan, 1996). The computed fraction of Cd<sup>2+</sup> to the total dissolved inorganic Cd species is about 0.5 (Stumm and Morgan, 1996). In exceptional cases, freshwaters may contain higher concentrations of ligands and lower free metal fractions. An example is the Lake IJssel in The Netherlands that was used for toxicity tests described below (Van Leeuwen et al., 1985). Lake IJssel is an artificial freshwater basin containing salts originating from the sea which was previously at that place. Complexation of Cd by dissolved organic ligands cannot be calculated unequivocally. Complexation is high at high concentrations of dissolved organic carbon and at low water hardness. Solution speciation of Cd undoubtedly affects toxicity but it is striking to note that the free metal ion is very rarely an order of magnitude smaller than the total concentration. Borg et al. (1989) studied Cd speciation in five soft water forest lakes in southern Sweden. Cadmium was predominantly in the soluble form in all of the lakes. In the circumneutral lakes, 35 to 82% of the soluble Cd was present in free ionic form, as inorganic complexes or as low molecular weight organic complexes. In the more acidic lakes, 83 to 100% of the soluble Cd was present in these forms. No data are available at the regional scale to account for Cd speciation in the dissolved fraction for risk assessment. In view of the much larger uncertainty of a toxic threshold concentration, we conclude that ignoring Cd speciation on the dissolved fraction will not cause large errors in risk assessment of Cd at a regional scale.

### Mixed pollution

In the data compilation given below, only tests with single Cd contamination are included. However, elevated Cd levels in the environment are often associated with elevated Zn levels. The interaction between Zn and Cd can be antagonistic (Zn protecting Cd to become toxic) at moderate Zn levels. At Zn concentrations reaching toxic levels, Cd toxicity is more readily observed. In addition to simultaneous Zn pollution, in many environments other toxic substances exist that may affect Cd toxicity. A widespread approach to account for combined metal toxicity is to use the sum of the toxic unit of each pollutant (the concentration of a pollutant divided by its EC<sub>50</sub>) as a gross toxicity indicator. In this approach it is assumed that the toxic actions of each contaminant are additive. The validity of such an approach was confirmed in a mesocosm experiment (Jak et al., 1996). The EC<sub>50</sub> values of combined toxicity of 7 different heavy metals (including Cd) and arsenic on several plankton species were found between 0.53 and 0.98 'sum of toxic units' (Jak et al., 1996).

### Acclimation

Populations previously exposed to Cd are more tolerant to elevated Cd than previously unexposed populations. An example of this process is found in a laboratory study with algae (Lawrence et al., 1989) reported in Section 3.2.2.4 and with slugs (Lam, 1996) reported in Section 3.2.2.3

### Toxic pathways for higher trophic levels

Most studies report single species tests where Cd was added as Cd<sup>2+</sup> salts. Cadmium toxicity in multi-species systems is certainly more complex because of altered food availability in toxic conditions and because of Cd exposure in various ways to higher trophic levels. The first process is illustrated in Section 3.2.2.3 by two studies reporting that the toxic action of Cd can decrease some populations and raise other populations in a multi-species system (Lawrence et al., 1989, DeNoyelles et al., 1980, Marshall and Mellinger, 1980). The question whether Cd in the diet or in water is the most toxic source is difficult to answer. Sørensen (1991) reports that in less contaminated environments, water rather than dietary uptake is the major route of Cd uptake. In contrast, as aquatic ecosystems become progressively more contaminated with Cd, the gastrointestinal route of Cd uptake becomes more important than the gill route (Sørensen, 1991). It must be stressed that this conclusion refers to Cd uptake and not to Cd toxicity. The importance of the food route on Cd toxicity can be indirectly found in data on Cd toxicity found in Sweden at very low Cd concentrations. In a field study in the River Emån (Sweden), sublethal toxicity was found in perch (*Perca fluviatilis*) collected downstream from a source of Cd pollution that ceased its discharge in the river in 1976 (Sjöbeck et al., 1984). The Cd concentrations downstream from the source were 0.1-0.2 µg L<sup>-1</sup> while upstream from the source the Cd concentrations were around 0.05 µg L<sup>-1</sup> (probably detection limit). The Cd concentrations in the liver of female downstream fish were 6-8 times higher than in those of upstream fish. Based on solution levels, no such large difference in liver Cd should be expected. Before 1976, solution Cd was however higher (about 1 µg L<sup>-1</sup>) and it is likely that the downstream river sediment and benthic organisms had a high Cd burden at the time of fish and solution sampling (1981). The higher Cd load in the food rather than in solution may be the reason for increased liver Cd and Cd toxicity in the downstream fish compared to the upstream fish. This example indicates that a solution based risk assessment could underestimate exposure on-sites with historical pollution.

### 3.2.2.2 Acute and chronic toxicity to fish/amphibians

Table 3.194 Selected data with RI 1-3 for acute and chronic Cd toxicity to fish/amphibians. Sixty-three tests were reviewed from 27 source documents and 51 tests were selected

	Min	Median	Max	n
Acute tests				
E(L)C <sub>x50</sub> (µg L <sup>-1</sup> )	0.9	1,500	40,200	31
Chronic tests				
NOEC (µg L <sup>-1</sup> )	0.47	4.2	62	19
LOEC (µg L <sup>-1</sup> )	0.78	11	132	20
E(L)C <sub>x50</sub> (µg L <sup>-1</sup> )	3.4	20	650	7

Results of cadmium toxicity studies with fish reveal that toxic concentrations vary from the sub µg L<sup>-1</sup> range to over 10 mg L<sup>-1</sup> (see **Table 3.194**). Larger values are less relevant as many of the organisms in the environment exposed to such cadmium concentrations are already affected (see Section 3.2.2.1). The variability in toxicity among tests can be attributed to varying water quality (e.g. hardness, pH and organic load), life stage investigated, species differences, exposure time and acclimation of the test organisms.

The marked effects of water hardness on cadmium toxicity have been studied extensively. Toxicity test results of Canton and Slooff (1982) demonstrate that cadmium toxicity decreases as water hardness increases. For *Oryzias latipes* a NOEC value of 30 µg L<sup>-1</sup> was recorded after 18 days exposure at a hardness of 200 mg CaCO<sub>3</sub>/L. This value was fivefold lower in water with hardness of 100 mg CaCO<sub>3</sub>/L. The effect of hardness became only significant after 4 days. McCarty et al. (1978) compared Cd toxicity to *Carassius auratus* in water with hardness 20 and 140 mg CaCO<sub>3</sub>/L. A 20-fold lower LC<sub>50</sub> value was recorded in soft test water. The effects of water hardness on the LC<sub>50</sub> values are confounded by precipitation reactions that occur at the very high Cd concentrations. Pickering and Henderson (1966) also found changes in pH and acidity of the test water when cadmium salts were added to hard water. The water became milky, insoluble hydroxide and/or basic salts of cadmium were precipitated and lowered the pH of the test water. Carroll et al. (1979) compared cadmium toxicity in the presence of either Ca, Mg or Na salts at equal total salt concentrations. Calcium salts were most efficient in reducing the toxic action of Cd. Hall et al. (1986) compared Cd toxicity to *Pimephales promelas* in synthetic water with hardness 120 mg CaCO<sub>3</sub>/L with that in well water with hardness 200 mg CaCO<sub>3</sub>/L. The LC<sub>50</sub> values were statistically not different in both media.

Toxicity values smaller than < 1 µg L<sup>-1</sup> are found in very soft waters. Rombough and Garside (1982) tested Cd toxicity for alevins of *Salmo salar* in soft water with hardness ranging between 19 and 28 mg CaCO<sub>3</sub>/L. Biomass production per female, an endpoint combining reproduction, survival of alevins and their growth, was significantly reduced at a Cd concentration of 0.78 µg L<sup>-1</sup>. Chapman (1978) tested mortality of different juvenile stages of *Oncorhynchus tshawytscha* in soft well water with hardness 23 mg CaCO<sub>3</sub>/L. After 8.3 days, LC<sub>50</sub> values of parr and smolts stages were found at Cd concentration of 0.9 and 1.6 µg Cd/L respectively. Benoit et al. (1976) exposed three generations of *Salvelinus fontinalis* to several concentrations of Cd in Lake Superior water (H 42-47 mg CaCO<sub>3</sub>/L). The total weight of young produced per female of the second generation was significantly reduced at a Cd concentration of 1.7 µg L<sup>-1</sup>. No effect was found at a concentration of 0.9 µg Cd/L. Sjöbeck et al. (1984) studied Cd toxicity to *Perca fluviatilis* in a field investigation of river Emån (Sweden, H 40-50 mg CaCO<sub>3</sub>/L).

Downstream from a former source of Cd pollution, an activated immune defence system was found in perch compared to reference perch living in the same river upstream of the contamination source. Upstream of the source, Cd concentration is below  $0.05 \mu\text{g L}^{-1}$  and downstream Cd concentrations are  $0.1\text{-}0.2 \mu\text{g L}^{-1}$ . This test calls for a detailed analysis because it shows the lowest LOEC value in the entire data set of reviewed tests. The test is, however, excluded in the current risk assessment (RI 4) for various reasons. First of all, only two test concentrations (upstream/downstream) were studied. Secondly, the statistics of the experimental design are questionable; as only one reference site but three contaminated sites were studied (confounding factors cannot be excluded). Thirdly, the river was contaminated in the past with both Cd and Ni and it is unknown how these two metals interact. A fourth remark is that the uptake of food with elevated Cd (benthic organisms dwelling in the sediment with elevated Cd due to the historical pollution) might have been an important Cd exposure in this investigation (see also above in Section 3.2.2.1.2). This implies that the solution LOEC does not reflect the risk. Last of all, the authors note that it is difficult to evaluate the ecological significance of the sub lethal endpoint (Sjöbeck et al., 1984).

Canton and Slooff (1982) illustrate to what extent sensitivity to Cd varies among several species. The  $\text{LC}_{50}$  values vary from 30 to  $3,800 \mu\text{g L}^{-1}$  at water hardness  $H = 100 \text{ mg CaCO}_3 \text{ L}^{-1}$  and from 20 to  $11,100 \mu\text{g L}^{-1}$  at  $H = 200 \text{ mg CaCO}_3 \text{ L}^{-1}$  between 6 fish species. Phipps and Holcombe (1985) studied acute cadmium toxicity to 6 fish species and recorded a fish sensitivity factor (highest fish 96h  $\text{LC}_{50}$ /lowest fish 96h  $\text{LC}_{50}$ ) of about 9. Dave et al. (1981) found rainbow trout to be more sensitive than zebrafish during their embryo-larval stage. Eaton et al. (1978) found greater sensitivity of two salmonid species, whereas Chapman (1978) noticed that steelhead was consistently more sensitive to cadmium than Chinook salmon. Pickering and Henderson (1966) found that 96h  $\text{LC}_{50}$  values for fathead minnows were significantly lower than those for bluegills. The  $\text{LC}_{50}$  values for fathead minnows were also lower than those for goldfish.

Different toxicity tests studied cadmium sensitivity at different life stages. Chapman (1978) found newly hatched alevins of both Chinook salmon and brook trout to be much more tolerant than later juvenile forms. Toxic Cd concentrations were very low (lowest  $\text{LC}_{50}$  value was found at  $0.9 \mu\text{g L}^{-1}$ ) but it should be noted that tests were performed in very soft well water of only  $23 \text{ mg CaCO}_3/\text{L}$ . The toxicity tests of Eaton et al. (1978) indicated that larvae or juveniles were in all cases more sensitive than embryos. In contrast, Spehar (1976) demonstrated that stages of spawning and embryo production were the most sensitive for *Jordanella floridae*. Benoit et al. (1976) found males of brook trout to be more sensitive than females. At a cadmium concentration of  $3.4 \mu\text{g L}^{-1}$ , both pre-exposed and not pre-exposed males became extremely hyperactive during spawning and suddenly died. Weights (growth) of 16-week old juveniles were also significantly less than weights of control fish. Hatch and survival of brook trout through the juvenile stage were not affected at  $6.4 \mu\text{g L}^{-1}$ . Pickering and Gast (1972) found a statistically significant effect of cadmium toxicity at  $27 \mu\text{g Cd/L}$  on hatchability of *Pimephales promelas*. At lower cadmium concentrations they also noticed a sudden increase in the number of eggs produced. Rombough and Garside (1982) found Atlantic salmon alevins to be considerably more sensitive to cadmium than the embryos. Alevins became substantially more sensitive near the completion of yolk absorption.

Increasing exposure time generally increases the Cd concentration in target organs, resulting in an increasing severity of observed effects (Pickering and Henderson 1966, Eaton et al., 1978, Spehar, 1976, Carroll et al., 1979, Phipps and Holcombe, 1985, McCarty et al., 1978). Carroll et al. (1979) recorded a 2- to 5-fold decrease in the  $\text{LC}_{50}$  value for *Salvelinus fontinalis* from 24 to 96 hours. McCarty et al. (1978) found a 2-fold reduction in the  $\text{LC}_{50}$ -value for *Carassius auratus* from 2 to 10 days.

Besides growth, reproduction and survival, other parameters have been studied when assessing toxicity of cadmium to fish. Muramoto (1981) observed vertebral column damage of *Cyprinus carpio* during 47 days. Bishop and McIntosh (1981) evaluated the use of ventilation rate and cough rate to predict the chronic toxicity of cadmium to bluegill. At cadmium concentrations lower than 1% of the LC<sub>50</sub> value of bluegill, the ventilation rate and cough rate of bluegill were increased. Changes in cough rate were correlated with cadmium exposure. This test has not been selected for the risk assessment since it is an acute test. Arillo et al. (1984) investigated the biochemical responses to low cadmium concentrations in *Salmo gairdneri*. Blood, liver and mitochondrial enzymes are sensitive to cadmium and their activity was altered when exposed to 10 µg Cd/L. The activity of the enzymes antioxidant and lipid peroxidase was only reduced at a Cd concentration of 620 µg Cd/L. This test was neither selected because of unknown ecological relevance of the test results. Venugopal et al. (1997) found a reduction of more than 50% at this concentration. Karlsson-Norrgren et al. (1985) recorded a change in gill morphology at 10 µg Cd/L after 6 weeks of exposure. Lowe-Jinde and Niimi (1984) found short- and long-term effects of cadmium on glycogen reserves and liver size of rainbow trout.

In conclusion, lowest effect concentrations for fish were found at 0.8 µg L<sup>-1</sup>. Toxicity is most pronounced in soft water. One reliable EC<sub>50</sub> and one LOEC value were found below 1 µg L<sup>-1</sup>. These values refer to tests performed at water hardness < 50 mg CaCO<sub>3</sub>/L. Reproduction parameters are most sensitively affected by Cd.

Table 3.195 Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC ( $\mu\text{g L}^{-1}$ )	Cat.*	LOEC ( $\mu\text{g L}^{-1}$ ) (%effect)	EC <sub>50</sub> ( $\mu\text{g L}^{-1}$ ) (%effect)	LC <sub>50</sub> ( $\mu\text{g L}^{-1}$ ) (%effect)	References	R.I.
CdCl <sub>2</sub>	<i>Salmo salar</i>	municipal water charcoal filtered and UV sterilised; BC 0.13 $\mu\text{g Cd/L}$ ; pH 6.5-7.3; T 5-10; DO 11.1-12.5; Al 14-17; H 19-28	semi-static	M	24	A	mortality					<u>34</u>	Rombough and Garside, 1982	2
					46	C	total biomass	<u>0.47</u>	1	<u>0.78(28)</u>				2
CdCl <sub>2</sub>	<i>Catostomus commersoni</i>	sand filtered Lake Superior Water; continuous flow; DO 10.3; H 45; Al 41; Ac 3; pH 7.6	T 18.1	M	30	C	standing crop (biomass)	<u>4.2</u>	1	<u>12</u>			Eaton et al., 1978	2
	<i>Esox lucius</i>		T 15.9		28	C	biomass	<u>4.2</u>	1	<u>12.9</u>				2
	<i>Oncorhynchus kisutch (sac fry)</i>		T 10.1		27	C	biomass	<u>1.3</u>	1	<u>3.4</u>				2
	<i>Oncorhynchus kisutch</i>		T 9.7		27	C	biomass	4.1	1	12.5				2
	<i>Salvelinus namaycush</i>		T 9.6		31	C	biomass	<u>4.4</u>	1	<u>12.3</u>				2
	<i>Salvelinus fontinalis</i>		T 9.7		126	C	biomass	<u>1.1</u>	1	<u>3.8</u>				2
	<i>Salmo trutta</i>		T 9.7		60	C	biomass	3.8	1	11.7				2
	<i>Salmo trutta (late eyed eggs)</i>		T 10		61	C	biomass	<u>1.1</u>	1	<u>3.7</u>				2

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.	
CdCl <sub>2</sub>	<i>Salvelinus fontinalis</i>	sterilised Lake Superior water; H 42-47; pH 7-8; Al 38-46; Ac 1-10; DO 4-12; T 9-15	continuous flow	M	3 years	C	mortality	1.7	1			3.4	Benoit et al., 1976	2	
							growth (weight) of 16 week old juveniles	1.7	1		<u>3.4</u> (56)				2
							total weight of young /female of the 2nd generation	<u>0.9</u>	1	<u>1.7</u> (31)		2			
							reproduction	6.4	1			2			
CdCl <sub>2</sub>	<i>Jordanella floridae</i>	untreated Lake Superior water; T 25; DO 8.3; H 44; Al 42; Ac 2.4; pH 7.1-7.8	continuous flow	M	4 100	A	mortality					<u>2,500</u>	Spehar, 1976	2	
							mortality	8.1	1			16(72)			2
							growth	8.1	1	<u>16</u> (27)		2			
							reproduction	<u>4.1</u>	1	<u>8.1</u> (52)		2			
CdCl <sub>2</sub>	<i>Salmo gairdneri</i>	aerated well water; T 10; O <sub>2</sub> 7.5; H 375-390; pH 8-8.6	continuous flow	M	84	C	mortality	<u>12</u>	1	<u>36</u> (10) HT		Lowe-Jinde and Niimi, 1984	2		
Cd	<i>Salvelinus fontinalis</i>	reconstituted soft water: T 14-16°C; DO 9.3-11.4 mg L <sup>-1</sup> ; Cd(BG) <0.2 µg L <sup>-1</sup> ; pH 6.3-7.6; H 20	static renewal	M	10	C	survival	<u>8</u>	1	<u>18</u>		Jop et al., 1995	2		
		river water: T 14-16°C; DO 8.7-12.2 mg L <sup>-1</sup> ; Cd(BG) <4 µg L <sup>-1</sup> ; pH 6.6-7.4; H 16-28	static renewal	M	10	C	survival	<u>62</u>	1	<u>132</u>				2	

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.	
CdCl <sub>2</sub>	<i>Lepomis macrochirus</i>	dechlorinated, carbon-filtered tap water	Static; T 22; DO 8.5; H 18; Al 16; pH 7.4-7.7	M	4	A	mortality					<u>2,300</u>	Bishop and McIntosh, 1981	2	
CdCl <sub>2</sub>	<i>Pimephales promelas</i>	lake water; T 22.5; DO 7.5; H 44.4; Al 45.4; pH 7.1-7.8	continuous flow	M	4	A	mortality					<u>1,500</u>	Phipps and Holcombe, 1985	2	
	<i>Carassius auratus</i>											<u>748</u>			2
	<i>Ictalurus punctatus</i>											<u>4,480</u>			2
	<i>Lepomis macrochirus(juv)</i>											<u>6,470</u>			2
CdCl <sub>2</sub>	<i>Barytelphusa guerini</i>	tap water; pH 7.2-7.4; DO 7.8-8 mg L <sup>-1</sup> , Al 102; H 112; male fish	semi-static	N	4	A	mortality					<u>1,820</u>	Venugopal et al., 1997	2	

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	<u>LC50</u> (µg L <sup>-1</sup> ) (%effect)	References	R.I.										
Cd-solution	<i>Oncorhynchus tsahwytsha</i>	continuous flow; aerated UV sterilised well water; T 11.6-12.8; AI 22; H 23; DO 10.2; pH 7.1; Cd < 0.2 µg L <sup>-1</sup>	newly hatched alevins	M	4	A	mortality					> 27	Chapman, 1978	3										
			swim-up alevins									A			1.3	3								
			5-8m old parr									A			1.0	3								
			smolts		A	> 2.9						3												
			newly hatched alevins		8.3	A						> 27			3									
			swim-up alevins			A						1.3			3									
	5-8m old parr		A			<u>0.9</u>						3												
	smolts		A		1.6	3																		
	<i>Salmo gairdneri</i>		newly hatched alevins		4	A						> 26			3									
			swim-up alevins			A						1.8			3									
			5-8m old parr			A						3.5			3									
			smolts			A						> 2.9			3									
			newly hatched alevins			8.3						A			> 26	3								
			swim-up alevins									A			<u>1.6</u>	3								
	5-8m old parr		A		2.0	3																		
	smolts		A		2.3	3																		
	CdCl <sub>2</sub>		<i>Brachydanio rerio</i>		synthetic water (changed ISO) ; T 24; DO >80%; H 100; pH 7.2	semi-static; adults						N			4	A	mortality					<u>3.500</u>	Bresch ., 1982	3
						larvae									24	C								
		36		C		reproduc tion	<u>1</u>	1																

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/Measured	Duration (d)	Acute/chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.		
CdCl <sub>2</sub>	<i>Salmo salar</i>	municipal water charcoal filtered and UV sterilised; BC 0.13 µg Cd/L; pH 6.5-7.3; T 5-10; DO 11.1-12.5; Al 14-17; H 19-28	semi-static	M	24	A	mortality					<u>34</u>	Rombough and Garside, 1982	2		
							total biomass	<u>0.47</u>	1	<u>0.78</u> (28)				2		
CdCl <sub>2</sub>	<i>Calostomus commersoni</i>	sand filtered Lake Superior Water; continuous flow; DO 10.3; H 45; Al 41; Ac 3; pH 7.6	T 18.1	M	30	C	standing crop (biomass)	<u>4.2</u>	1	<u>12</u>			Eaton et al., 1978	2		
	<i>Esox lucius</i>						biomass	<u>4.2</u>	1	<u>12.9</u>			2			
	<i>Oncorhynchus kisutch</i> (sac fry)						biomass	<u>1.3</u>	1	<u>3.4</u>			2			
	<i>Oncorhynchus kisutch</i>						biomass	4.1	1	12.5			2			
	<i>Salvelinus namaycush</i>						biomass	<u>4.4</u>	1	<u>12.3</u>			2			
	<i>Salvelinus fontinalis</i>						biomass	<u>1.1</u>	1	<u>3.8</u>			2			
	<i>Salmo trutta</i>						biomass	3.8	1	11.7			2			
	<i>Salmo trutta</i> (late eyed eggs)						biomass	<u>1.1</u>	1	<u>3.7</u>			2			
CdCl <sub>2</sub>	<i>Salvelinus fontinalis</i>	sterilised Lake Superior water; H 42-47; pH 7-8; Al 38-46; Ac 1-10; DO 4-12; T 9-15	continuous flow	M	3 years	C	mortality	1.7	1			3.4	Benoit et al., 1976	2		
							growth (weight) of 16 week old juveniles	1.7	1		<u>3.4</u> (56)		2			
							total weight of young /female of the 2nd generation	<u>0.9</u>	1	<u>1.7</u> (31)			2			
							reproduction						2			
CdCl <sub>2</sub>	<i>Jordanella floridae</i>	untreated Lake Superior water; T 25; DO 8.3; H 44; Al 42; Ac 2.4; pH 7.1-7.8	continuous flow	M	4	A	mortality					<u>2,500</u>	Spehar, 1976	2		
							100	C	mortality	8.1	1				16(72)	2
								C	growth	8.1	1	<u>16</u> (27)				2
								C	reproduction	<u>4.1</u>	1			<u>8.1</u> (52)		2
CdCl <sub>2</sub>	<i>Salmo gairdneri</i>	aerated well water; T 10; O <sub>2</sub> 7.5; H 375-390; pH 8-8.6	continuous flow	M	84	C	mortality	<u>12</u>	1	<u>36</u> (10) HT		Lowe-Jinde and Niimi, 1984	2			

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.
Cd	<i>Salvelinus fontinalis</i>	reconstituted soft water: T 14-16°C; DO 9.3-11.4 mg L <sup>-1</sup> ; Cd(BG) <0.2 µg L <sup>-1</sup> ; pH 6.3-7.6; H 20	static renewal	M	10	C	survival	<u>8</u>	1	<u>18</u>			Jop et al., 1995	2
							C	growth	18	1				2
		river water: T 14-16°C; DO 8.7-12.2 mg L <sup>-1</sup> ; Cd(BG) <4 µg L <sup>-1</sup> ; pH 6.6-7.4; H 16-28	static renewal	M	10	C	survival	<u>62</u>	1	<u>132</u>				2
CdCl <sub>2</sub>	<i>Lepomis macrochirus</i>	dechlorinated, carbon-filtered tap water	Static; T 22; DO 8.5; H 18; Al 16; pH 7.4-7.7	M	4	A	mortality					<u>2,300</u>	Bishop and McIntosh, 1981	2
CdCl <sub>2</sub>	<i>Pimephales promelas</i> <i>Carassius auratus</i> <i>Ictalurus punctatus</i> <i>Lepomis macrochirus</i> (juv)	lake water; T 22.5; DO 7.5; H 44.4; Al 45.4; pH 7.1-7.8	continuous flow	M	4	A	mortality					<u>1,500</u>	Phipps and Holcombe, 1985	2
						A				<u>748</u>	2			
						A				<u>4,480</u>	2			
						A	mortality			<u>6,470</u>	2			
CdCl <sub>2</sub>	<i>Barytelphusa guerinii</i>	tap water; pH 7.2-7.4; DO 7.8-8 mg L <sup>-1</sup> ; Al 102; H 112; male fish	semi-static	N	4	A	mortality					<u>1,820</u>	Venugopal et al., 1997	2

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.
Cd-solution	<i>Oncorhynchus tsahwyttscha</i>	continuous flow; aerated UV sterilised well water; T 11.6-12.8; Al 22; H 23; DO 10.2; pH 7.1; Cd < 0.2 µg L <sup>-1</sup>	newly hatched alevins	M	4	A	mortality					> 27	Chapman, 1978	3
			swim-up alevins			A		1.3	3					
			5-8m old parr			A		1.0	3					
			smolts		A	> 2.9		3						
			newly hatched alevins		8.3	A		> 27	3					
			swim-up alevins			A		1.3	3					
	5-8m old parr		A			<u>0.9</u>		3						
	smolts		A		1.6	3								
	<i>Salmo gairdneri</i>		newly hatched alevins		4	A		> 26	3					
			swim-up alevins			A		1.8	3					
			5-8m old parr			A		3.5	3					
			smolts			A		> 2.9	3					
			newly hatched alevins			8.3		A	> 26	3				
			swim-up alevins					A	<u>1.6</u>	3				
			5-8m old parr					A	2.0	3				
			smolts			A		2.3	3					

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.				
CdCl <sub>2</sub>	<i>Brachydanio rerio</i>	synthetic water (changed ISO) ; T 24; DO >80%; H 100; pH 7.2	semi-static; adults larvae	N	4	A	mortality					<u>3,500</u>	Bresch ., 1982	3				
					24	C	reproduction			<u>10(35)</u>								
					36	C	reproduction	<u>1</u>	1									
CdCl <sub>2</sub>	<i>Brachydanio rerio</i>	tap water; continuous flow; T 20	H 170	M	1	A	mortality					7,000	Canton and Slooff, 1982	3				
					2	A					<u>4,200</u>							
					<i>Oryzias latipes</i>	synthetic water (Dutch standard water); semi-static; T 24	H 200	1	A	mortality								> 2,600
								2	A							1,800		
								3	A							170		
								4	A							130		
								1	A	mortality and abn. behaviour						> 2,600		
								2	A							470		
	3	A								160								
	4	A								<u>70</u>								
	H 100	1	A	mortality														
		2	A								>2,800							
		3	A								350							
		4	A								350							
	<i>Poecilia reticulata</i>	synthetic water (Dutch standard water); semi-static; T 24	H 200	1	A	mortality and abn. behaviour				> 2,800								
				2	A				320									
				3	A					120								
				4	A					<u>70</u>								
				1	A	mortality				33,000								
				2	A					20,500								
3				A					14,400									
4				A					11,100									

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206).  
Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.
					1	A						31,000		
					2	A						19,500		
					3	A	mortality					12,100		
					4	A						<u>11,100</u>		
			H 100		1	A						10,400		
					2	A	mortality and abn. behaviour					5,700		
					3	A						4,300		
					4	A						3,800		
		tap water; continuous flow; T 20			1	A						7,100		
					2	A						5,900		
					3	A	mortality					3,700		
					4	A						<u>3,400</u>		
			H 200		18	C	mortality and abn. behaviour	30	1	35(25)		50		
			H 100			C		6	1	23(25)		40		
			H 200		18	C		<u>6</u>	1	<u>7</u> (25)		<u>20</u>		
			H 100			C		<u>3</u>	1	<u>13</u> (25)		<u>30</u>		
	<i>Oryzias latipes</i>													
		tap water; continuous flow; T 20	H 170		1	A	mortality					4,000		
					2	A						3,200		
	<i>Xenopus laevis</i>				100	C	mortality	30	1			1,500		
							inhibition of larvae developmen t	<u>9</u>	1		<u>650</u>			
							body weight	30	1					

Table 3.195 continued overleaf

Table 3.195 continued Toxicity to fish/amphibians. All underlined data are selected to discuss the critical concentrations (Table 3.194). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.		
CdSO <sub>4</sub>	<i>Brachydanio rerio</i>	synthetic water (ISO 1977) ; T 25; pH 8.3; H 100	static; juvenile fish (0.25g each)	N	1	A	mortality					2,400	Dave et al., 1981	3		
					4	A						1,700		3		
	<i>Salmo gairdneri</i>		semi-static; T 8; embryo-larva	N	6	A							<u>1,700</u>		3	
					48	C	median survival time	<u>4</u>	1	<u>5</u> (15)					3	
CdSO <sub>4</sub>	<i>Pimephales promelas</i>	pond water diluted with carbon filtered demineralised tap water: H 201-204; DO 6.5-6.6; pH 7.6-7.7; Al 145-161; Ac 8-12; T 16-27	continuous flow;	M	60	C	survival of developing embryos	37	1	57(26)			Pickering and Gast, 1972	3		
			pond fish													
						C	growth	37	1	57					3	
			reproduction													
						C	mortality	350	1						3	
			survival of developing embryos				<u>13</u>	1	<u>37</u> (26)					3		
						C	reproduction	104	1						3	
			continuous flow; 3 week old fry from laboratory				60	C	growth	27	1	57(22)			<u>68</u>	3
						C	mortality									3
							30	C		<u>14</u>	1	<u>27</u> (24)				3
	A	static	4	1	110	1				30,000		3				
		4	A							<u>2,000</u>		3				
CdCl <sub>2</sub>	<i>Brachydanio rerio</i>	synthetic water; T 25; pH 6.9-7.2; H 12.4	continuous flow	N	42	C	mortality			<u>3</u> (40)LT		<u>10</u> (60)	Karlsson-Norrgren et al., 1985	3		
CdCl <sub>2</sub>	<i>Cyprinus carpio</i>	tap water; T 18-19; pH 6.8; Al 14.8; H 18, BC 0.001 mg L <sup>-1</sup> ; food < 0.05 µg L <sup>-1</sup>	semi-static	N	47	C	vertebral column damage			<u>10</u> LT			Muramoto, 1981	3		

Table 3.195 continued overleaf

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Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.	
CdSO <sub>4</sub>	<i>Salvelinus fontinalis</i>	synthetic soft water (EPA); pH 7.3 - 7.7; T 12	+ 3.10 <sup>-3</sup> M CaCO <sub>3</sub>	N	4	A	mortality					<u>26</u>	Carroll et al., 1979	3	
			H 340 - 344; AI 327-332												
			+ 3.10 <sup>-3</sup> M CaSO <sub>4</sub>			A							<u>29</u>		3
			H 332 - 348; AI 28-30												
			+ 3.10 <sup>-3</sup> M MgCO <sub>3</sub>			A							<u>3.8</u>		3
			H 348 - 360; AI 314-324												
+ 3.10 <sup>-3</sup> M MgSO <sub>4</sub>			A								<u>4.4</u>		3		
H 324 - 336; AI 27-32															
+ 3.10 <sup>-3</sup> M Na <sub>2</sub> SO <sub>4</sub>			A									<u>2.4</u>		3	
H 44 -46; AI 27-34															
CdCl <sub>2</sub>	<i>Pimephales promelas</i>	well water; pH 7.7; H 200; AI 140; T 22; BC negligible	static	N	2	A	mortality					100	Hall et al., 1986	3	
					4	A						<u>90</u>			
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Gambusia affinis</i>	0.15µm filtered pond water rich in TOC; continuous flow; DO > 90%; AI 4; H 10; pH 5.6; Cd 0.02 µg L <sup>-1</sup>	T 30.2	N	4	A	mortality					<u>1,300</u>	Giesy et al., 1977	3	
			T 30.7			A						<u>1,500</u>		3	
			T 28			A						<u>2,600</u>		3	
			0.15 µm filtered well water pour in TOC; continuous flow; ; DO > 90%; AI 9.7; H 11.1; pH 6.5; Cd 0.023 µg L <sup>-1</sup>												
			T 30.2			A							<u>900</u>		3
			T 28			A							<u>2,200</u>		3
CdCl <sub>2</sub>	<i>Carassius auratus</i>	aerated dechlorinated and aged city water; T 22-25; Cd < 10 µg L <sup>-1</sup> ; AI 14-18; DO 90%	static; H 20	N	2	A	mortality					2,760	McCarty et al., 1978	3	
					4	A						2,130		3	
					10	A						<u>1,780</u>		3	
			H 140		2	A						46,900		3	
					4	A						46,800		3	
					10	A						<u>40,200</u>		3	

Table 3.195 continued overleaf

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Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.
Supporting data														
CdCl <sub>2</sub>	<i>Salmo gairdneri</i>	water; T 15; pH 7.4; DO 90%; H 320	continuous flow	N	4 months	C	activity of:	1	1	10(10)	10(75)		Arillo et al., 1984	4
							liver enzymes							4
							blood enzymes							4
							mitochondrial enz							4
							gill sialic acid content							4
C	mucus lysozyme	1	1	10(20)			4							
C		10	1				4							
CdSO <sub>4</sub>	<i>Brachydanio rerio</i>	synthetic water (ISO 1977) ; T 25; pH 8.3; H 100	semi-static; embryo-larva	N	10	C	median survival	50(HT)					Dave et al., 1981	4
Cd	<i>Brachydanio rerio</i>	OECD-203-test water; T 22; pH 7.42; DO 9.3; H 233.4	static	M	4	A	mortality			320(20)			Janssen Pharmaceutica, 1993a	4
CdO	<i>Brachydanio rerio</i>	OECD-203-test water; T 22; pH 7.82; DO 9.5; H 243.6	static	M	4	A	mortality	1600 (HT)					Janssen Pharmaceutica, 1993b	4
Cd	<i>Salvelinus fontinalis</i>	river water: T 14-16°C; DO 8.7-12.2 mg L <sup>-1</sup> ; Cd(BG) <4 µg L <sup>-1</sup> ; pH 6.6-7.4; H 16-28	static renewal	M	10	C	growth	132 (HT)					Jop et al., 1995	4
CdCl <sub>2</sub>	<i>Lepomis macrochirus</i>	dechlorinated, carbon-filtered tap water	continuous flow; T 14.5-16; pH 7.8-8.2; DO 6.2-8.1; H 340-360; Al 248-264; Cd < 1 µg L <sup>-1</sup>	N	3	A	cough rate			50(35)LT			Bishop and McIntosh, 1981	4
CdCl <sub>2</sub>	<i>Barytelphusa guertini</i>	tap water; pH 7.2-7.4; DO 7.8-8 mg L <sup>-1</sup> ; Al 102; H 112; male fish	semi-static	N	30	C	activity of				620(80)		Venugopal et al., 1997	4
							antioxidase				620(52)			4
C						C	lipid peroxidase							4

Table 3.195 continued overleaf

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Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	R.I.	
CdCl <sub>2</sub>	<i>Pimephales promelas</i>	synthetic water (5% natural limestone spring water + 95% deionised water); static	T 25; DO 7.8; pH 7.5; Al 18; H 20	N	4	A	mortality					630-1,050	Pickering and Henderson, 1966	4	
	<i>Lepomis macrochirus</i>											1,940			4
	<i>Carassius auratus</i>														
	<i>Lebistes reticulatus</i>														
	<i>Lepomis cyanellus</i>											2,340			4
	<i>Pimephales promelas</i>														
	<i>Lepomis cyanellus</i>	1,270	4												
		hard limestone spring water	T 25; DO 7.8; pH 8.2; Al 300; H 360								2,840		4		
	72,600-73,500										4				
	66,000										4				
Soluble Cd	<i>Perca fluviatilis</i>	River Emån water; T 20-22; H 40-50; pH 6.7; female fish	field study	M	whole life	C	immune defence				0.1-0.2(45-100)LT		Sjöbeck et al., 1984	4	

- T Temperature (°C);  
H Hardness (as mg CaCO<sub>3</sub>/L);  
DO Dissolved oxygen (mg O<sub>2</sub>/L);  
Al Alkalinity (mg CaCO<sub>3</sub>/L);  
Ac Acidity (mg CaCO<sub>3</sub>/L);  
LT LOEC value found at lowest concentration tested  
HT NOEC value found at highest concentration tested  
\* NOEC classification (see section 3.2.1.2);  
\*\* Days of exposure of embryos and larvae-juveniles

### 3.2.2.3 Acute and chronic toxicity to aquatic invertebrates

Table 3.196 Selected data with RI 1-3 for acute and chronic Cd toxicity to aquatic invertebrates. One hundred and two tests were reviewed from 42 source documents and 97 tests were selected

	Min	Median	Max	n
Acute tests				
E(L)C <sub>x≥50</sub> (µg L <sup>-1</sup> )	7	166	74,000	61
Chronic tests				
NOEC (µg L <sup>-1</sup> )	0.16	2.0	11	22
LOEC (µg L <sup>-1</sup> )	0.28	1.9	25	19
E(L)C <sub>x≥50</sub> (µg L <sup>-1</sup> )	1	5	32	14

A large number of acute tests were found for invertebrates. Only few chronic studies met all criteria for classification as RI 2. Certain invertebrates e.g. *Daphnia* and *Ceriodaphnia*, appear to be particularly sensitive to cadmium. Most chronic LOEC values of *Daphnia* range between 1 and 10 µg L<sup>-1</sup>. The lowest LOEC value is found in well water (H 103 mg CaCO<sub>3</sub> /L, background Cd 0.08 µg L<sup>-1</sup>, Chapman et al., 1980). The mean number of young per adult after 21 days exposure was reduced at only 0.29 µg L<sup>-1</sup> (measured concentration). The NOEC in this test was 0.16 µg L<sup>-1</sup>.

Toxicity of CdO powder was tested in the 48-hour acute test with *Daphnia magna*. The filtrate of a CdO dispersion was diluted in several series (57-750 µg Cd/L). There were no toxic effects up to 250 µg Cd/L and there was 70% mortality at 750 µg Cd/L).

A wide range of concentrations at which cadmium is toxic to freshwater invertebrates (see **Table 3.196**) is found. The acute E(L)C<sub>x≥50</sub> values vary from 5 µg L<sup>-1</sup> to 74 10<sup>3</sup> µg L<sup>-1</sup>. Canton and Slooff (1982) found a lower LC<sub>50</sub> value of 0.67 µg Cd/L and a NOEC value of 0.37 µg Cd/L. Both values are, however, unreliable because the authors state that it is an extrapolated value below the lowest test concentration (tested concentration range not reported). The extrapolation is based on concentration measurements with flame atomic absorption spectrophotometry (detection limit ~20 µg L<sup>-1</sup>) does therefore not warrant reliable data. Differences in species, life stage, exposure time, type of flow system in which experiments were performed, changes in water quality, hardness, pH, alkalinity, temperature and organic fractions, impact cadmium toxicity.

Van Leeuwen et al. (1985) compared both mortality and reproduction characteristics in synthetic water and 50 µm filtered and sterilised IJssel water. The LC<sub>50</sub> and LOEC values were both 7 times higher in natural water than in synthetic water. They explain the differences found by differences in speciation of cadmium. In natural water bioavailability of cadmium is reduced through sorption on suspended particles so that biological responses occur at higher cadmium levels. Giesy et al. (1977) also report the influence of particles on bioavailability of cadmium. They compare cadmium toxicity in soft well water containing low organic carbon concentrations to toxicity in soft surface waters containing high concentrations of naturally occurring organic compounds. Toxicity of cadmium was significantly smaller in the organic surface water than in the well water (LC<sub>50</sub> values were 35 µg L<sup>-1</sup> and 7 µg L<sup>-1</sup> respectively). Different molecular organic fractions of this surface water were isolated by ultracentrifugation and were added to the well water. Addition of these fractions resulted in a decrease in Cd toxicity (an increase of the

LC<sub>50</sub> value from 7 µg L<sup>-1</sup> to 16.5 µg L<sup>-1</sup>). Adding the smallest fraction (< 0.9 nm) however increased Cd toxicity. Both effects of cadmium sorption to suspended particles and cadmium complexation by dissolved organic carbon confirm the free ion theory as described above (see Section 3.2.2, introduction). Schuyttema et al. (1984) compared Cd toxicity in soft well water with toxicity in a water-sediment system. In well water toxic concentrations were expressed as total measured concentrations, in the sediment-water system as dissolved measured concentrations. They found similar LC<sub>50</sub> values in both systems demonstrating that the dissolved fraction in sediment-water systems is the bioavailable fraction. Hall et al. (1986) tested cadmium toxicity on different water flea species in both synthetic and well water. They report that the different water types did not affect the cadmium toxicity to the different species tested.

Acclimation of a species or a population generally decreases the sensitivity to toxic compounds. Lam (1996) collected adolescent *Brotia hainanensis* (snails) from sites either upstream or downstream of a Cd polluting source. The downstream snails were more tolerant to cadmium than upstream snails even after laboratory acclimation for one week. Similar interpopulation differences persisted in the first generation (F1) juveniles (< 2-day-olds) which were descendants of laboratory-cultured snails. These differences in metal tolerance in the F1 juveniles disappeared after the juveniles had been cultured under identical laboratory conditions for one week. Bodar et al. (1990) found *Daphnia magna* pre-exposed to sublethal Cd concentrations to become more resistant to cadmium.

Cadmium toxicity generally increases with increasing exposure time. Van Leeuwen et al. (1985) report a gradual decline in the LC<sub>50</sub> values for daphnids with time from 10 µg L<sup>-1</sup> to 2 µg L<sup>-1</sup> in synthetic water until a constant level was reached after about 2 weeks. In 50 µm filtered Lake IJssel water the LC<sub>50</sub> declined from 24 µg L<sup>-1</sup> after 14 days to 14 µg L<sup>-1</sup> after 21 days. Attar and Maly (1982) obtained LC<sub>50</sub> values, which varied between 204 µg L<sup>-1</sup> if calculated at 36 hours and 5 µg L<sup>-1</sup> if calculated at 96 hours. Biesinger and Christensen (1972) found a fourteen-fold decrease of the LC<sub>50</sub> value for *Daphnia magna*, in filtered Lake Superior water, from exposure day 2 to 21. Canton and Slooff (1982) performed a similar test in synthetic water and found an even bigger decrease of the LC<sub>50</sub> value, from 30 µg Cd/L to 0.67 µg Cd/L. In the same test the NOEC data for mortality showed a similar trend. The background Cd of the test medium and test concentration range is unknown. Furthermore, it is not known if thresholds below 1 µg L<sup>-1</sup> are calculated by extrapolation outside the tested concentration range. Therefore, these data are considered as unreliable. Spehar et al. (1978) record an eleven-fold decrease of the LC<sub>50</sub> value for snails between 7 days and 28 days. For mayfly no significant effects on mortality were observed until the fourth week of exposure at which 3 µg L<sup>-1</sup> caused 70% mortality.

The marked effects of increasing water hardness reducing cadmium toxicity are extensively reported (see Section 3.2.2.6.4).

The importance of species differences, over and within different trophic levels, is illustrated by the experiments of Canton and Slooff (1982), Baudouin and Scoppa (1974), Warnick and Bell (1969), Williams et al. (1985), Winner (1988), Fennikoh et al. (1978), Hall et al. (1986) and Ingersoll and Kemble (2000). Canton and Slooff (1982) studied short- and long-term toxicity of cadmium to different freshwater organisms of different trophic levels. Bacteria, algae, crustaceans, fishes and amphibians were studied. In both short- and long-term studies, *Daphnia magna* was the most sensitive organism. Baudouin and Scoppa (1974) compared cadmium toxicity to three most representative freshwater zooplankton (*Cyclops abyssorum prealpinus*, *Eudiaptomus padanus padanus*, *Daphnia hyalina*) of Lake Monate -an unpolluted subalpine lake of Italy- and also found *Daphnia sp.* to be the most sensitive. Williams et al. (1985) studied cadmium toxicity on ten freshwater macroinvertebrates. Results indicated a wide range of species sensitivity. Members of the crustacean (*Gammarus sp.*) appear the most sensitive

( $LC_{50} 20 \mu\text{g L}^{-1}$ ) whilst insect species of the orders *Plecoptera* and *Trichoptera* exhibit high short-period tolerance to cadmium poisoning ( $LC_{50} 520 \cdot 10^3 \mu\text{g L}^{-1}$ ). Warnick and Bell (1969) studied 3 aquatic insects from which mayfly (*Ephemera subvaria*) is the most sensitive. Hall et al. (1986) compared the sensitivity of different water flea species to cadmium. No difference in species sensitivity was reported. Ingersoll and Kemble (2000) compared Cd toxicity to *Hyaella azteca* and *Chironomus tentans* in well water. They found *Hyaella azteca* to be the most sensitive.

Different toxicity tests demonstrate cadmium sensitivity to be depended on life stages. Wier and Walter (1976) found mature *Physa gyrina* to be much more tolerant than immature snails. Nebeker et al. (1986a) noted new-born *Daphnia*'s to be more resistant to Cd than test organisms of several days old. Sensitivity to Cd was also found to be dependent on the size of the neonates. Enserink et al. (1990) demonstrated larger neonates to be more resistant than smaller neonates.

Several reproduction parameters are used as toxic endpoints. Van Leeuwen et al. (1985) tested the effects of Cd on the number of offspring and the delay in the reproduction. Both parameters are based on individuals. From a 3-week life table study the authors calculated 'the intrinsic rate of natural reproduction' which integrates both age-specific survival and reproduction and found this a better test parameter. Bertram and Hart (1979) investigated the effect of cadmium on survival and reproduction capacity of *Daphnia pulex*. Cadmium at  $5 \mu\text{g L}^{-1}$  reduced the average longevity. Reproduction parameters such as the number of broods per adult, the number of young per brood, the number of progeny per adult, the intrinsic rate of natural increase or the mean generation time were already affected at  $1 \mu\text{g L}^{-1}$ . Elnabarawy et al. (1986) also found reproduction to be more sensitive to Cd than mortality for several daphnids. Both LOEC- and NOEC-values were below  $1 \mu\text{g L}^{-1}$ . The same conclusion is drawn for the very low effect values on reproduction and growth found by Biesinger and Christensen (1972). A LOEC value of  $0.17 \mu\text{g Cd/L}$  for reproduction was found by extrapolation beyond the test concentrations. Bodar et al. (1988a) note the change in the reproduction strategy of *Daphnia magna* which produce larger broods with smaller neonates at low cadmium concentrations ( $< 5 \mu\text{g L}^{-1}$ ). At higher cadmium concentrations ( $> 5 \mu\text{g L}^{-1}$ ) brood size and body size decline and the average number of days to the first brood increases.

Sublethal endpoints of *Daphnia* can be very sensitive to Cd. The haemoglobin content decreased by 20% when *Daphnia* was exposed to only  $0.1 \mu\text{g L}^{-1}$  Cd for 16 days (Berglund, 1985). However, at Cd exposure between  $0.2$ - $1.6 \mu\text{g L}^{-1}$ , no differences with the control value were found. Bodar et al. (1988b) found a decrease of 60% in the chlorella consumption rate of *Daphnia magna* at a cadmium concentration of  $5 \mu\text{g L}^{-1}$ .

In conclusion, Cd can affect primary consumers in the  $\mu\text{g L}^{-1}$  range and below. Reproduction was found to be the most sensitive endpoint. Different effect data smaller than  $1 \mu\text{g L}^{-1}$  were found. However, several of those values are considered unreliable because they were obtained by extrapolation, or because they are expressed as nominal concentrations without information on background Cd concentration in the test medium.

Table 3.197 Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC <sub>50</sub> (µg L <sup>-1</sup> ) (%effect)	LC <sub>50</sub> (µg L <sup>-1</sup> ) (%effect)	References	RI			
Cd (filtrate of dispersion)	<i>Daphnia magna</i>	OECD 202-test medium; pH 7.76; DO 9.6; H 274; T 20.2	static	M	2	A	mortality			40(30)		<u>110</u> (70)	Janssen Pharmaceutica, 1993c	1			
														2			
CdCl <sub>2</sub>	<i>Daphnia magna</i>	synthetic water; T 25; pH 8; H 11; DO 69%	semi-static	M	1	A	mortality	<u>0.6</u>	1	<u>1.9</u>		<u>1900</u>	Kühn et al., 1989	2			
					21	C	reproduction							2			
CdCl <sub>2</sub>	<i>Daphnia magna</i>	aerated well water; DO >70%; pH 8; T 22; H 300; Al 250	continuous	M	21	C	mortality	4.3	1			7.2 (100)	Knowles and McKee, 1987	2			
							reproduction							<u>0.8</u>	1	<u>2.1</u> (54)	2
CdCl <sub>2</sub>	<i>Aplexa hypnorum</i> <i>mature</i> <i>immature</i>	Lake Superior water; DO 7.5; T 24	continuous flow	M	4	A	mortality					93	Holcombe et al., 1984	2			
							growth							<u>4.41</u>	1	<u>4.79</u> (47)	2
							mortality+hatchability							4.41	1	4.79(62)	2
CdCl <sub>2</sub>	<i>Physa integra</i> <i>Ephemera sp.</i>	untreated Lake Superior water; pH 7.1-7.7; T 15; DO 10-11; H 44-48; Al 40-44; Ac 1.9-3	semi-static	M	21	C	mortality	<u>8.3</u>	1					Spehar et al., 1978	2		
					28										C	10.4	2
					28										C	<u>3</u> (70)	2
CdO (filtrate of dispersion)	<i>Daphnia magna</i>	OECD 202-test medium; pH 8.05; DO 9.3; H 226; T 19.1	static	M	2	A	mortality					<u>750</u> (70)	Janssen Pharmaceutica, 1993d	2			
CdCl <sub>2</sub>	<i>Daphnia magna</i>	dechlorinated Montreal city water; pH 6.95; T 20; Al 80; H 130; Cd 1µg L <sup>-1</sup>	continuous flow	N	1.5	A	mortality					203.8	Attar and Maly, 1982	2			
					2	A								58.16	2		
					2.5	A								15.8	2		
					3	A								8.88	2		
					4	A								<u>5</u>	2		
CdCl <sub>2</sub>	<i>Daphnia magna</i> <i>Daphnia pulex</i>	synthetic water; static; pH 8-8.5	H 160-180; T 20 H 80-100; T 20	N	2	A	mortality					<u>38</u> <u>42</u>	Lewis and Horning, 1991	2			
														2			

Table 3.197 continued overleaf

Table 3.197 continued Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	RI	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	soft well water; H 26-32; AI 30; T 20; DO 7.5-9; pH 6.6-7.8  slurry; T 20; H 15-23; AI 10-15; DO 7.5-9; pH 6.1-7.1 (LC50 expressed on dissolved fraction)	static	M	2	A	mortality					<u>36</u>	Schuytema et al., 1984	2	
			continuous							<u>49</u>	2				
			100 mg L <sup>-1</sup> total solids, static							39	2				
			continuous							144	2				
			1000 mg L <sup>-1</sup> total solids, static							44	2				
		continuous				A					44		2		
						A					97		2		
Cd	<i>Ceriodaphnia dubia</i>	reconstituted soft water: T 14-16°C; DO 9.3-11.4 mg L <sup>-1</sup> ; Cd(BG) <0.2 µg L <sup>-1</sup> ; pH 6.3-7.6; H 20  river water: T 14-16°C; DO 8.7-12.2 mg L <sup>-1</sup> ; Cd(BG) <4 µg L <sup>-1</sup> ; pH 6.6-7.4; H 16-28	static renewal	M	7	C	survival	19	1	41			Jop et al., 1995	2	
														2	
				M	7	C	survival	19	1	39				2	
			reproduction				<u>10</u>	1	<u>19</u>			2			
													2		
														2	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	well water: T 20±2°C; DO 4.9-7.9; Cd(BG) 0.08  pH 7.5, H 53  pH 7.9, H 103  pH 8.2, H 209	static renewal	M	21	C	reproduction (mean number of young per adult)						Chapman et al., 1980	3	
											<u>0.29</u>	3			
											<u>0.16</u>	3		<u>0.28</u>	3
											<u>0.21</u>	3		<u>0.91</u>	3
Cd	<i>Hyalella azteca</i>	well water: T 23°C; pH 7.8; H 280	flow-through	M	42	C	survival	<u>0.51</u>	1	<u>1.9</u>			Ingersoll and Kemble, 2000	3	
															3
			M	20	C	reproduction	1.9	1	3.2					3	
	weight					<u>5.8</u>	1	<u>17.4</u>			3				
	biomass					5.8	1	17.4			3				
	%emergence					5.8	1	17.4			3				
%hatch	5.8	1	17.4			3									
													3		

Table 3.197 continued overleaf

Table 3.197 continued Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	RI	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	unchlorinated, carbon filtered well water, aerated to saturation; H 240; Al 230; pH 8; DO >5; T 23; Cd < 0.01 µg Cd/L	static	N	2	A	mortality					178	Einabarawy et al., 1986	3	
	A									319	3				
	A									<u>184</u>	3				
	<i>Daphnia magna</i> <i>Daphnia pulex</i>		semi-static		14	C	reproductive impairment	<u>2.5</u>	1		<u>7.5</u> (75)				3
						C		<u>7.5</u>	1	<u>25</u> (32)		3			
	<i>Ceriodaphnia reticulata</i>				7	C		<u>0.25</u>	1	<u>0.75</u> (20)				3	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	20 µm cloth filtered Lake Superior water; pH 7.7; H 45.3; Al 42.3; DO 9; T 18;	semi-continuous flow; without food	N	2	A	mortality						65	Biesinger and Christensen, 1972	3
						C	mortality					<u>5</u>	3		
			with food		C	weight/animal	<u>1</u>	3					3		
					C	protein conc./animal	<u>1</u>	3					3		
					C	GOT activity/animal					<u>1</u> (15)		3		
CdCl <sub>2</sub>	<i>Daphnia pulex</i>	Whatman N° 1 filtered Lake Champlain water; pH 7.7; Al 42.4; H 65; Cd < 1µg L <sup>-1</sup>	static	N	3	A	mortality					62	Bertram and Hart, 1979	3	
						A	mortality					<u>47</u>		3	
			semi-continuous flow		104	C	longevity	<u>1</u>	3			<u>5</u> (57)			3
						C	brood size				1(37)LT			3	
						C	generation time in days				<u>1</u> (19)LT			3	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	Dutch standard water; T 19	semi-static H 200 H 100	M(>20µg L <sup>-1</sup> )	2 2	A	mortality					<u>30</u>	Canton and Slooff, 1982	3	
						A	mortality					<u>30</u>		3	
CdSO <sub>4</sub>	<i>Ceriodaphnia dubia</i>	Synthetic water; H 90; Al 65; T 25	static	N	7	C	mortality	<u>1.5</u>	1	<u>2</u> (40)		<u>3</u> (70)	Winner, 1988	3	
	C					reproduction	<u>2</u>	1	<u>3</u> (30)			3			

Table 3.197 continued overleaf

Table 3.197 continued Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	RI	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	NPR synthetic water; pH 8.4; T 20; H 200	semi-static	N	21	C	intrinsic rate of natural increase	1	1	1.8(32.5)	32(100)		Van Leeuwen et al., 1985	3	
							C	mortality	1	1	<u>1.8</u> (17)		<u>3.2</u> (88)		3
			50 µm filtered and sterilised Lake IJssel water; pH 8.1; T 20; H 224	semi-continuous flow	M	21	C	yield			<u>0.3</u> (36)LT				3
				semi-static	N	21	C	intrinsic rate of natural increase	<u>3.2</u>	1	<u>10</u> (14.5)	<u>32</u> (100)			3
CdCl <sub>2</sub>	<i>Daphnia galeata mendotae</i>	10 µm filtered Lake Michigan water; T 18.5 H 120	semi-continuous flow	N	154	C	carrying capacity				7.7(50)		Marshall, 1978	3	
							C	number of individuals	<u>2</u>	1	4(23)	8(58)			3
							C	average biomass							3
							C	average birth rate	2	1	4(9)				3
							C	average death rate	2	1		<u>4</u> (71)			3
							C	brood size	2	1		4(70)			3
							C	dry weight	2	1	<u>4</u> (36)	5(54)			3
							C	life expectancy	4	1		8(71)			3
CdCl <sub>2</sub>	<i>Daphnia magna</i>	culture medium; pH8.4; H 150; T 20	semi-continuous flow	N	25	C	mortality	2.5	4			10(60)	Bodar et al., 1988a	3	
							C								3
							C	biomass production/female	<u>2.5</u>	4		<u>10</u> (71)			3
													3		
							intrinsic rate of natural increase	5	3	10(34)	20(72)			3	

Table 3.197 continued overleaf

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Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L-1)	Cat.*	LOEC (µg L-1) (%effect)	EC50 (µg L-1) (%effect)	LC50 (µg L-1) (%effect)	References	RI
CdCl <sub>2</sub>	<i>Simocephalus serrulatus</i>	synthetic water; H 39-48; Al 26-42; Ac 1.9-5.7; pH 7-7.9	static T 20; <1d old	M	2	A	mortality					<u>24.5</u>	Spehar and Carlson, 1984	3
	<i>Gammarus pseudolimnaeus</i>	unfiltered river water; static; H 55-79 Ac 2.4-2; Al 41-65; pH 7.2-7.8	T 17; 0.1g		4	A						<u>68.3</u>		3
	<i>Daphnia magna</i>		T 20; <1d old		2	A						<u>166</u>		3
	<i>Ceriodaphnia reticulata</i>		T 20; <1d old		2	A	reproduction					<u>129</u>		3
	<i>Simocephalus vetulus</i>		T 20; <1d old		2	A	mortality	<u>3.4</u>	1	<u>7.2</u>		<u>89.3</u>		3
	<i>Simocephalus serrulatus</i>		T 20; <1d old		2	A						<u>123</u>		3
	<i>Gammarus pseudolimnaeus</i>		T 17; 0.1g		4	A						<u>54.4</u>		3
	<i>Hyalella azteca</i>		T 7; 1µg		4	A						<u>285</u>		3
	<i>Paraleptophlebia praepepida</i>		T 12; 2µg		4	A						<u>449</u>		3
CdCl <sub>2</sub>	<i>Dugesia sp.</i>		non aerated spring water; T 23; H 20	static	N	4	A	mortality					<u>4.900</u>	Fennikoh et al., 1978
	<i>Cyclops sp.</i>	A					<u>340</u>						3	
	<i>Cypridopsis sp.</i>	A					<u>190</u>						3	
	<i>Hyalella sp.</i>	A					<u>85</u>						3	
	<i>Procambarus sp.</i>	A					<u>5.000</u>						3	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	Dutch Standard water NPR 6503 (1980); pH 8.4; H 150; T 20	semi-continuous flow	N	2	A	mean survival time of embryos			1000(37) (LT)	10000(87)		Bodar et al., 1989	3

Table 3.197 continued overleaf

Table 3.197 continued Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	RI	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	Dutch Standard water NPR 6503 (1980); pH 8.4; H 150; T 20	semi-continuous flow	N	14	C	body weight	1	1		1(56)		Bodar et al., 1988b	3	
							consumption rate				5(60)			3	
CdSO <sub>4</sub>	<i>Tubifex tubifex</i>	dilution water for BOD without phosphate buffer  dilution water for BOD with phosphate buffer:  drinking water	pH 6.85; H 34.2; Al 1.5	N	2	A	mortality					<u>31</u>	Brkovic-Popovic and Popovic, 1977	3	
			pH 6.85; H 34.2; Al 22.5				A					<u>45</u>		3	
			pH 7.32; H 261; Al 234; T 20				A					<u>720</u>		3	
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Simocephalus serrulatus</i>	filtered (0.15µm ) well water; Cd 0.023 µg L <sup>-1</sup> ; pH 6.5; H 11.1; Al 9.7; T 22; DO >80%  Skinface pond water; filtered through 0.15µm; Cd 0.02 µg L <sup>-1</sup> ; pH 5.6; H 10; Al 4; T 22; DO >80%	filtered well water	N	2	A	mortality					<u>7</u>	Giesy et al., 1977	3	
			filtered well water + F1**				A					8.6		3	
			filtered well water + F2**				A					12		3	
			filtered well water + F3**				A					16.5		3	
			filtered well water + F4**				A					3.6		3	
							A					<u>35</u>		3	
Cd-solution	<i>Gammarus pulex</i> <i>Asellus aquaticus</i> <i>Baetis rhodani</i> <i>Physa fontinalis</i> <i>Limnodrilus hoffmeisteri</i> <i>Ephemerella ignita</i> <i>Leuctra inermis</i> <i>Polycelis tenuis</i> <i>Chironomus riparius</i> <i>Hydropsyche angustipennis</i>	dechlorinated tap water; pH 7.7; T 12; H 152; DO >96%	continuous flow	M	4	A	mortality					<u>20</u>	Williams et al., 1985	3	
												A		<u>600</u>	3
												A		<u>500</u>	3
												A		<u>800</u>	3
												A		<u>2,400</u>	3
												A		<u>13,000</u>	3
												A		<u>32,000</u>	3
												A		<u>74,000</u>	3
												A		<u>30,000</u>	3
												A		<u>52,000</u>	3

Table 3.197 continued overleaf

Table 3.197 continued Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	<u>LC50 (µg L<sup>-1</sup>) (%effect)</u>	References	RI
CdCl <sub>2</sub>	<i>Daphnia magna</i>	well water; T 19.5; H 32-76; AI 31-69; pH 6.8-7.8	semi-static <4h old	M	2	A	mortality					109	Nebeker et al., 1986a	3
			<24h old			A						46		3
			1d old			A						48		3
			2d old			A						164		3
			3d old			A						63		3
			4d old			A						82		3
			5d old			A						49		3
6d old	A	<u>23</u>	3											
CdCl <sub>2</sub>	<i>Daphnia pulex</i>	synthetic water; pH 7.8; T 22	static; H 120; AI 110	N	2	A	mortality					<u>90</u>	Hall et al., 1986	3
	<i>Daphnia magna</i>					A						<u>35</u>		3
	<i>Ceriodaphnia reticulata</i>					A						<u>110</u>		3
	<i>Daphnia pulex</i>	well water; pH 7.7; T 22	static; H 200; AI 140;	2	A	<u>90</u>	3							
	<i>Daphnia magna</i>				A	<u>65</u>	3							
	<i>Ceriodaphnia reticulata</i>				A	<u>80</u>	3							
CdSO <sub>4</sub>	<i>Daphnia magna</i>	synthetic water (ISO 1977); pH 7.8; H 200; T 20-23	static	N	1	A	mortality					309	Dave et al., 1981	3
					2	A						69		3
					3	A						<u>40</u>		3
CdSO <sub>4</sub>	<i>Cyclops abyssorum prealpinus</i>	5µm filtered Lake Monate water; pH 7.2; H 40.7; T 10		N	2	A	mortality					<u>3,800</u>	Baudouin and Scoppa, 1974	3
	<i>Eudaptomus padanus padanus</i>					A						<u>550</u>		3
	<i>Daphnia hyalina</i>					A						<u>55</u>		3
CdCl <sub>2</sub>	<i>Daphnia magna</i>	synthetic water; T 20; pH 8.3; H 250	semi-static; small neonates	N	2	A	mortality					<u>98</u>	Enserink et al., 1990	3
			large neonates			A						294		3

Table 3.197 continued overleaf

Table 3.197 continued Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	<u>LC50 (µg L<sup>-1</sup>) (%effect)</u>	References	RI
CdCl <sub>2</sub>	<i>Daphnia magna</i>	synthetic water; T 20; pH 8.4; H 150	static;	N	2	A	mortality					<u>320</u>	Bodar et al., 1990	3
			pre-exposed to control											
			pre-exposed to 1µg Cd/L											
			pre-exposed to 5 µg Cd/L											
Cd-solution	<i>Physa gyrina</i> <i>mature</i>	synthetic water; T 20-22; DO 10-14; H 200; Al 130; pH 6.73; Cd < 0.5µg L <sup>-1</sup>	static	N	1	A	mortality					7,600	Wier and Walter, 1976	3
					2	A				4,250	3			
					4	A				1,370	3			
					9.5	A				830	3			
					2	A				690	3			
					4	A				<u>410</u>	3			
CdCl <sub>2</sub>	<i>Brotia hainanensis</i>	aerated artificial pond water; T 20; pH 7.4;H 200	upstream adolescents	N	4	A	mortality					15,210	Lam, 1996	3
			downstream adolescents			A				35,940	3			
			upstr. juv. <2d			A				<u>770</u>	3			
			downstr. juv. <2d			A				1,090	3			
			upstr. juv. >7d			A				1,180	3			
			downstr. juv. >7d			A				1,220	3			
CdSO <sub>4</sub>	<i>Daphnia magna</i>	filtered aerated tubewell hard water; H 240, T 13; pH 7.6; DO 5.6; Al 400	static	M	2	A	mortality					<u>1,880</u>	Khangarot and Ray, 1989	3
CdSO <sub>4</sub>	<i>Acroneuria lycorias</i>	carbon filtered Lake Superior tap water; pH 7-7.3; T 18.5; DO 8; Al 54-60; Ac 6-12; H 52-56		N	14	A	mortality					<u>32,000</u>	Warnick and Bell, 1969	3
	<i>Ephemereilla subvaria</i>		4		A				<u>2,000</u>	3				
	<i>Hydropsyche betteni</i>		10		A				<u>32,000</u>	3				

Table 3.197 continued overleaf

Table 3.197 continued Toxicity to aquatic invertebrates. All underlined data are selected to discuss the critical concentrations (Table 3.196). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Acute/ chronic	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC50 (µg L <sup>-1</sup> ) (%effect)	LC50 (µg L <sup>-1</sup> ) (%effect)	References	RI
Supporting data														
CdCl <sub>2</sub>	<i>Pteronarcys dorsata</i> <i>Hydropsyche betteni</i>	untreated Lake Superior water; pH 7.1-7.7; T 15; DO 10-11; H 44-48; Al 40-44; Ac 1.9-3	semi-static	M	28	C	mortality	238 (HT)					Spehar et al., 1978	4
					28	C		238 (HT)						4
CdCl <sub>2</sub>	<i>Daphnia magna</i> <i>Daphnia pulex</i> <i>Ceriodaphnia reticulata</i>	unchlorinated, carbon filtered well water, aerated to saturation; H 240; Al 230; pH 8; DO >5; T 23; Cd < 0.01 µg L <sup>-1</sup>	semi-static	N	14	C	mortality	25(HT)					Einabarawy et al., 1986	4
						C		25(HT)				4		
					7	C		25(HT)				4		
CdCl <sub>2</sub>	<i>Daphnia magna</i>	20 µm cloth filtered Lake Superior water; pH 7.7; H 45.3; Al 42.3; DO 9; T 18;	semi-continuous flow	N	21	C	reproductive impairment			0.17 (16)	0.7		Biesinger and Christensen, 1972	4
CdCl <sub>2</sub>	<i>Daphnia magna</i>	Dutch standard water; T 19	semi-static H200	M(>20µg L <sup>-1</sup> )	20	C	mortality	0.37	5			0.67	Canton and Slooff, 1982	4
					20	C	reproduction	0.5	1		<u>4.2</u>			4/3
Cd	<i>Hyalella azteca</i>	well water: T 23°C; pH 7.8; H 280	flow-through	M	42	C	length	3.2 (HT)					Ingersoll and Kemble, 2000	4
						C	weight	3.2 (HT)				4		
	20		C	biomass	3.2 (HT)				4					
				survival	17.4 (HT)				4					
<i>Chironomus tentans</i>	M	number of eggs	17.4 (HT)				4							
CdSO <sub>4</sub>	<i>Daphnia magna</i> <i>Ceriodaphnia dubia</i>	synthetic water; H 90; Al 65; T 25	static	N	7	C	mortality	3(HT)					Winner, 1988	4
						C	reproduction	0.5	2	<u>1(45)</u>			4/3	
CdCl <sub>2</sub>	<i>Daphnia magna</i>	hard synthetic water; H 250; T 20; DO 66-100%; pH 7.2-8.2	semi-static	N	16	C	growth	1.6(HT)					Berglund, 1985	4
CdCl <sub>2</sub>	<i>Tetrahymena sp.</i>	Osterhouts medium		N	15 min.	A	ciliate chemotactic response inhibition			250	475		Berk et al., 1985	4

T Temperature (°C);

Al Alkalinity (mg CaCO<sub>3</sub>/L);

\*\* Organic fractions

F3 0.0032 - 0.0009 µm;

H Hardness (as mg CaCO<sub>3</sub>/L);

Ac Acidity (mg CaCO<sub>3</sub>/L);

F1 > 0.0183 µm;

F4 < 0.0009 µm;

DO Dissolved oxygen (mg O<sub>2</sub>/L);

\* NOEC classification (see section 3.2.1.2);

F2 0.0183 - 0.0032 µm;

GOT Glutamic oxalacetic transaminase;

LT LOEC value found at lowest concentration tested

HT NOEC value found at highest concentration tested

### 3.2.2.4 Toxicity to primary producers

Table 3.198 Selected data with RI 1-3 for Cd toxicity to primary producers. Twenty-nine tests were reviewed from 21 source documents and 20 tests were selected. All tests were considered to represent chronic exposure to Cd

	Min	Median	Max	n
NOEC ( $\mu\text{g L}^{-1}$ )	0.85	6.9	31	8
LOEC ( $\mu\text{g L}^{-1}$ )	1.9	18	100	9
E(L) $C_{x=50}$ ( $\mu\text{g L}^{-1}$ )	6.1	59	1,000	12

Various studies reveal the toxicity of Cd, added as soluble salts, on algae, diatomic species, floating weeds and bacteria (see **Table 3.198**). Two studies are dealing with toxicity of CdO following the OECD-201 protocol for testing growth inhibition of algae (Janssen Pharmaceutica, 1993f, LISEC 1998b). These tests were performed in filtrates (0.1  $\mu\text{m}$  or 0.45  $\mu\text{m}$  pore size) of a CdO dispersion made up in the test medium. The metal oxide was dispersed in the test medium and membrane filtered. The Cd concentration in the filtrate was analysed and dilutions of the filtrate in test solution were inoculated with algae cells. Growth rate of *Selenastrum capricornutum* was reduced by 50% at Cd concentrations between 80-120  $\mu\text{g L}^{-1}$  with CdO as test substance (LISEC 1998b, Janssen Pharmaceutica 1993f). A similar test was performed with filtrates of a dispersion of metallic Cd powder (LISEC 1998a, Janssen Pharmaceutica 1993e). The EC<sub>50</sub> values for growth were 70-89  $\mu\text{g L}^{-1}$  with Cd as test substance, similar to the values obtained with the CdO filtrates. This indicates that the filtrates of the CdO and metallic Cd dispersions have the same Cd speciation, i.e. predominantly Cd<sup>2+</sup> ions.

Most reported LOEC values for algae or diatomic species range between 10 and 50  $\mu\text{g L}^{-1}$  with some exceptions. Four effect concentrations were noted below that range. In general terms, metal toxicity to algae increases with decreasing nutrient supply, decreasing cell density and with decreasing concentrations of chelating agents (Chen and Lin, 1997). Those studies in which synthetic chelates have been used in solution are omitted from this review except when these concentrations are low enough to warrant little Cd complexation. It appears that Cd toxicity is far more pronounced in flow through systems compared to static experiments (Chen and Lin, 1997). The type of Cd<sup>2+</sup> salts (Cl, NO<sub>3</sub><sup>-</sup>, acetate or carbonate) was found not to affect Cd<sup>2+</sup> toxicity (Wong et al., 1979).

Wong and co-workers (1979) followed growth (as cell number) in static conditions of *Ankistrodesmus falcatus* during 10 days after applying Cd<sup>2+</sup> salts to a synthetic medium. The cell number was reduced to 60% of the control after 6 days exposure to 1,000  $\mu\text{g L}^{-1}$ . At 500  $\mu\text{g L}^{-1}$ , no toxic effect was yet clear. A NOEC of Cd at 500  $\mu\text{g L}^{-1}$  is rather high compared to that of other studies (see **Table 3.199**). This could be attributed to a species effect: in a further comparative study on photosynthetic activity (<sup>14</sup>CO<sub>2</sub> uptake) of four algae species (*Ankistrodesmus falcatus*, *Chlorella vulgaris*, *Scenedesmus quadricauda*, *Chlorella pyrenoidosa*) it was found that *A. falcatus* and *C. vulgaris* are rather tolerant to Cd (EC<sub>50</sub> values at 700 and 600  $\mu\text{g L}^{-1}$ ) whereas *S. quadricauda* or *C. pyrenoidosa* are sensitive species (EC<sub>50</sub> values below 20 and at 100  $\mu\text{g L}^{-1}$ , Wong et al., 1979). Another factor that may explain the high NOEC in this test is the cell density. Metal toxicity often reduces at higher cell density because an increasing amount of metal becomes immobilised in the algal cell wall. A maximal initial cell density of 10,000 cells mL<sup>-1</sup> is defined in the OECD-201 algal growth inhibition tests. The initial cell density in the test *A. falcatus* is about 20 fold above this limit (190,000 cells mL<sup>-1</sup>). Therefore, we chose to define this test as unreliable. Klass et al. (1974) and Bringmann and Kühn (1980) also illustrate the sensitivity of *Scenedesmus quadricauda* to Cd. In the study of Klass et al. cell

number was reduced to 48% of control at  $6.1 \mu\text{g L}^{-1}$ . In this static experiment, cell density was rather low (ca.  $10^5$  cells/mL) and water hardness also low ( $25 \text{ mg L}^{-1}$ ), both factors contributing to high sensitivity. A drawback in the data interpretation of the test results is that average cell number (between 2-16 days after exposure) of the growing population is used as endpoint rather than cell number at one occasion. Bringmann and Kühn (1980) report a toxicity threshold concentration of Cd to *Scenedesmus quadricauda* of  $31 \mu\text{g L}^{-1}$ . The effect at that concentration is very low (3%) and is considered as a NOEC here. Another *Scenedesmus* species (*S. subspicatus*) is affected by Cd concentrations around  $30 \mu\text{g L}^{-1}$  ( $\text{EC}_{10}$  values in this case, Kühn and Pattard, 1990).

Toxicity of Cd to *Chlorella vulgaris* in static tests was reported by Wong et al. (1979), see above, Rosko and Rachlin (1977), Jouany et al. (1983) and Kosakowska et al. (1988). The study of Rosko and Rachlin reports an  $\text{EC}_{50}$  value for growth at  $60 \mu\text{g L}^{-1}$  after 33 days of exposure. Neither pH (which increased from 7.5 to 9.5) nor Cd concentrations were monitored during growth in this static test. In the tests of Jouany et al. (1983)  $\text{EC}_{50}$  values for growth are  $550\text{-}1,220 \mu\text{g L}^{-1}$ . In these tests, cell density was about two orders of magnitude higher than in the test of Rosko and Rachlin (1977). The test systems of Jouany et al. (1983) were either static or pseudodynamic (periodic addition of fresh medium). The Cd toxicity in the latter system was twofold higher ( $\text{EC}_{50}$  value twofold lower) than in the static system. In the tests of Kosakowska et al. (1988), the chlorophyll a content of the static system reduced by 77% compared to control in the presence of  $393 \mu\text{g Cd/L}$ , the only concentration tested.

A very high sensitivity to Cd was reported for the diatomic species *Asterionella formosa* by Conway (1978). The test system was dynamic (continuous culture system, also called chemostat) in which the Cd addition starts when steady state conditions are reached, i.e. when algae growth rate matches the dilution rate. In an artificial medium matching the Lake Michigan composition, Cd reduced growth rate by an order of magnitude when measured steady state Cd concentration reached  $2 \mu\text{g L}^{-1}$ . Unfortunately, the authors did not include a zero Cd treatment to show that steady state conditions were maintained during a further 9 days after initial steady state conditions. Therefore, these data are not included here. Nevertheless, static studies with the same diatomic species in (almost) the same medium revealed that significant inhibition of growth by 17% is reached at  $4.1 \mu\text{g L}^{-1}$  after 24 hours (Conway and Williams, 1979). Another diatomic species, *Fragilaria crotonensis*, was unaffected by Cd up to  $8.5 \mu\text{g L}^{-1}$ , the highest concentration tested.

The alga *Selenastrum capricornutum* is used in various standard algae tests (U.S. EPA, 1985, OECD, 1984). The static studies reported by Bartlett et al. (1974), Turbak et al. (1986), Lin et al. (1996), Chen and Lin (1997), Janssen Pharmaceutica (1993e&f) and LISEC (1998a,b) yield  $\text{EC}_{50}$  values for that species ranging between 18 and  $341 \mu\text{g L}^{-1}$ . Lin et al. (1996) indicated that most standard tests have high P concentrations ( $> 0.1 \text{ mg L}^{-1}$ ) and showed that sensitivity to Cd increases tenfold under P limiting conditions. Chen and Lin (1997) compared Cd toxicity to *Selenastrum capricornutum* between a continuous system and the U.S. EPA static test. In an artificial medium, the growth rate declined to 50% of control at  $13 \mu\text{g L}^{-1}$  in the continuous system within 24 hours. In the static experiment, the  $\text{EC}_{50}$  value for growth was  $341 \mu\text{g L}^{-1}$ . The medium composition differed in the concentrations of  $\text{NaNO}_3$ ,  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{EDTA}$ . The EDTA concentrations in both systems were low enough (below  $1 \mu\text{M}$ ) to ensure that almost no Cd is complexed by EDTA. Solution speciation calculation revealed that the difference in  $\text{EC}_{50}$  values between static and continuous systems is similar, whether based on total Cd concentration or on free metal ( $\text{Cd}^{2+}$ ) concentration.

Lawrence et al. (1989) used a serial construction of two continuous systems. In the first continuous system, the green alga *Chlamydomonas reinhardtii* was grown and that suspension

was pumped into the second where the protozoan *Tetrahymena vorax* was grown. Once steady state cell numbers were reached in both continuous systems, Cd was added at various concentrations. LOEC's on cell number after 7 days were  $10 \mu\text{g L}^{-1}$  and it appeared that the algae were a bit more sensitive to Cd than the protozoa. As a result of reduced grazing, the cell number of algae temporarily increased in the second continuous system at  $40 \mu\text{g L}^{-1}$  Cd. Acclimation of the algae to  $20 \mu\text{g L}^{-1}$  allowed the population to respond less drastically to  $40 \mu\text{g L}^{-1}$  than increasing Cd from 0 to  $40 \mu\text{g L}^{-1}$  in one step. It is unclear why the authors deliberately omitted Zn from the artificial solutions. It is likely that in Zn deficient conditions, Cd toxicity will be more pronounced. In a continuous *in situ* culture, shifts in populations of phytoplankton were observed upon Cd exposure. At Cd concentrations ranging between 2.9 and  $4.2 \mu\text{g L}^{-1}$  (measured concentrations, almost all Cd soluble), cell densities of two *Dinobryon* species were reduced to less than 10% of control values. The densities of other plankton species (*Elakatothrix sp.* and *Rhabdoderma gorskii*) were increased significantly above those in the control systems (DeNoyelles et al., 1980). Since only one concentration was tested above the background, the data of this experiment cannot be used for the current risk assessment.

Varying solution pH between 4.3 and 6.2 marginally affected Cd toxicity to the green alga *Coelastrum proboscideum*. LOEC values were found at  $27 \mu\text{g L}^{-1}$  (Müller and Payer, 1979).

Effects of Cd to duckweed (*Lemna paucicostata*) were assessed in three artificial media at varying pH (Nasu and Kugimoto, 1981). Toxic effects on the number of fronds after 1 week of growth started at  $10 \mu\text{g L}^{-1}$  Cd and Cd toxicity was generally higher at higher pH.

In conclusion, Cd can affect primary producers in the  $1\text{-}10 \mu\text{g L}^{-1}$  range but no tests showed toxicity below  $1 \mu\text{g L}^{-1}$ . At nutrient limiting conditions and low cell density, species are likely to be most sensitive to Cd. With one exception, all tests were performed in artificial media, some of which had very similar composition as freshwater samples.

Table 3.199 Toxicity to aquatic primary producers. All underlined data are selected to discuss the critical concentrations (Table 3.198). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC <sub>50</sub> (µg L <sup>-1</sup> ) (%effect)	References	RI	
Cd filtrate of dispersion	<i>Selenastrum capricornutum</i>	modified ISO 6341 medium; 0.2 µm filtered; T 20.3-25.6; pH 7.7-10.4 H 49	static	M	3	cell number	<u>2.4</u>	1	<u>5(11)</u>	<u>23</u>	LISEC, 1998a	1	
						growth rate	9.0	4	89	1			
CdO filtrate of dispersion	<i>Selenastrum capricornutum</i>	modified ISO 6341 medium; 0.2 µm filtered; H 49;pH 7-10		M	3	cell number			9.5(37)LT	18	LISEC, 1998b	1	
						growth rate	10.9	1	48(39)	79		1	
Cd filtrate of dispersion	<i>Selenastrum capricornutum</i>	AM; H 23; pH 7-9		M	3	growth rate	15	4	60(46)	70	Janssen Pharmaceutica, 1993e	1	
CdO filtrate of dispersion	<i>Selenastrum capricornutum</i>	AM H 23; pH 7-8		M	3	growth rate	50	1		120	Janssen Pharmaceutica, 1993f	1	
CdSO <sub>4</sub>	<i>Coelastrum proboscideum</i>	AM;H 32;T 31;pH 5.3;	static	M	1	biomass	<u>6.3</u>	1	<u>27(36)</u>		Müller and Payer 1979	2	
CdCl <sub>2</sub>	<i>Asterionella formosa</i>	AM; pH 8; H 121	static	M	1	growth rate	<u>0.85</u>	2	<u>1.9(18)LT</u>		Conway and Williams 1979	2	
CdCl <sub>2</sub>	<i>Chlamydomonas reinhardtii</i>	AM;H 42;pH 6.7; T 20	continuous	N	7	steady state cell number	<u>7.5</u>	1	<u>10(22)</u>		Lawrence et al., 1989	3	
CdCl <sub>2</sub>	<i>Scenedesmus subspicatus</i>	AM;H 60;T 24; pH 8	static	N	3	biomass				<u>62</u>	Kühn and Pattard 1990	3	
						growth rate (0-3d)				136		3	
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Scenedesmus quadricauda</i>	AM; pH 7	static; T 27; H 55	N	7	biomass (OD)	<u>31</u>	1			Bringmann and Kühn, 1980	3	
CdCl <sub>2</sub>	<i>Lemna paucicostata</i>	AM; T 25	static; pH > 6; H 120 pH 5.1; H 120 pH 5.1; H 700	N	7	number of fronds						Nasu and Kugimoto, 1981	
								<u>5</u>	2	<u>10(19)</u>			3
								<u>10</u>	3	<u>100(35)</u>			3
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Chlorella vulgaris</i>	AM; H=34;T=20	static	N	1	<sup>14</sup> CO <sub>2</sub> uptake				<u>600(50)</u>	Wong et al., 1979	3	
		AM; H=34;T=20	static		1					700(50)		3	
	<i>Scenedesmus quadricauda</i>	AM; H=34;T=20	static		1					<u>20(80)LT</u>		3	
	<i>Chlorella pyrenoidosa</i>	AM; H=34;T=20	static		1					<u>100(50)</u>		3	

Table 3.199 continued overleaf

Table 3.199 continued Toxicity to aquatic primary producers. All underlined data are selected to discuss the critical concentrations (Table 3.198). Bold data are used to estimate the HC<sub>5</sub> (Table 3.206). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Endpoint	NOEC (µg L <sup>-1</sup> )	Cat.*	LOEC (µg L <sup>-1</sup> ) (%effect)	EC <sub>50</sub> (µg L <sup>-1</sup> ) (%effect)	References	RI
CdCl <sub>2</sub>	<i>Selenastrum capricornutum</i>	AM;H=15;pH=7.1;T=24	static	N	4	biomass			<u>50(32)LT</u>		Bartlett et al., 1974	3
CdCl <sub>2</sub>	<i>Selenastrum capricornutum</i>	AM; pH 7.6; H 15; T 24	continuous	N	1	growth rate				<u>13</u>	Chen and Lin, 1997	3
			static		1	growth rate			<u>341</u>	3		
CdCl <sub>2</sub>	<i>Selenastrum capricornutum</i>	AM; pH 7.5; H 15;T24;	static	N	1	growth rate				<u>32</u>	Lin et al., 1996	3
CdCl <sub>2</sub>	<i>Selenastrum capricornutum</i>	AM;H=15;pH=7.1	static	N	14-21	biomass				<u>57</u>	Turbak et al., 1986	3
Supporting data												
CdCl <sub>2</sub>	<i>Scenedesmus quadricauda</i>	AM; H 28; T 21-30	static	N	2-16	average cell number	0.6	1		<u>6.1(52%)</u>	Klass et al., 1974	4/3
CdCl <sub>2</sub>	<i>Fragilaria crotonensis</i>	AM; pH 8; H 121	static	M	1	growth rate	8.5HT				Conway and Williams 1979	4
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Ankistrodesmus falcatus</i>	AM; H=34;T=20	static	N	6	cell number	500	3		<u>1000(60%)</u>	Wong et al., 1979	4/3
CdCl <sub>2</sub>	<i>Chlorella vulgaris</i>	AM;H=82;T=21	static	N	33	cell number	0.75	3	<u>18(28)</u>	<u>60(50)</u>	Rosko and Rachlin, 1977	4/3/3
			pseudo-dynamic		4	biomass (OD)			1220	Jouany et al., 1983		4
Cd-salt	<i>Dinobryon bavaricum</i> <i>Dinobryon sertularia</i> <i>Elakatothrix sp</i> <i>Rhabdoderma gorskii</i>	lake water	in situ continuous; epilimnion	M	12	cell density				3.5(>90)	DeNoyelles F. et al., 1980	4
												4
												4
												4
CdCl <sub>2</sub>	<i>Chlorella vulgaris</i> <i>Anabaena variabilis</i>	AM;H33;T 28	static	N	7	chlorophyll a content				393(77)LT	Kosakowska et al., 1988	4
										393(79)LT		

T Temperature (°C);  
H Water hardness (mg CaCO<sub>3</sub>/L);  
AM Artificial medium;  
OD Optical density;  
LT LOEC value found at lowest concentration tested  
HT NOEC value found at highest concentration tested  
\* NOEC classification (see Section 3.2.1.2).

### 3.2.2.5 Discussion

**Table 3.200** lists all toxicity data of primary producers, aquatic invertebrates and fish/amphibians. This data set contains all individual data (i.e. no species means) that were underlined in **Tables 3.195, 3.197 and 3.199**. This selection is based on data quality, i.e. data with RI 1-3 only. The selected data are retrieved from 168 different tests. This selection of results is used in this section to identify the factors that affect Cd toxicity, i.e. type of organism and environmental conditions.

Table 3.200 Summary of selected Cd toxicity data ( $\mu\text{g Cd/L}$ ). All data have  $\text{RI} \leq 3$  and are underlined in Tables 3.195, 3.197 and 3.199

	NOEC (chronic tests only)				
	min	5 <sup>th</sup> perc.	median	max	n
fish/amphibians	0.47	0.86	4.2	62	19
aquat. invertebrates	0.16	0.21	2.0	11	22
primary producers	0.85	1.4	6.9	31	8
	LOEC (chronic tests only)				
	min	5 <sup>th</sup> perc.	median	max	n
fish/amphibians	0.78	1.7	11	132	20
aquat. invertebrates	0.28	0.29	1.9	25	19
primary producers	1.9	3.1	18	100	9
	E-LC <sub>x≥50</sub> (chronic tests only)				
	min	5 <sup>th</sup> perc.	median	max	n
fish/amphibians	3.4	4.8	20	650	7
aquat. invertebrates	1	1.7	5	32	14
primary producers	6.1	9.9	59	1,000	12
	E-LC <sub>x≥50</sub> (acute tests only)				
	min	5 <sup>th</sup> perc.	median	max	n
fish/amphibians	0.9	2	1,500	40,200	31
aquat. invertebrates	7	24.5	166	74,000	61

The summary of selected data from chronic Cd tests reveals that the sensitivity to Cd decreases as:

aquatic invertebrates > fish/amphibians > primary producers.

The LOEC values indicate a considerably lower sensitivity of algae towards Cd than invertebrates or fish/amphibians. However, many of the tests with algae are performed in static (batch) conditions where high LOEC/NOEC values are associated with high cell densities. The much higher sensitivity obtained in the continuous systems (chemostats) indicates that algae may indeed be sensitively affected in the  $\mu\text{g L}^{-1}$  range (Conway, 1978; Chen and Lin, 1997).

The toxic effects of Cd become pronounced above  $1 \mu\text{g L}^{-1}$ . In the selected data set with  $\text{RI} \leq 3$ , only 6 of the 48 LOEC values and 1 of the 125 E(L)C<sub>50</sub> values can be found below  $1 \mu\text{g L}^{-1}$ . Two of these data refer to tests on fish in soft water ( $< 28 \text{ mg CaCO}_3/\text{L}$ ). In the data with RI 4, at least

three more effect concentrations are found below  $1 \mu\text{g L}^{-1}$ . These data were considered as not reliable, mainly because Cd background concentrations were unknown. Detecting Cd in solution below about  $0.5 \mu\text{g L}^{-1}$  is intricate with conventional methods (i.e. flameless atomic absorption spectrometry, detection limit  $\approx 0.1 \mu\text{g L}^{-1}$ ). The source document of Rombough and Garside (1982) is the only that mentions details on pre-concentration steps. These authors found a LOEC at  $0.78 \mu\text{g L}^{-1}$ , significantly above the background of  $0.13 \mu\text{g L}^{-1}$ . More information should be gathered using more sensitive techniques such as Inductively Coupled Plasma, Mass Spectrometry (ICP-MS detection limits around  $0.05 \mu\text{g L}^{-1}$ ) to assess possible toxic effects of Cd in the  $< 0.5 \mu\text{g L}^{-1}$  range. Some authors however stressed that threshold toxic Cd effects may not be found in chronic studies with Cd (Marshall, 1978; Van Leeuwen et al., 1985).

### 3.2.2.6 The $\text{PNEC}_{\text{water}}$

#### 3.2.2.6.1 The NOEC data

Different species sensitivity distributions (SSD's) can be calculated for different selections of the data since the NOEC values have attached information such as data quality (the Reliability Index, RI) and properties of the test (species, water characteristics and endpoint). All data with  $\text{RI} = 4$  (unreliable) were not included because critical information of the test was lacking. Statistical properties of the selected NOEC data are given in **Table 3.201**. The selected NOEC data are summarised in **Table 3.202**.

Table 3.201 Summary of the NOEC values ( $\mu\text{g Cd/L}$ ) of chronic tests in the aquatic compartment for various levels of reliability (RI, defined in the introduction of Section 3.2.2)

	NOEC				
	min	5 <sup>th</sup> perc. of NOEC data	median	max	n
RI 1-3	0.16	0.34	3.4	62	49
RI 1-2	0.47	0.60	4.2	62	21
RI 1			2.4		1

#### 3.2.2.6.2 Species sensitivity distributions at different levels of data quality

There are enough data from all three trophic levels to calculate the  $\text{PNEC}_{\text{water}}$  by the assessment factor method (AFM) using the lowest assessment factor 10 (TGD, 1996, p. 330). The lowest NOEC value with a  $\text{RI} \leq 3$  is  $0.16 \mu\text{g L}^{-1}$ . This would yield a  $\text{PNEC}_{\text{water}} = 0.016 \mu\text{g L}^{-1}$  (see **Table 3.206**). Rather than making a risk assessment based on one single NOEC value, it is possible to use the statistical extrapolation method (TGD, 1996, p. 469) if enough NOEC data are available. This condition is certainly met in the case of Cd and is preferred over the assessment factor method. The  $\text{PNEC}_{\text{water}}$ , derived with the assessment factor method, is in the range of background concentrations of membrane filtered freshwaters. The Cd toxicity has not been tested in that range. Moreover, Cd concentrations below  $0.1\text{-}0.2 \mu\text{g L}^{-1}$  are difficult to measure with conventional methods (see Section 3.2.2.4.).

To evaluate the toxicity data, the statistical extrapolation method is used (Aldenberg and Slob, 1993). The fifth percentile ( $\text{HC}_5$ ), with 50% confidence, of a species sensitivity distribution is calculated using the software package ETX 1.3a (RIVM, Bilthoven, The Netherlands). The  $\text{HC}_5$  is calculated for 4 different approaches of data selection. The first approach is by using all the

data (see **Table 3.202**), without calculation of species geometric mean values. The second method is by calculating ‘geometric mean’ NOEC values for each species, resulting in one NOEC per species (see **Table 3.203**). The third approach is by calculating ‘geometric mean’ NOEC’s on a case-by-case basis (see **Table 3.204**). At a special workshop, held in January 2001, in the framework of the EU Existing Substances programme, it was agreed that “for comparable data on the same endpoint and species the geometric mean should be used as the input value for the calculation using the SSD. If this is not thought to be possible, perhaps because results that are considered valid, are too variable, then consider grouping and combining the values, e.g. by pH ranges, and using reduced numbers of values. The full data set could also be used if necessary”. Geometric mean NOEC’s are thus calculated for the same species and the same endpoint, tested in similar media<sup>¶</sup>. This approach does not result in one NOEC per species. The fourth approach is by selecting the lowest NOEC for each species, resulting in one NOEC per species (see **Table 3.205**).

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<sup>¶</sup> Test media are considered to be similar if the difference in pH is 5% or less, if the difference in water hardness is 15% or less and if the difference in dissolved oxygen concentration, aluminium concentration, and temperature is 10% or less. Biomass and total weight of young per female are considered to be the same endpoint. Pond fish and laboratory fry (*P. promelas*) are considered to be the same species.

Table 3.202 Selected NOEC data of effects of Cd in freshwater. Data derived from Tables 3.195, 3.197 and 3.199 within quality class RI 1-3

Organism	Phylum/class	Order	Family	Medium	H	Nominal/ Measured	Duration (d)	Endpoint	NOEC ( $\mu\text{g L}^{-1}$ )	References	R.I.
<i>Salmo gairdneri</i>	Chordata	Salmoniformes	Salmonidae	aerated well water; T 10; O <sub>2</sub> 7.5; pH 8-8.6	375-390	M	84	mortality	12	Lowe-Jinde and Niimi, 1984	2
<i>Salmo gairdneri</i>	Chordata	Salmoniformes	Salmonidae	synthetic water (ISO 1977); T 25; pH 8.3	100	N	50	median survival time	4	Dave et al., 1981	3
<i>Oncorhynchus kisutch</i>	Chordata	Salmoniformes	Salmonidae	sand filtered Lake Superior Water; continuous flow; DO 10.3; Al 41; Ac 3; pH 7.6	45	M	27	biomass	1.3	Eaton et al., 1978	2
<i>Salvelinus fontinalis</i>	Chordata	Salmoniformes	Salmonidae	sand filtered Lake Superior Water; continuous flow; DO 10.3; Al 41; Ac 3; pH 7.6	45	M	126	biomass	1.1	Eaton et al., 1978	2
<i>Salvelinus fontinalis</i>	Chordata	Salmoniformes	Salmonidae	sterilised Lake Superior water; pH 7-8; Al 38-46; Ac 1-10; DO 4-12; T 9-15	42-47	M	3 years	total weight of young /female of the 2nd generation	0.9	Benoit et al, 1976	2
<i>Salvelinus fontinalis</i>	Chordata	Salmoniformes	Salmonidae	reconstituted soft water; T 14-16°C; DO 9.3-11.4 mg L <sup>-1</sup> ; Cd(BG) <0.2 $\mu\text{g L}^{-1}$ ; pH 6.3-7.6; H 20	20	M	10	survival	8	Jop et al., 1995	2
<i>Salvelinus fontinalis</i>	Chordata	Salmoniformes	Salmonidae	river water; T 14-16°C; DO 8.7-12.2 mg L <sup>-1</sup> ; Cd(BG) <4 $\mu\text{g L}^{-1}$ ; pH 6.6-7.4; H 16-28	16-28	M	10	survival	62	Jop et al., 1995	2
<i>Salmo salar</i>	Chordata	Salmoniformes	Salmonidae	municipal water charcoal filtered and UV sterilised; BC 0.13 $\mu\text{g Cd/L}$ ; pH 6.5-7.3; T 5-10; DO 11.1-12.5; Al 14-17	19-28	M	46	total biomass	0.47	Rombough and Garside, 1982	2
<i>Catostomus commersoni</i>	Chordata	Cypriniformes	Catostomidae	sand filtered Lake Superior Water; continuous flow; DO 10.3; Al 41; Ac 3; pH 7.6	45	M	30	standing crop (biomass)	4.2	Eaton et al., 1978	2
<i>Esox lucius</i>	Chordata	Esociformes	Esocidae				28	biomass	4.2		2
<i>Salvelinus namaycush</i>	Chordata	Salmoniformes	Salmonidae				31		4.4		2
<i>Salmo trutta</i> (late eyed eggs)	Chordata	Salmoniformes	Salmonidae				61		1.1		2
<i>Jordaniella floridiae</i>	Chordata	Cyprinodontiformes	Cyprinodontidae	untreated Lake Superior water; T 25; DO 8.3; Al 42; Ac 2.4; pH 7.1-7.8	44	M	100	reproduction	4.1	Spehar, 1976	2
<i>Brachydanio rerio</i>	Chordata	Cypriniformes	Cyprinidae	synthetic water (changed ISO); T 24; DO >80%; pH 7.2	100	N	36	reproduction	1	Bresch., 1982	3
<i>Oryzias latipes</i>	Chordata	Beloniformes	Adrianichthyidae	tap water; continuous flow; T 20	200	M	18	mortality and abn. behaviour	6 3	Canton and Slooff, 1982	3
<i>Xenopus laevis</i>	Chordata	Anura	Pipidae	tap water; continuous flow; T 20	170		100	inhibition of larvae development	9		3
<i>Pimephales promelas</i>	Chordata	Cypriniformes	Cyprinidae	pond water diluted with carbon filtered demineralised tap water; DO 6.5-6.6; pH 7.6-7.7; Al 145-161; Ac 8-12; T 16-27	201-204	M	60 60	reproduction (pond fish) reproduction (laboratory fry)	13 14	Pickering and Gast, 1972	3 3
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	50 $\mu\text{m}$ filtered and sterilised Lake IJssel water; pH 8.1; T 20; H 224	224	N	21	intrinsic rate of natural increase	3.2	Van Leeuwen et al., 1985	3
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	NPR synthetic water; pH 8.4; T 20	200	N	21	mortality	1	Van Leeuwen et al., 1985	3

Table 3.202 continued overleaf

Table 3.202 continued Selected NOEC data of effects of Cd in freshwater. Data derived from Tables 3.195, 3.197 and 3.199 within quality class RI 1-3

Organism	Phylum/class	Order	Family	Medium	H	Nominal/ Measured	Duration (d)	Endpoint	NOEC (µg L-1)	References	R.I.
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	synthetic water; T 25; pH 8; DO 69%	11	M	21	reproduction	0.6	Kühn et al., 1989	2
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	Synthetic water; Al 65; T 25	90	N	7	reproduction	2	Winner, 1988	3
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	well water: T 20±2°C; DO 4.9-7.9; Cd(BG) 0.08; pH 7.9	103	M	21	reproduction	0.16	Chapman et al., 1980	3
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	well water: T 20±2°C; DO 4.9-7.9; Cd(BG) 0.08; pH 8.2	209	M	21	reproduction	0.21	Chapman et al., 1980	3
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	unchlorinated, carbon filtered well water, aerated to saturation; Al 230; pH 8; DO >5; T 23; Cd < 0.01 µg Cd/L	240	N	14	reproductive impairment	2.5	Elnabarawy et al., 1986	3
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	aerated well water; DO >70%; pH 8; T 22; Al 250	300	M	21	reproduction	0.8	Knowles and McKee, 1987	2
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	culture medium; pH8.4; T 20	150	N	25	biomass production/female	2.5	Bodar et al., 1988a	3
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	20 µm cloth filtered Lake Superior water; pH 7.7; Al 42.3; DO 9; T 18	45.3	N	21	weight/animal	1	Biesinger and Christensen, 1972	3
<i>Daphnia pulex</i>	Arthropoda	Cladocera	Daphnidae	Whatman N° 1 filtered Lake Champlain water; pH 7.7; Al 42.4; Cd < 1 µg L <sup>-1</sup>	65	N	104	longevity	1	Bertram and Hart, 1979	3
<i>Daphnia pulex</i>	Arthropoda	Cladocera	Daphnidae	unchlorinated, carbon filtered well water, aerated to saturation; Al 230; pH 8; DO >5; T 23; Cd < 0.01 µg Cd/L	240	N	14	reproductive impairment	7.5	Elnabarawy et al., 1986	3
<i>Aplexa hypnorum: immature</i>	Mollusca	Basommatophora	Physidae	Lake Superior water; DO 7.5; T 24		M	26	growth	4.41	Holcombe et al., 1984	2
<i>Physa integra</i>	Mollusca	Basommatophora	Physidae	untreated Lake Superior water; pH 7.1-7.7; T 15; DO 10-11; Al 40-44; Ac 1.9-3	44-48	M	21	mortality	8.3	Spehar et al., 1978	2
<i>Daphnia galeata mendotae</i>	Arthropoda	Cladocera	Daphnidae	10 µm filtered Lake Michigan water; T 18.5	120	N	154	number of individuals	2	Marshall, 1978	3
<i>Ceriodaphnia reticulata</i>	Arthropoda	Cladocera	Daphnidae	unfiltered river water; static; Ac 2-4.2; Al 41-65; pH 7.2-7.8	55-79	M	9	reproduction	3.4	Spehar and Carlson, 1984	3
<i>Ceriodaphnia reticulata</i>	Arthropoda	Cladocera	Daphnidae	unchlorinated, carbon filtered well water, aerated to saturation; Al 230; pH 8; DO >5; T 23; Cd < 0.01 µg L <sup>-1</sup>	240	N	7	reproductive impairment	0.25	Elnabarawy et al., 1986	3
<i>Ceriodaphnia dubia</i>	Arthropoda	Cladocera	Daphnidae	Synthetic water; Al 65; T 25	90	N	7	mortality	1.5	Winner, 1988	3
<i>Ceriodaphnia dubia</i>	Arthropoda	Cladocera	Daphnidae	reconstituted soft water: T 14-16°C; DO 9.3-11.4 mg L <sup>-1</sup> ; Cd(BG) <0.2 µg L <sup>-1</sup> ; pH 6.3-7.6; H 20	20	M	7	reproduction	10	Jop et al., 1995	2
<i>Ceriodaphnia dubia</i>	Arthropoda	Cladocera	Daphnidae	river water: T 14-16°C; DO 8.7-12.2 mg L <sup>-1</sup> ; Cd(BG) <4 µg L <sup>-1</sup> ; pH 6.6-7.4; H 16-28	16-28	M	7	reproduction	11	Jop et al., 1995	2
<i>Hyalella azteca</i>	Arthropoda	Amphipoda	Hyalellidae	well water: T 23; pH 7.8	280	M	42	Survival	0.51	Ingersoll and Kemble, 2000	3
<i>Chironomus tentans</i>	Arthropoda	Diptera	Chironomidae	well water: T 23; pH 7.8	280	M	20	weight	5.8	Ingersoll and Kemble, 2000	3
<i>Selenastrum capricornutum</i>	Chlorophyceae	Chlorococcales	Scenedesmeceae	modified ISO 6341 medium; 0.2 µm filtered; T 20.3-25.6; pH 7.7-10.4	49	M	3	cell number	2.4	LISEC, 1998a	1

Table 3.202 continued overleaf

Table 3.202 continued Selected NOEC data of effects of Cd in freshwater. Data derived from Tables 3.195, 3.197 and 3.199 within quality class RI 1-3

Organism	Phylum/class	Order	Family	Medium	H	Nominal/ Measured	Duration (d)	Endpoint	NOEC (µg L-1)	References	R.I.		
<i>Coelastrum proboscideum</i>	Chlorophyceae	Chlorococcales	Coelastraceae	AM;T 31;pH 5.3;	32	M	1	biomass	6.3	Müller and Payer 1979	2		
<i>Asterionella formosa</i>	Bacillariophyceae	Pennales	Diatomaceae	AM; pH 8	121	M	1	growth rate	0.85	Conway and Williams 1979	2		
<i>Chlamydomonas reinhardtii</i>	Chlorophyceae	Volvocales	Chlamydomonaceae	AM; pH 6.7; T 20	42	N	7	steady state cell number	7.5	Lawrence et al., 1989	3		
<i>Scenedesmus quadricauda</i>	Chlorophyceae	Chlorococcales	Scenedesmaceae	AM; pH 7		N	7	biomass (OD)	31	Bringmann and Kühn, 1980	3		
<i>Lemna paucicostata</i>	Liliopsida	Arales	Lemnaceae	AM; T 25		N	7	number of fronds		Nasu and Kugimoto, 1981			
				pH>6	120							5	3
				pH 5.1	120							10	3
				pH 5.1	700							10	3

- T Temperature (°C);
- H Hardness (as mg CaCO<sub>3</sub>/L);
- DO Dissolved oxygen (mg O<sub>2</sub>/L);
- Al Alkalinity (mg CaCO<sub>3</sub>/L);
- Ac Acidity (mg CaCO<sub>3</sub>/L);
- AM Artificial medium.

Table 3.203 'One species, one NOEC': selected NOEC data of effects of Cd in freshwater and calculation of 'geometric mean NOEC's. Data derived from Table 3.202

Organism	Phylum/class	Order	Family	NOEC ( $\mu\text{g L}^{-1}$ )	
<i>Salmo gairdneri</i>	Chordata	Salmoniformes	Salmonidae	6.9	geometric mean of 4 and 12
<i>Oncorhynchus kisutch</i>	Chordata	Salmoniformes	Salmonidae	1.3	
<i>Salvelinus fontinalis</i>	Chordata	Salmoniformes	Salmonidae	4.7	geometric mean of 0.9, 1.1, 8 and 62
<i>Salmo salar</i>	Chordata	Salmoniformes	Salmonidae	0.47	
<i>Catostomus commersoni</i>	Chordata	Cypriniformes	Catostomidae	4.2	
<i>Esox lucius</i>	Chordata	Esociformes	Esocidae	4.2	
<i>Salvelinus namaycush</i>	Chordata	Salmoniformes	Salmonidae	4.4	
<i>Salmo trutta</i> (late eyed eggs)	Chordata	Salmoniformes	Salmonidae	1.1	
<i>Jordanella floridae</i>	Chordata	Cyprinodontiformes	Cyprinodontidae	4.1	
<i>Brachydanio rerio</i>	Chordata	Cypriniformes	Cyprinidae	1	
<i>Oryzias latipes</i>	Chordata	Belontiiformes	Adrianichthyidae	4.2	geometric mean of 3 and 6
<i>Xenopus laevis</i>	Chordata	Anura	Pipidae	9	
<i>Pimephales promelas</i>	Chordata	Cypriniformes	Cyprinidae	13.5	geometric mean of 13 and 14
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	1.0	geometric mean of 0.16, 0.21, 0.6, 0.8, 1, 1, 2, 2.5, 2.5 and 3.2
<i>Daphnia pulex</i>	Arthropoda	Cladocera	Daphnidae	2.7	geometric mean of 1 and 7.5
<i>Aplexa hypnorum</i> : immature	Mollusca	Basommatophora	Physidae	4.41	
<i>Physa integra</i>	Mollusca	Basommatophora	Physidae	8.3	
<i>Daphnia galeata mendotae</i>	Arthropoda	Cladocera	Daphnidae	2	
<i>Ceriodaphnia reticulata</i>	Arthropoda	Cladocera	Daphnidae	0.9	geometric mean of 0.25 and 3.4
<i>Ceriodaphnia dubia</i>	Arthropoda	Cladocera	Daphnidae	5.5	geometric mean of 1.5, 10 and 11
<i>Hyalella azteca</i>	Arthropoda	Amphipoda	Hyalellidae	0.51	
<i>Chironomus tentans</i>	Arthropoda	Diptera	Chironomidae	5.8	
<i>Selenastrum capricornutum</i>	Chlorophyceae	Chlorococcales	Scenedesmaceae	2.4	
<i>Coelastrum proboscideum</i>	Chlorophyceae	Chlorococcales	Coelastraceae	6.3	
<i>Asterionella formosa</i>	Bacillariophyceae	Pennales	Diatomaceae	0.85	
<i>Chlamydomonas reinhardtii</i>	Chlorophyceae	Volvocales	Chlamydomonaceae	7.5	
<i>Scenedesmus quadricauda</i>	Chlorophyceae	Chlorococcales	Scenedesmaceae	31	
<i>Lemna paucicostata</i>	Liliopsida	Arales	Lemnaceae	7.9	geometric mean of 5, 10 and 10

Table 3.204 'Case-by-case selection': selected NOEC data of effects of Cd in freshwater and case-by-case calculation of 'geometric mean NOEC's. Bold, underlined data are selected for the HC<sub>5</sub> calculation. Data derived from Table 3.202

Organism	Medium	H	Endpoint	NOEC (µg L <sup>-1</sup> )		References
<i>Salmo gairdneri</i>	aerated well water; T 10; O <sub>2</sub> 7.5; pH 8-8.6	375-390	mortality	<u>12</u>	<i>S. gairdneri</i> : no geometric mean calculation: different test medium	Lowe-Jinde and Niimi, 1984
<i>Salmo gairdneri</i>	synthetic water (ISO 1977) ; T 25; pH 8.3	100	median survival time	<u>4</u>		Dave et al., 1981
<i>Oncorhynchus kisutch</i>	sand filtered Lake Superior Water; continuous flow; DO 10.3; Al 41; Ac 3; pH 7.6	45	biomass	<u>1.3</u>		Eaton et al., 1978
<i>Salvelinus fontinalis</i>	sand filtered Lake Superior Water; continuous flow; DO 10.3; Al 41; Ac 3; pH 7.6	45	biomass	1.1	<i>S. fontinalis</i> : geometric mean calculation: same test medium, same endpoint (biomass)	Eaton et al., 1978
<i>Salvelinus fontinalis</i>	sterilised Lake Superior water; pH 7-8; Al 38-46; Ac 1-10; DO 4-12; T 9-15	42-47	total weight of young /female of the 2nd generation	0.9	geometric mean = <u>1.0</u>	Benoit et al., 1976
<i>Salvelinus fontinalis</i>	reconstituted soft water: T 14-16°C; DO 9.3-11.4 mg L <sup>-1</sup> ; Cd(BG) <0.2 µg L <sup>-1</sup> ; pH 6.3-7.6; H 20	20	survival	8	<i>S. fontinalis</i> : geometric mean calculation: similar test medium, same endpoint (survival)	Jop et al., 1995
<i>Salvelinus fontinalis</i>	river water: T 14-16°C; DO 8.7-12.2 mg L <sup>-1</sup> ; Cd(BG) <4 µg L <sup>-1</sup> ; pH 6.6-7.4; H 16-28	16-28	survival	62	geometric mean = <u>22</u>	Jop et al., 1995
<i>Salmo salar</i>	municipal water charcoal filtered and UV sterilised; BC 0.13 µg Cd/L; pH 6.5-7.3; T 5-10; DO 11.1-12.5; Al 14-17	19-28	total biomass	<u>0.47</u>		Rombough and Garside, 1982
<i>Catostomus commersoni</i> <i>Esox lucius</i> <i>Salvelinus namaycush</i> <i>Salmo trutta</i> (late eyed eggs)	sand filtered Lake Superior Water; continuous flow; DO 10.3; Al 41; Ac 3; pH 7.6	45	standing crop (biomass) biomass	<u>4.2</u> <u>4.2</u> <u>4.4</u> <u>1.1</u>		Eaton et al., 1978
<i>Jordaniella floridae</i>	untreated Lake Superior water; T 25; DO 8.3; Al 42; Ac 2.4; pH 7.1-7.8	44	reproduction	<u>4.1</u>		Spehar, 1976
<i>Brachydanio rerio</i>	synthetic water (changed ISO) ; T 24; DO >80%; pH 7.2	100	reproduction	<u>1</u>		Bresch., 1982
<i>Oryzias latipes</i>	tap water; continuous flow; T 20	200 100	mortality and abn. behaviour	<u>6</u> <u>3</u>	<i>O. latipes</i> : no geometric mean calculation: different test medium	Canton and Slooff, 1982
<i>Xenopus laevis</i>	tap water; continuous flow; T 20	170	inhibition of larvae development	<u>9</u>		Canton and Slooff, 1982
<i>Pimephales promelas</i>	pond water diluted with carbon filtered demineralised tap water; DO 6.5-6.6; pH 7.6-7.7; Al 145-161; Ac 8-12; T 16-27	201-204	reproduction (pond fish) reproduction (laboratory fry)	13 14	<i>P. promelas</i> : geometric mean calculation: same test medium, same endpoint (reproduction) geometric mean = <u>13.5</u>	Pickering and Gast, 1972
<i>Daphnia magna</i>	50 µm filtered and sterilised Lake IJssel water; pH 8.1; T 20; H 224	224	intrinsic rate of natural increase	<u>3.2</u>	<i>D. magna</i> : no geometric mean calculation: different endpoints	Van Leeuwen et al., 1985
<i>Daphnia magna</i>	NPR synthetic water; pH 8.4; T 20	200	mortality	<u>1</u>		Van Leeuwen et al., 1985
<i>Daphnia magna</i>	synthetic water; T 25; pH 8; DO 69%	11	reproduction	<u>0.6</u>	<i>D. magna</i> : no geometric mean calculation: different medium	Kühn et al., 1989
<i>Daphnia magna</i>	Synthetic water; Al 65; T 25	90	reproduction	2	<i>D. magna</i> : geometric mean calculation: similar medium, same endpoint (reproduction)	Winner, 1988

Table 3.204 continued overleaf

Table 3.204 continued 'Case-by-case selection': selected NOEC data of effects of Cd in freshwater and case-by-case calculation of 'geometric mean NOEC's. Bold, underlined data are selected for the HCs calculation. Data derived from Table 3.202

Organism	Medium	H	Endpoint	NOEC ( $\mu\text{g L}^{-1}$ )		References
<i>Daphnia magna</i>	well water: T 20±2°C; DO 4.9-7.9; Cd(BG) 0.08; pH 7.9	103	reproduction	0.16	geometric mean = <u>0.6</u>	Chapman et al., 1980
<i>Daphnia magna</i>	well water: T 20±2°C; DO 4.9-7.9; Cd(BG) 0.08; pH 8.2	209	reproduction	<u>0.21</u>	<i>D. magna</i> : no geometric mean calculation: different medium	Chapman et al., 1980t
<i>Daphnia magna</i>	unchlorinated, carbon filtered well water, aerated to saturation; Al 230; pH 8; DO >5; T 23; Cd < 0.01 $\mu\text{g Cd/L}$	240	reproductive impairment	<u>2.5</u>		Elnabarawy et al., 1986
<i>Daphnia magna</i>	aerated well water; DO >70%; pH 8; T 22; Al 250	300	reproduction	<u>0.8</u>		Knowles and McKee, 1987
<i>Daphnia magna</i>	culture medium; pH8.4; T 20	150	biomass production/female	<u>2.5</u>	<i>D. magna</i> : no geometric mean calculation: different medium	Bodar et al., 1988a
<i>Daphnia magna</i>	20 $\mu\text{m}$ cloth filtered Lake Superior water; pH 7.7; Al 42.3; DO 9; T 18	45.3	weight/animal	<u>1</u>		Biesinger and Christensen, 1972
<i>Daphnia pulex</i>	Whatman N° 1 filtered Lake Champlain water; pH 7.7; Al 42.4; Cd < 1 $\mu\text{g L}^{-1}$	65	Longevity	<u>1</u>	<i>D. pulex</i> : no geometric mean calculation: different medium	Bertram and Hart, 1979
<i>Daphnia pulex</i>	unchlorinated, carbon filtered well water, aerated to saturation; Al 230; pH 8; DO >5; T 23; Cd < 0.01 $\mu\text{g Cd/L}$	240	reproductive impairment	<u>7.5</u>		Elnabarawy et al., 1986
<i>Aplexa hypnorum: immature</i>	Lake Superior water; DO 7.5; T 24		Growth	<u>4.41</u>		Holcombe et al., 1984
<i>Physa integra</i>	untreated Lake Superior water; pH 7.1-7.7; T 15; DO 10-11; Al 40-44; Ac 1.9-3	44-48	Mortality	<u>8.3</u>		Spehar et al., 1978
<i>Daphnia galeata mendotae</i>	10 $\mu\text{m}$ filtered Lake Michigan water; T 18.5	120	Number of individuals	<u>2</u>		Marshall, 1978
<i>Ceriodaphnia reticulata</i>	unfiltered river water; static; Ac 2-4.2; Al 41-65; pH 7.2-7.8	55-79	Reproduction	<u>3.4</u>	<i>C. reticulata</i> : no geometric mean calculation: different medium	Spehar and Carlson, 1984
<i>Ceriodaphnia reticulata</i>	unchlorinated, carbon filtered well water, aerated to saturation; Al 230; pH 8; DO >5; T 23; Cd < 0.01 $\mu\text{g L}^{-1}$	240	reproductive impairment	<u>0.25</u>		Elnabarawy et al., 1986
<i>Ceriodaphnia dubia</i>	Synthetic water; Al 65; T 25	90	Mortality	<u>1.5</u>	<i>C. dubia</i> : no geometric mean calculation: different medium, different endpoint	Winner, 1988
<i>Ceriodaphnia dubia</i>	reconstituted soft water: T 14-16°C; DO 9.3-11.4 $\text{mg L}^{-1}$ ; Cd(BG) < 0.2 $\mu\text{g L}^{-1}$ ; pH 6.3-7.6; H 20	20	Reproduction	10	<i>C. dubia</i> : geometric mean calculation: similar medium, same endpoint (reproduction)	Jop et al., 1995
<i>Ceriodaphnia dubia</i>	river water: T 14-16°C; DO 8.7-12.2 $\text{mg L}^{-1}$ ; Cd(BG) < 4 $\mu\text{g L}^{-1}$ ; pH 6.6-7.4; H 16-28	16-28	Reproduction	11	geometric mean = <u>10.5</u>	Jop et al., 1995
<i>Hyalella azteca</i>	well water: T 23; pH 7.8	280	Survival	<u>0.51</u>		Ingersoll and Kemble, 2000
<i>Chironomus tentans</i>	well water: T 23; pH 7.8	280	Weight	<u>5.8</u>		Ingersoll and Kemble, 2000
<i>Selenastrum capricornutum</i>	modified ISO 6341 medium; 0.2 $\mu\text{m}$ filtered; T 20.3-25.6; pH 7.7-10.4	49	cell number	<u>2.4</u>		LISEC, 1998a
<i>Coelastrum proboscideum</i>	AM; T 31; pH 5.3;	32	Biomass	<u>6.3</u>		Müller and Payer 1979
<i>Asterionella formosa</i>	AM; pH 8	121	growth rate	<u>0.85</u>		Conway and Williams 1979
<i>Chlamydomonas reinhardtii</i>	AM; pH 6.7; T 20	42	steady state cell number	<u>7.5</u>		Lawrence et al., 1989
<i>Scenedesmus quadricauda</i>	AM; pH 7		biomass (OD)	<u>31</u>		Bringmann and Kühn, 1980

Table 3.204 continued overleaf

Table 3.204 continued 'Case-by-case selection': selected NOEC data of effects of Cd in freshwater and case-by-case calculation of 'geometric mean NOEC's. Bold, underlined data are selected for the HC<sub>5</sub> calculation. Data derived from Table 3.202

Organism	Medium	H	Endpoint	NOEC (µg L <sup>-1</sup> )		References
<i>Lemna paucicostata</i>	AM; T 25		number of fronds		<i>L. paucicostata</i> : no geometric mean calculation: different medium	Nasu and Kugimoto, 1981
	pH>6	120		<u>5</u>		
	pH 5.1	120		<u>10</u>		
	pH 5.1	700		<u>10</u>		

- T Temperature (°C);
- H Hardness (as mg CaCO<sub>3</sub>/L);
- DO Dissolved oxygen (mg O<sub>2</sub>/L);
- Al Alkalinity (mg CaCO<sub>3</sub>/L);
- Ac Acidity (mg CaCO<sub>3</sub>/L);
- AM Artificial medium.

Table 3.205 'One species, one NOEC': lowest NOEC selection. Data derived from Table 3.202

Organism	Phylum/class	Order	Family	NOEC ( $\mu\text{g L}^{-1}$ )
<i>Salmo gairdneri</i>	Chordata	Salmoniformes	Salmonidae	4
<i>Oncorhynchus kisutch</i>	Chordata	Salmoniformes	Salmonidae	1.3
<i>Salvelinus fontinalis</i>	Chordata	Salmoniformes	Salmonidae	0.9
<i>Salmo salar</i>	Chordata	Salmoniformes	Salmonidae	0.47
<i>Catostomus commersoni</i>	Chordata	Cypriniformes	Catostomidae	4.2
<i>Esox lucius</i>	Chordata	Esociformes	Esocidae	4.2
<i>Salvelinus namaycush</i>	Chordata	Salmoniformes	Salmonidae	4.4
<i>Salmo trutta</i> (late eyed eggs)	Chordata	Salmoniformes	Salmonidae	1.1
<i>Jordanella floridae</i>	Chordata	Cyprinodontiformes	Cyprinodontidae	4.1
<i>Brachydanio rerio</i>	Chordata	Cypriniformes	Cyprinidae	1
<i>Oryzias latipes</i>	Chordata	Beloniformes	Adrianichthyidae	3
<i>Xenopus laevis</i>	Chordata	Anura	Pipidae	9
<i>Pimephales promelas</i>	Chordata	Cypriniformes	Cyprinidae	13
<i>Daphnia magna</i>	Arthropoda	Cladocera	Daphnidae	0.16
<i>Daphnia pulex</i>	Arthropoda	Cladocera	Daphnidae	1
<i>Aplexa hypnorum: immature</i>	Mollusca	Basommatophora	Physidae	4.41
<i>Physa integra</i>	Mollusca	Basommatophora	Physidae	8.3
<i>Daphnia galeata mendotae</i>	Arthropoda	Cladocera	Daphnidae	2
<i>Ceriodaphnia reticulata</i>	Arthropoda	Cladocera	Daphnidae	0.25
<i>Ceriodaphnia dubia</i>	Arthropoda	Cladocera	Daphnidae	1.5
<i>Hyalella azteca</i>	Arthropoda	Amphipoda	Hyalellidae	0.51
<i>Chironomus tentans</i>	Arthropoda	Diptera	Chironomidae	5.8
<i>Selenastrum capricornutum</i>	Chlorophyceae	Chlorococcales	Scenedesmaceae	2.4
<i>Coelastrum proboscideum</i>	Chlorophyceae	Chlorococcales	Coelastraceae	6.3
<i>Asterionella formosa</i>	Bacillariophyceae	Pennales	Diatomaceae	0.85
<i>Chlamydomonas reinhardtii</i>	Chlorophyceae	Volvocales	Chlamydomonaceae	7.5
<i>Scenedesmus quadricauda</i>	Chlorophyceae	Chlorococcales	Scenedesmaceae	31
<i>Lemna paucicostata</i>	Liliopsida	Arales	Lemnaceae	5

The statistical extrapolation method (SEM, Aldenberg and Slob, 1993) was applied to the NOEC data (some grouped per species, see previous section), calculating the median 5<sup>th</sup> percentile (HC<sub>5</sub>) of both the log-logistic and the log-normal distribution with the software package ETX 1.3a RIVM, Bilthoven, The Netherlands) (see **Table 3.206**).

Table 3.206 Calculation of critical concentrations ( $\mu\text{g L}^{-1}$ ) using the assessment factor method (AFM) or the statistical extrapolation method (SEM, Aldenberg and Slob, 1993) for various levels of data quality

Data quality group	AFM: NOEC/AF $\mu\text{g Cd/L}$	
	AF=10	
RI 1-3	0.016	
RI 1-2	0.047	
	SEM: HC <sub>5</sub> at 50% (and 95%) confidence $\mu\text{g Cd/L}$	
	Logistic distribution	Normal distribution
Selection of all data, RI 1-2 (Table 3.202); n = 21	0.39 (0.15)	0.40 (0.16)
Selection of all data, RI 1-3 (Table 3.202); n = 49	0.35 (0.19)	0.34 (0.20)
One species, one value: geometric mean NOEC's (Table 3.203); n = 28	0.59 (0.30)	0.59 (0.32)
Case-by-case geometric mean calculation (Table 3.204); n = 44	0.38 (0.21)	0.38 (0.22)
One species, one value: lowest NOEC selection (Table 3.205); n = 28	0.31 (0.14)	0.31 (0.15)

Selection on data quality does affect the value of HC<sub>5</sub> between groups RI 1-3 and RI 1-2. The NOEC data with RI 1-3 yield a smaller HC<sub>5</sub> than those with RI 1-2. The group with RI 1-2 has obviously a higher quality label than the group RI 1-3. The latter group of data is, on the other hand, derived based on 28 species whereas the former is derived on 16 species (see **Table 3.202**). Many test results are classified as RI 3 mainly because the source document did not give statistical data analysis or because only nominal concentrations were given. These tests are still considered to be reliable (no critical information is missing). The choice between these two data groups is therefore a trade off between complete background information on tests with fewer species or more species with less complete background information. The latter is preferred here because the statistical extrapolation is based on the modelling of the species sensitivity distribution.

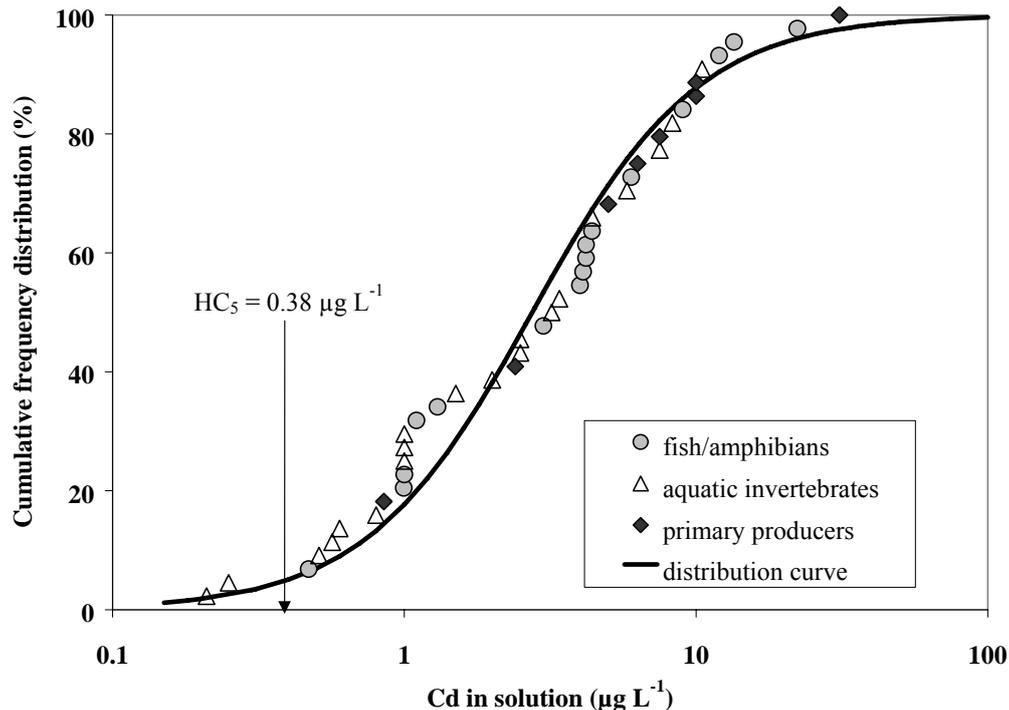
The choice of SSD (log-logistic or log-normal) does not affect the HC<sub>5</sub> (see **Table 3.206**). The choice of data selection (geometric mean calculation or not, lowest NOEC selection or not) influences the HC<sub>5</sub> by a factor two. The lowest HC<sub>5</sub> ( $0.31 \mu\text{g L}^{-1}$ ) is calculated when only the lowest NOEC value is selected for each species. The highest HC<sub>5</sub> ( $0.59 \mu\text{g L}^{-1}$ ) is calculated when the geometric mean NOEC is calculated for each species. The main drawback of both approaches is that they reduce information from the database. The lowest NOEC values are often found at low water hardness, in synthetic water or carbon filtered water. Selecting only these values creates a bias in the database which should be avoided for a generic risk assessment. However, hardness correction of the data may be used to set standards that vary by region (see Section 3.2.2.6.4). Selecting a geometric mean NOEC for each species may not be protective for that species in all conditions. As an example, the geometric mean NOEC of *D. magna* is  $1 \mu\text{g Cd/L}$  whereas several LOEC's of that species have been detected below  $1 \mu\text{g Cd/L}$  (see **Table 3.197**). The alternatives for data selection are therefore using all RI 1-3 data or data of RI 1-3 with case-by-case averaging. Some species might be overrepresented compared to others when all data are selected to calculate the HC<sub>5</sub>. This is partly overcome by calculating geometric mean NOEC values on a case-by-case basis, where NOEC's are only averaged for the same

species tested on the same endpoint in the same or a similar medium. As a trade-off between the last 2 alternatives, we propose to use the HC<sub>5</sub> of the largest group (RI 1-3), calculated based on case-by-case selected (geometric mean) NOEC values, i.e.

$$HC_5 = 0.38 \mu\text{g L}^{-1}$$

The frequency distribution and HC<sub>5</sub> are illustrated in **Figure 3.14**.

Figure 3.14 The cumulative frequency distribution of the NOEC values of Cd toxicity tests of data quality group and RI 1-3 used to calculate the HC<sub>5</sub> (case-by-case geometric mean calculation; n = 44). Selected data and logistic distribution curve fitted on the data



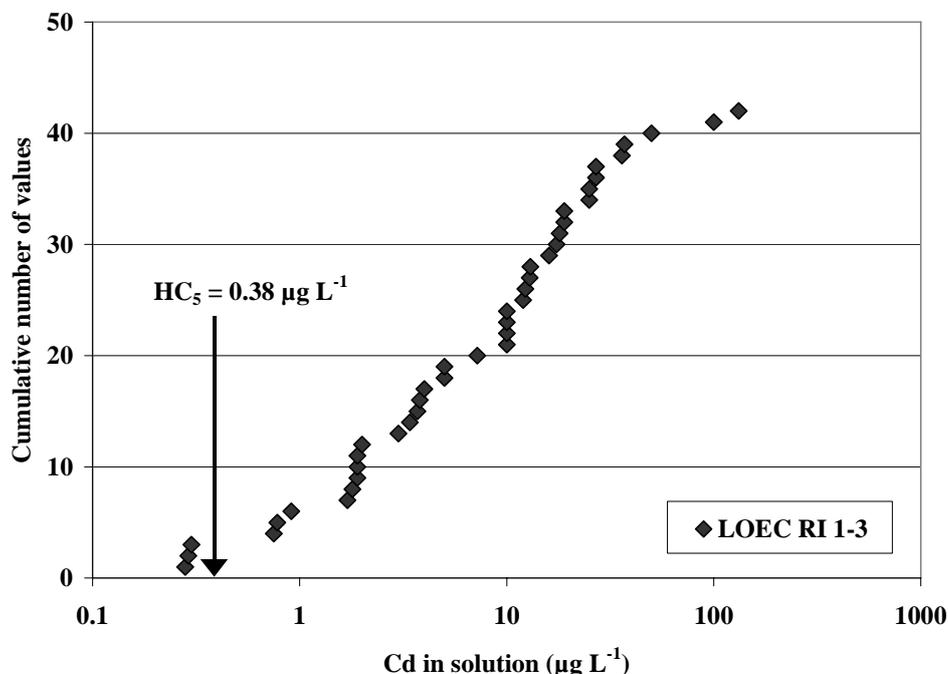
**Figure 3.15** gives the cumulative number of the LOEC values of data quality group RI 1-3. LOEC values are found at higher Cd concentrations than NOEC values (not shown). Three LOEC's are found below the HC<sub>5</sub>. Yield of a *Daphnia* population was reduced by 36% at 0.3 µg L<sup>-1</sup> (measured concentration) after 21 days exposure in Lake IJssel water (Van Leeuwen et al., 1985). There was no statistical evaluation of the data and no NOEC value could be derived from that test (the LOEC was found at the lowest concentration tested). Furthermore, reproduction *Daphnia magna* was also significantly affected at 0.28 and 0.29 µg L<sup>-1</sup> in well water at a hardness of 53 and 103 mg CaCO<sub>3</sub>/L (Chapman et al., 1980).

A small number of other chronic tests has also demonstrated Cd toxicity at solution Cd concentrations below 0.5 µg Cd/L (e.g. Biesinger and Christensen, 1972; Sjöbeck et al., 1984). These data are less reliable as discussed in the Sections 3.2.2.2 and 3.2.2.3. Nevertheless, this review of toxicity data indicates that a toxicity threshold Cd concentration in freshwater, if detectable, may be very close to background Cd concentrations (typically 0.05-0.2 µg Cd/L in filtered freshwater). The number of ecological processes affected in the 0.1-0.5 µg Cd/L is, however, small as indicated by the LOEC frequency distribution.

The HC<sub>5</sub> is likely not overestimated due to speciation of Cd in the test media that would reduce Cd toxicity in the tests. One NOEC value of 0.8 µg L<sup>-1</sup> was found in unfiltered well water

(Knowles and McKee, 1987). All other data (both NOEC or effect data) at concentrations below  $1 \mu\text{g L}^{-1}$  were found in either synthetic media or in filtered environmental samples. Therefore, almost no Cd in these solutions has reduced availability due to sorption on suspended solids. This again justifies the use of filtered solutions in risk assessment of Cd in aquatic systems (see exposure section).

Figure 3.15 The cumulative number of LOEC values of selected tests of data quality group RI 1-3



### 3.2.2.6.3 Calculation of the generic PNEC<sub>water</sub>

The EU workshop on statistical extrapolation (17-18 January, 2001) proposed that the statistical extrapolation technique can be applied to derive a PNEC, but that an additional assessment factor should be applied to the HC<sub>5</sub>. In order to derive a PNEC, this extra assessment factor should be between 5 and 1, to be judged on a case by case basis, and should remove uncertainty in extrapolating the PNEC to the field situation.

The data on which the HC<sub>5</sub> is calculated are selected NOEC's or geometric mean NOEC's, calculated on a case-by-case basis (see **Table 3.204**). The diversity of the data (44 NOEC values from 28 species and 16 different families, including warm and cold water fish, amphibians, crustaceans, algae and higher plants) is large enough to use the statistical extrapolation method to calculate the PNEC. Many of the tests are performed in synthetic water resulting in a lower degree of Cd complexation than in natural conditions.

All NOEC data are derived from real chronic studies. Test durations are between 7 days and 3 years, except for some algae tests, which should cover different life stages. The goodness-of-fit of the SSD's is tested with the Kolmogorov-Smirnov test. It indicated that the log-logistic distribution is accepted at the 1-5% and the log-normal distribution at the 1-10% significance levels when applied on the selected NOEC's.

Field data on Cd can hardly be used to derive threshold values for Cd in the environment because of the usual mixed metal pollution where Cd is found at high concentrations. Microcosm (model)

ecosystems offer an alternative way of testing effects of Cd in field conditions. Results from such multi-species studies should be evaluated regarding their reliability, reproducibility, representativeness and relevance. Furthermore, the evaluation should include consideration of the reported endpoints, species and/or indices, including the statistical power of the test design. **Table 3.207** gives an overview of the description and results of nine multi-species (MS) studies. Using the US-EPA hardness correction (see next section), the NOEC and LOEC values of these MS studies can be compared to the HC<sub>5</sub> of single species NOECs (see **Table 3.208**). This reveals that the hardness corrected HC<sub>5</sub> values are within the range of the reported MS-NOEC values and below the reported MS-LOEC values, with one exception in the study of Marshall and Mellinger (1980). The study revealed a significant effect on 1 of the 16 species at 0.2 µg L<sup>-1</sup> (nominal concentration, measured concentrations unknown).

Table 3.207 Overview of multi-species studies about effects of Cd (added as Cd<sup>2+</sup>+salt) in the aquatic environment

Reference (chronological order)	Test system	Replicates	Cd conc. range ( $\mu\text{g L}^{-1}$ , Nominal or Measured)	Water chemistry	Period	Results	Conclusion for Multi-Species study (MS)
1. Giesy et al., 1979	artificial streams; 91.5 m long, 0.3 m depth; mean water retention time = 2h; sediment present	2 for each treatment	0, 5, 10 (N) 0.02, 4-5, 8-10 (M)	hardness 11 mg L <sup>-1</sup> as CaCO <sub>3</sub> ; pH = 6.5	1 year	at 5 and 10 $\mu\text{g Cd/l}$  significant reductions in macrophytes biomass and periphyton;  some invertebrate taxa eliminated, while other taxa increased in density  chronic toxicity in crayfish and snails	5 $\mu\text{g L}^{-1}$ is a MS-LOEC  a MS- NOEC can not be derived (extrapolation factors > 2 are considered not reliable in Cd/CdO RAR)  effects of Cd at 5 $\mu\text{g Cd/l}$ in this very soft water is expected from single species studies
2. Marshall and Mellinger, 1980	closed 8 l carboys at 3-5 m or 6-8 m depth in Lake Michigan	2 for each treatment	0, 0.6, 1.2, 2.5, 5.0 (N, exp. 1-4) 0, 0.2, 0.4, 0.8, 1.6 (N, exp. 5-6)	hardness 120 mg L <sup>-1</sup> as CaCO <sub>3</sub> ; background Cd <0.1 $\mu\text{g Cd/l}$	3 weeks	for 16 species/categories of crustacean plankton  sign. increases in density of 4 categ. at 0.6 or 1.2 $\mu\text{g Cd/l}$  sign. decrease in density of 2 species at 0.6 $\mu\text{g Cd/l}$ , one species sign. affected at 0.2 $\mu\text{g Cd/l}$  lowest LOEC for total zooplankton density at 0.8 $\mu\text{g Cd/l}$ - NOEC's varying with experiments (0.4-2.5 $\mu\text{g Cd/l}$ )  LOEC for 1 species at 0.2 $\mu\text{g L}^{-1}$  LOEC for percentage similarity (biodiversity index): 1.2 $\mu\text{g L}^{-1}$ (exp. 1&2), 0.6 $\mu\text{g L}^{-1}$ (lowest tested conc., exp. 3&4) 0.4 $\mu\text{g L}^{-1}$ (exp. 5&6)	less reliable because no measured Cd concentrations in the critical Cd concentration range (<1 $\mu\text{g Cd/l}$ )  MS-NOEC's of total zooplankton density: 0.4-2.5 $\mu\text{g L}^{-1}$  1 individual species can be sign. affected at Cd = 0.2 $\mu\text{g L}^{-1}$
3. Marshall and Mellinger, 1980	10 m diameter open surface enclosures in L 223 of Canada's experimental lake area (~2m depth)	no	0, 1, 3, 10, 30 (N)	background Cd <0.1 $\mu\text{g Cd/l}$ ; hardness unknown	44-87 days	reduction in density of most of the 8 species/categories of crustacean plankton at lowest Cd concentration tested  increased density of 8 species/categories of rotifers at 1 or 3 $\mu\text{g L}^{-1}$  LOEC for percentage similarity (biodiversity index) is 1 $\mu\text{g L}^{-1}$ (lowest tested)  EC1 of percent similarity is extrapolated from L223 and Lake Michigan enclosure data and is predicted 0.12 added Cd (background not included)	unreliable because no measured Cd concentrations, no replicates and no known water characteristics
4. DeNoyelles et al., 1980	continuous 5 l culture chambers, retention time 92-110 h, incubated at 1.74 m depth in L 239 of Canada's experimental lake area	2 for each treatment	0, 4 (N) unknown and 2.9-4.2 (M)	background Cd unknown; hardness unknown	188 h	density of 4 phytoplankton species:  increased for 2 species and decreased for 2 other species	MS-NOEC is below 2.9-4.2 $\mu\text{g L}^{-1}$ if based on most sensitive species  less reliable because water hardness unknown
5. DeNoyelles et al., 1980	10 m diameter open surface enclosures in L 223 of Canada's experimental lake area (~2m depth)	no	0, 1, 3, 10, 30 (N) measured Cd : declined to half of nominal in 2 weeks (no other details available) <sup>a</sup>	background Cd <0.1 $\mu\text{g Cd/l}$ ; hardness unknown	2 weeks	density of 3 phytoplankton species:  increased for 2 species at Cd = 1 and 3 $\mu\text{g L}^{-1}$ , decreased for 1 species at lowest Cd rate and above (LOEC = 1 $\mu\text{g L}^{-1}$ )	MS-NOEC is below 1 $\mu\text{g L}^{-1}$ if based on most sensitive species  unreliable because no measured Cd, hardness unknown and no replicates

Table 3.207 continued overleaf

Table 3.207 continued Overview of multi-species studies about effects of Cd (added as Cd<sup>2+</sup>salt) in the aquatic environment.

Reference (chronological order)	Test system	Replicates	Cd conc. range ( $\mu\text{g L}^{-1}$ , Nominal or Measured)	Water chemistry	Period	Results	Conclusion for Multi-Species study (MS)
6. Niederlehner et al., 1985	colonisation of barren polyurethane foam substrates by protozoan from a species source (collected on foam in a pond)	2 per treatment	0, 0.6, 1.3, 2.5, 5, 10 (N) 0.2, 0.4, 1.4, 2.7, 5.6, 9.5 (M)	dechlorinated tap water; hardness 70 mg L <sup>-1</sup> as CaCO <sub>3</sub> ; background Cd 0.2 $\mu\text{g Cd/l}$	28 days	NOEC colonisation tests 0.4 $\mu\text{g L}^{-1}$ , LOEC=1.4 $\mu\text{g L}^{-1}$ (22% inhibition) <sup>2</sup>	reliable MS-NOEC=0.4 $\mu\text{g L}^{-1}$
7. Borgmann et al., 1989	3400 l indoor ecosystems (4 tanks) inoculated with <i>Daphnia magna</i> and phytoplankton	none at 5 and 15 $\mu\text{g L}^{-1}$ , 2 at 1 $\mu\text{g L}^{-1}$ , 3 at control*	0, 1, 5, 15 (N) 0.08-0.2, 1, 4.7, 12 (M)	tap water; hardness 130 mg L <sup>-1</sup> as CaCO <sub>3</sub> ; background Cd < 0.3 $\mu\text{g Cd/l}$ ; pH 8.2-8.6	>10 weeks	no effects at 1 $\mu\text{g Cd/l}$ on <i>Daphnia</i> ash free dry weight or chlorophyll concentration  collapse of <i>Daphnia</i> population and increase in Chlorophyll conc. at 5 $\mu\text{g/L}$  both endpoints affected at 15 $\mu\text{g L}^{-1}$	less reliable MS-NOEC of 1 $\mu\text{g L}^{-1}$ because no continuous replicates of control and 1 $\mu\text{g Cd/l}$ treatment
8. Lawrence and Holoka, 1991	continuous 41 l culture chambers, retention time 2 days, incubated at 2 m depth in L 382, 302, 204 of Canada's experimental lake area	2 per treatment	paired studies: 0, 0.2 (10 exp.) 0, 0.4 (3 exp) 0, 1 (2 exp) 0, 3 (2 exp)	background Cd in L 382 is < 0.002 $\mu\text{g L}^{-1}$ ,  other lakes unknown; hardness less than about 10 mg L <sup>-1</sup> as CaCO <sub>3</sub> <sup>§</sup>  DOC < 1.2 mmol/l	2 weeks	6 categories of crustacean species  calanoid and cyclopoid copepods: NOEC=1.0 $\mu\text{g L}^{-1}$  2 species: NOEC = 0.2 $\mu\text{g Cd/l}$  2 species ( <i>D. galeata mendotae</i> & <i>Holopedium gibberum</i> ): LOEC = 0.2 $\mu\text{g L}^{-1}$ (lowest tested, 40% and 38% inhibition)	MS-NOEC below 0.2 $\mu\text{g L}^{-1}$ if based on most sensitive species  less reliable: no measured Cd concentrations in the critical Cd concentration range (<1 $\mu\text{g Cd/l}$ )
9. Malley and Chang, 1991	lake 382 of Canada's experimental lake area	no	0.002 (pre-contamination years 1985-1986); 0.05-0.08 $\mu\text{g Cd/l}$ (experimental years 1987-1988)	hardness less than about 10 mg L <sup>-1</sup> as CaCO <sub>3</sub> <sup>§</sup>  DOC < 0.7 mmol/l	2 years	zooplankton community structure: no adverse effects on composition and population abundances	MS-NOEC = 0.08 $\mu\text{g L}^{-1}$ , highest tested (less reliable-no replicates and unbounded, authors have indirect evidence for predicting effects at 0.2 $\mu\text{g Cd/l}$ in soft water lakes)

\* Control;

1 Continuous control,

2 Controls for the period before Cd was added; Cd in 4<sup>th</sup> unit (designed as 2<sup>nd</sup> continuous control) increased in time to 1  $\mu\text{g Cd/l}$  (contamination ascribed to a welding joint);§ The test reports Ca concentrations of about 2.2 mg L<sup>-1</sup> but data on Mg are lacking, i.e. the hardness cannot be calculated unequivocally. The Ca/Mg molar ratio is typically about 3:1 in freshwater, yielding a hardness of about 7 mg CaCO<sub>3</sub>/L. We have used a larger estimated Mg concentration (Ca/Mg molar ratio of 1), i.e. hardness of about 10 mg L<sup>-1</sup>.

Table 3.208 Summarising table for multi-species studies (numbers refer to those in Table 3.207). The water hardness correction is described in Section 3.2.2.6.4. The HC<sub>5</sub> at the water hardness of the MS study is calculated based on hardness corrected NOEC data and retransformation with a lower hardness limit of H = 40 mg l<sup>-1</sup> as CaCO<sub>3</sub>). The model for the hardness correction is discussed in Section 3.2.2.6.4

Study number	Reliability	MS-NOEC (µg L <sup>-1</sup> )	MS-LOEC (µg L <sup>-1</sup> )	Hardness (mg L <sup>-1</sup> )	HC <sub>5</sub> at that hardness (µg L <sup>-1</sup> )
1	reliable	-	5	11	0.16
2	less reliable	< 0.2 (most sensit. species) 0.4-2.5 (crustacean density)	0.2 (most sensit. species) ≥ 0.8 (crustacean density)	120	0.34
3	unreliable	< 1 (most sensit species)	1 (most sensit. species)	no data	-
4	less reliable	< 2.9-4.2	2.9-4.2	no data	-
5	unreliable	< 1	1	no data	-
6	reliable	0.4	1.4	70	0.23
7	less reliable	1.0	5.0	130	0.37
8	less reliable	< 0.2 (most sensit. species)	0.2 (most sensit. species)	~10	0.16
9	less reliable	0.08	-	~10	0.16

The database of the 168 reliable tests on single species contains 3 reliable LOEC's below the HC<sub>5</sub> whereas the 9 multi species studies identified 1 LOEC below the hardness corrected HC<sub>5</sub>. This suggests that NOEC and LOEC distributions overlap in the lower concentration range and that an additional assessment factor may be necessary. Therefore, we propose to include a assessment factor of 2 on the HC<sub>5</sub>, yielding

$$PNEC_{\text{water}} = HC_5/2 = 0.19 \mu\text{g L}^{-1}$$

One NOEC from the laboratory toxicity tests (RI 1-3) and one NOEC from the multi-species studies are below this PNEC<sub>water</sub>. No LOEC's of the reliable single species or multi species studies is found below this PNEC<sub>water</sub>. However, this generic PNEC<sub>water</sub> might not be protective for water with a very low water hardness (see Section 3.2.2.6.4). Finally, we note that the PNEC<sub>water</sub> derived with the Assessment Factor (AF) method is 4-14-fold below the value proposed above. This is related to the emphasis on the lowest NOEC value (with AF=10) with the AF method whereas the Statistical Extrapolation method uses the weight of evidence.

#### 3.2.2.6.4 PNEC<sub>water</sub> as a function of water characteristics

Water characteristics affect Cd toxicity. Toxicity of Cd generally increases with reducing water hardness, reducing concentrations of dissolved organic matter and increasing solution pH. Effects of dissolved organic matter on Cd toxicity cannot be described using the tests that are reviewed here since most tests did not report this water characteristic.

Toxicity of Cd<sup>2+</sup> in solution is lower in more acid conditions because of H<sup>+</sup>/Cd<sup>2+</sup> competition at the membrane (e.g. data on *Lemna paucicostata*, Nasu and Kugimoto, 1981). Acidification leads to higher Cd emissions from catchments into water, but this is an effect on exposure, not on ecotoxicology of soluble Cd. In the presence of soluble Cd complexes (Cd complexed by dissolved organic matter), the situation is more complex because pH has effects on affinity of Cd<sup>2+</sup> for the membrane and for the dissolved organic matter. Data suggesting that the effect of acidification is larger on releasing Cd<sup>2+</sup> from soluble complexes than the opposite effect of

decreasing  $\text{Cd}^{2+}$  affinity for the biota, have not been found. However, John et al. (1987) studied  $^{109}\text{Cd}$  uptake (not toxicity) at varying pH and aquatic humus concentrations by *Salmo salar* in water reconstituted from a small marsh area in Oslo. The  $^{109}\text{Cd}$  uptake was lowest at lowest pH at all but one DOC-level (Dissolved Organic Carbon). The pH effect was not significant at that DOC-level. The effects of pH on Cd toxicity were not identified in the selected tests of this report: a regression between the log ( $\text{EC}_{x \geq 50}$ ) and pH showed non-significant effects for both the acute as chronic tests ( $P > 0.05$  for both regressions). The absence of effects of pH on Cd toxicity in this report might be due to the bias towards higher pH values ( $\text{pH} > 7$ ) of the aqueous media used in the selected tests.

Biotic ligand models (BLM's) have been developed to account for abiotic factors affecting metal toxicity. This model has been constructed and successfully validated to explain acute Cd toxicity to fish (fathead minnow and rainbow trout). Data for invertebrates (*C. dubia*) were not reliable enough to allow validation of a BLM and no BLM for algae was constructed (Hydroqual, 2003). Most of the data with fish show the importance of hardness on Cd toxicity, while effects of pH are of minor importance at  $\text{pH} > 6.2$ . This BLM model can, however not be used in this document because the modifying factors for acute toxicity are not necessarily identical in chronic exposure and because the model is missing for invertebrates which are, most likely, the most sensitive group.

Considerable regional differences in water hardness of surface waters exist within the EU (see **Table 3.209**). Half of the surface waters in the northern European countries have a water hardness below  $10 \text{ mg CaCO}_3 \text{ L}^{-1}$ , while in the western European countries almost 50% of the surface waters have a hardness above  $200 \text{ mg CaCO}_3 \text{ L}^{-1}$ . Therefore, a water hardness correction of the  $\text{PNEC}_{\text{water}}$  for risk characterisation at a local or regional scale might be useful.

Table 3.209 Water hardness (in  $\text{mg CaCO}_3 \text{ L}^{-1}$ ) distribution of surface waters in some EU countries

	10 <sup>th</sup> percentile	25 <sup>th</sup> percentile	50 <sup>th</sup> percentile	90 <sup>th</sup> percentile
Finland <sup>(a)</sup>	6.5	9	12	25
Sweden <sup>(b)</sup>	5	8	14	107
Norway <sup>(a)</sup>	0.7	1.7	4	18
Denmark <sup>(a)</sup>	14	86	155	272
France	48	83 <sup>(e)</sup> 217	335	
Belgium (Flanders) <sup>(c)</sup>	109	-	240,500	
Germany <sup>(d)</sup>	30	105	210	

a) Source: Skjelkvåle et al. (2001);

b) Source: Swedish University of agriculture;

c) Source: VMM;

d) Water hardness of groundwater instead of surface water (Hannappel et al., 2000);

e) 20<sup>th</sup> percentile.

The effect of water hardness (H) on Cd toxicity has been quantified by the US-EPA (US-EPA, 2001). For *Daphnia magna*, *Pimephales promelas* and *Salmo trutta* an increasing trend of chronic values with increasing water hardness was observed (see **Table 3.210**). The chronic value is the geometric mean of the NOEC and LOEC value for a given endpoint. To account for the apparent relationship of Cd chronic toxicity to hardness, an analysis of covariance was performed to calculate the pooled slope for hardness using the natural logarithm of the chronic value as the dependent variable, species as the treatment or grouping variable and the natural logarithm of hardness as the covariate or independent variable. This analysis was fit to the data

of the 3 species for which chronic values are available over a range of hardness such that the highest hardness is at least 3 times the lowest, and the highest is also 100 mg L<sup>-1</sup> higher than the lowest. Regression of the natural logarithm of the chronic value against the natural logarithm of water hardness gave a slope of 0.7712 for *D. magna*, 1.0034 for *P. promelas* and 0.5212 for *S. trutta*. The pooled slope for the three species is 0.7409, with 95% confidence limits of 0.3359 and 1.1459. The slope of 0.7409 was then used to adjust a range of chronic values to a reference hardness of 50 mg CaCO<sub>3</sub> L<sup>-1</sup> following

$$\text{Chronic value}_{H=50} = \text{Chronic value}_H \left( \frac{50}{H} \right)^{0.7409} \quad \text{Equation 3.1}$$

The water hardness correction covers a hardness range of 44-209 mg CaCO<sub>3</sub>/L.

Table 3.210 Chronic values as a function of water hardness as reported by US-EPA (2001)

Species	Hardness (mg L <sup>-1</sup> as CaCO <sub>3</sub> )	Chronic value (µg L <sup>-1</sup> )
<i>Daphnia magna</i>	53	0.152
<i>Daphnia magna</i>	103	0.212
<i>Daphnia magna</i>	209	0.437
<i>Salmo trutta</i>	44	6.668
<i>Salmo trutta</i>	250	16.49
<i>Pimephales promelas</i>	44	10.0
<i>Pimephales promelas</i>	201	45.92

The effect of water hardness on Cd toxicity can also be observed in the current database. It has been frequently described in Sections 3.2.2.2-3.2.2.4 that water hardness is an important factor influencing Cd toxicity in water. Lowest LOEC or EC<sub>x≥50</sub> values are often found in soft waters. The intrinsic variability of NOEC's across different studies limits the identification of the underlying relationship between hardness and toxicity in a meta-analysis in this report. Therefore, it is preferred to use the mean slope as used by US-EPA for the water hardness correction.

The water hardness correction equation of the US-EPA (US EPA, 2001; see above) is used to calculate the HC<sub>5</sub> as a function of water hardness. All NOEC values at hardness H are converted to NOEC values at a reference hardness of 50 mg CaCO<sub>3</sub> L<sup>-1</sup> (NOEC<sub>H=50</sub>) following

$$\text{NOEC}_{H=50} = \text{NOEC}_H \left( \frac{50}{H} \right)^{0.7409} \quad \text{Equation 3.2}$$

Geometric mean values are calculated on the same data as in **Table 3.204** after normalisation of the data. The software package ETX 1.3a (RIVM, Bilthoven, The Netherlands) is used to calculate the HC<sub>5</sub> at the reference hardness of 50 mg CaCO<sub>3</sub> L<sup>-1</sup>, assuming a log-logistic distribution. This HC<sub>5</sub> value is then divided by a assessment factor of 2 to yield a PNEC<sub>water, regional</sub> that is valid for waters with hardness of 50 mg CaCO<sub>3</sub> L<sup>-1</sup>. The arguments to include an assessment factor 2 to convert a HC<sub>5</sub> to PNEC were given in the previous paragraph. Finally, Equation 3.2 is used again to recalculate the PNEC<sub>water, regional</sub> at different values of water hardness as:

$$\text{PNEC}_{\text{water, regional}} = 0.09 (H/50)^{0.7409} \quad \text{Equation 3.3}$$

It is proposed that this equation is not extrapolated below  $H = 40 \text{ mg CaCO}_3/\text{L}$ , i.e. the  $\text{PNEC}_{\text{water,regional}}$  for  $H < 40 \text{ mg CaCO}_3/\text{L} = 0.08 \text{ } \mu\text{g Cd/L}$ . The  $\text{PNEC}_{\text{water,regional}}$  is graphically represented in **Figure 3.16**.

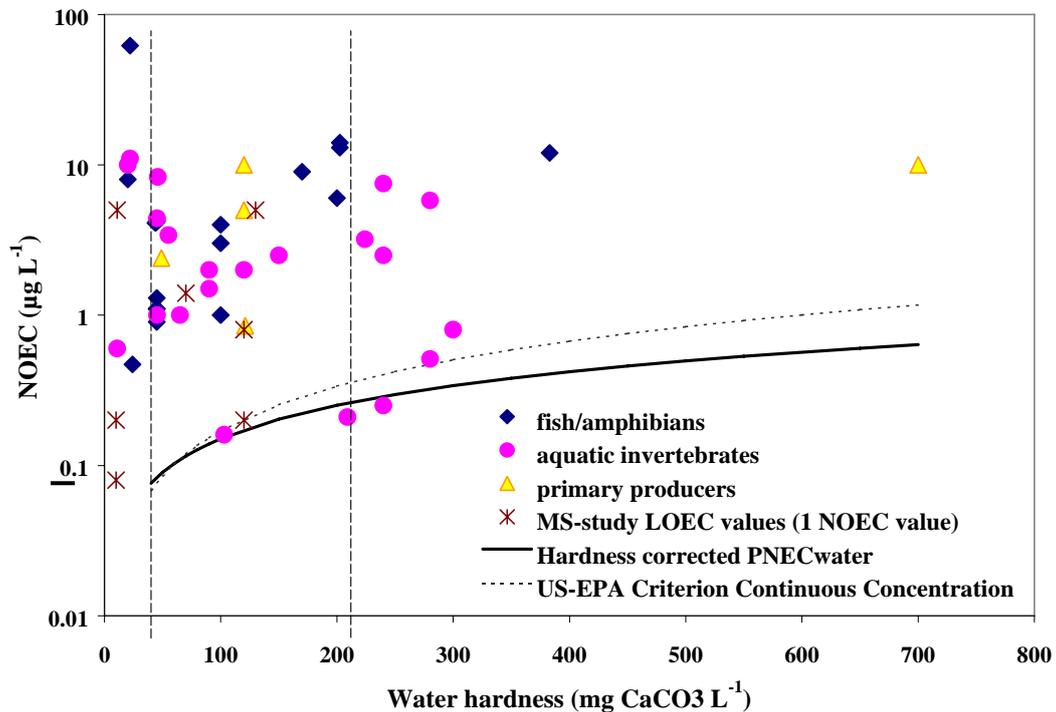
The extrapolation of the hardness correction below  $H = 40 \text{ mg CaCO}_3/\text{L}$  is not proposed because this equation has not been tested in that hardness range. The  $\text{PNEC}_{\text{water,regional}} = 0.08 \text{ } \mu\text{g Cd/L}$  should then be evaluated for soft water. It is observed that:

- none of the 37 Cd toxicity tests in the database of the Cd RAR (including data with lower quality) that were performed between  $H = 7\text{-}10^1$  and  $H=40 \text{ mg CaCO}_3/\text{L}$  have identified adverse effects below the threshold of  $0.08 \text{ } \mu\text{g Cd/L}$
- there are 2 multi-species studies (see **Table 3.207**) carried out in soft water lakes of Canada and which were designed to study fate and effects of Cd at low concentrations ( $0.05\text{-}0.2 \text{ } \mu\text{g Cd/L}$ ). The chemical properties of these waters ( $\text{Ca} = 2.2 \text{ mg L}^{-1}$ , neutral pH, DOC about  $8 \text{ mg C/L}$ ) are similar to that of soft water lakes in Scandinavian countries. The tests allow to conclude that  $0.08 \text{ } \mu\text{g Cd/L}$  is protective whereas adverse effects are found at about  $0.20 \text{ } \mu\text{g Cd/L}$ .
- We conclude that down to a water hardness of  $7\text{-}10 \text{ mg CaCO}_3/\text{L}$  there is no indication of Cd toxicity below  $0.08 \text{ } \mu\text{g Cd/L}$ .
- There are no data for the very soft waters ( $H$  below about  $10 \text{ mg CaCO}_3/\text{L}$ ) and these areas may be unprotected by the proposed  $\text{PNEC}_{\text{water}}$  for soft water.

Table 3.211 The  $\text{PNEC}_{\text{water,regional}}$  ( $\mu\text{g L}^{-1}$ ) for different values of water hardness ( $H$ ,  $\text{mg CaCO}_3/\text{L}$ ). The NOEC data were all first normalised to  $H=50$  from which the  $\text{HC}_5$  at a reference hardness was found. The  $\text{PNEC}_{\text{water}}$  at that hardness contains a assessment factor of 2. The normalisation was then used to calculate the  $\text{PNEC}_{\text{water,regional}}$  values at other values of  $H$

	N	min. NOEC	median NOEC	$\text{PNEC}_{\text{water}}$
Data normalised to H 50 (method 2)	34	0.07		0.09
retransformed $\text{PNEC}_{\text{water}} = 0.09 (H/50)^{0.7409}$				
H 40				0.08
H50				0.09
H100				0.15
H200				0.25

Figure 3.16 NOEC values of the laboratory studies , LOEC of multi-species studies (1 NOEC), water hardness corrected  $PNEC_{water}$  and the US-EPA chronic criterion (US-EPA, 2001) as a function of water hardness. The dashed lines indicate the range of water hardness for which the US EPA (2001) hardness correction was derived



The water hardness correction method yields a  $PNEC_{water,regional}$  at  $H = 50 \text{ mg CaCO}_3/\text{L}$  of  $0.09 \text{ µg Cd/L}$ . Transforming this value to other water hardness using the slope of 0.7409, increases this threshold more than threefold between  $H = 40$  and  $H = 200$  (see **Figure 3.16**). We note that the US-EPA Cd criterion continuous concentration is very close to the regional  $PNEC_{water}$ .

Sorption of  $\text{Cd}^{2+}$  on suspended particles is higher in soft water than in hard water. As a result, the difference in  $HC_5$  values between soft and hard water becomes smaller if the concentrations are based on total concentrations (dissolved and sorbed).

Although there is a relationship between Cd toxicity and water hardness, no correction of the  $PNEC_{water}$  will be made to derive the generic  $PNEC_{water}$ . However, we suggest that for risk characterisation on a local/regional scale,  $PNEC_{water}$  should be corrected to water hardness in order to better correspond to local/regional environmental conditions.

### 3.2.2.7 Conclusion

The  $PNEC_{water}$  of Cd is derived from the median  $HC_5$  value (Aldenberg and Slob, 1993) from 44 chronic NOEC values, some of which are geometric species means. These data are derived from 19 tests with fish/amphibians, 22 tests with aquatic invertebrates and 8 tests with primary producers, and represent 28 species in total. All these tests belong to data quality group RI 1-3. The NOEC values were obtained from laboratory based, single species studies and refer to the dissolved fraction. An assessment factor of two is applied on the  $HC_5$ . The  $PNEC_{water}$  is

$$PNEC_{water} = 0.19 \text{ µg Cd L}^{-1}$$

No adverse effect of Cd below this PNEC was found in the 168 tests with RI 1-3 that have been reviewed. There is a trend that dissolved Cd is more toxic at lower water hardness. A correction of the PNEC for water hardness has been proposed that may be useful for local or regional risk characterisation. Multi-species NOEC's have been reported between 0.08 and 4.2  $\mu\text{g Cd L}^{-1}$ . The lowest NOEC was found at very low water hardness. The hardness corrected PNEC<sub>water</sub> was within the range of MS NOEC values and below all MS LOEC's. This indicates that the HC<sub>5</sub> method is protective for ecosystem structure in case of Cd. No data were, however, found for very soft waters, i.e. at water hardness below about 10 mg CaCO<sub>3</sub>/L. Current data suggest that a significant number of freshwaters in Norway, Finland and Sweden have water hardness below this threshold. So, a **conclusion (i)** is reached because there is a need for better information regarding the toxic effects of cadmium to aquatic organisms under low water hardness conditions (Cd toxicity testing in very soft waters).

### 3.2.3 Terrestrial compartment

#### 3.2.3.1 General

##### 3.2.3.1.1 Data quality: definitions of Reliability Indices (RI's)

For each test, a RI is given according to the following criteria:

- **RI 1:** standard test. Two such tests included are the OECD 207 acute toxicity test with *Eisenia fetida* in OECD-soil and the ISO 1994 "Soil quality effects of soil pollutants on Collembolla (*Folsomia candida*)" method for the determination of effects on reproduction.
- **RI 2:** no standard test but complete background information is given, i.e. the following information is present:
  - a) soil pH
  - b) soil organic matter or carbon content
  - c) texture (class or texture fractions)
  - d) total Cd content of the soil at zero Cd application if the NOEC or LOEC value is below  $2\mu\text{g g}^{-1}$
  - e) equilibration time after soil contamination and prior to the test
  - f) statistical analysis of the dose-response relationship
  - g) no varying metal contamination along with increasing Cd application
  - h) the control soil must be tested along with at least two Cd concentrations above the background concentration
  - i) the soil must be homogeneously mixed with the metal prior to the test
- **RI 3:** no standard test and one or more of the following information from the above-mentioned list is missing as background information: b), c), e) or f). All other information from that list is present.
- **RI 4:** no standard test and one or more of the following information from the above-mentioned list is missing as background information: a), d), g), h) or i). The requirement d) is critical since some tests reporting LOEC values  $< 2\mu\text{g g}^{-1}$  are considered unreliable. Background Cd concentrations in soil typically range between 0.1 and  $0.5\mu\text{g g}^{-1}$  and the

lack of reporting the background concentration may underestimate the total Cd concentration in soil at which the first toxic effects are found. Some tests were included that did not show Cd toxicity up to the highest Cd concentration tested. These tests cannot be used for risk assessment (no NOEC can be found) and were considered unreliable (RI4) but were quoted in the tables for illustration.

Tests performed in substrates that were judged as not representative for soils (e.g. pure quartz sand or farmyard manure) were not included in this effects assessment.

### 3.2.3.1.2 Source of data and its limitations for risk assessment

The original HEDSET contained no toxicity data for terrestrial organisms. A literature review was made on Cd toxicity to soil or litter microflora, soil fauna and higher plants.

Almost no tests have been made on the toxicity of CdO in soil. Many tests have however been performed with soluble Cd<sup>2+</sup> salts. The relevance of soil toxicity tests with metal salts for a risk assessment of the metal oxide is discussed below. The tests with mixed metal pollution or with sludge are generally avoided in this review in order to avoid confounding factors for assessing the dose-response relationship. Mixed metal pollution is, however, more often found in the environment than single metal pollution. Other metals may have a synergistic or antagonistic effect on Cd toxicity. Increasing soil zinc is known to reduce Cd availability to plants. It has been advocated that plant Cd uptake studies at soil Cd:Zn ratio's that are strongly different from the usual 1:100 weight ratio are not relevant (Chaney et al., 1996). Antagonistic effects of Zn on Cd toxicity were shown for growth of the collembollan *Folsomia candida* in artificial soil (Van Gestel and Hensbergen, 1997). The EC<sub>50</sub> for growth was found at 1.5 of toxic units of Cd and Zn. The effects of Zn on Cd toxicity to reproduction were, however, only additive. Due to the lack of information on Cd:Zn interactions in Cd toxicity to soil microflora, soil fauna or higher plants, no predictions can be made to what extent single Cd toxicity studies may overestimate the Cd related toxicity at sites with moderate Cd-Zn metal contamination.

#### Toxicity of Cd<sup>2+</sup> salts versus toxicity of CdO

Only one reliable study was found in which the toxicity of CdO was tested (Khan and Frankland, 1983). All other data are derived from studies using soluble Cd<sup>2+</sup> salts in soil.

The toxicity of CdO in soil can be overestimated based on studies with soluble Cd<sup>2+</sup> salts. Depending on the conditions prevailing in the soil, CdO transforms in soil to Cd<sup>2+</sup> that sorbs to the soil sorption-sites. In this way, Cd derived from CdO becomes equally available as soluble Cd<sup>2+</sup> salts after a certain equilibration time.

In order to quantify the transformation rate of CdO in soil, an experiment was set up in which 2 soils were amended with CdO at 50 µg Cd g<sup>-1</sup> (Smolders et al., unpublished). The soil solution Cd concentration was monitored during a 3 month incubation period. The soil solution Cd concentrations were compared with these in soils that were amended with a Cd<sup>2+</sup> salt at an equivalent total Cd application. The Cd concentrations in the CdO treated soil were between 71 and 86% of those in soil applied with the Cd<sup>2+</sup> salt after 3 months incubation. Both soils were acids (pH CaCl<sub>2</sub> 4.4 and 5.4) which may have contributed to the rapid transformation.

Other evidence on the fate of CdO in soil can be found in studies on comparative toxicity of CdO versus Cd<sup>2+</sup> salts and in isotopic exchange of Cd in soils contaminated with CdO. Calculations with MINTEQA2 (Allison et al., 1991) can provide the equilibrium speciation of CdO in soils but no model has yet been developed predicting its reaction rate.

Table 3.212 The Cd concentrations in membrane filtered soil solution of soils amended with CdO. The solution Cd concentrations are expressed as a percentage of the Cd concentration in the soil solution of the Cd(NO<sub>3</sub>)<sub>2</sub> treated soil for corresponding soil types and equilibration times. Data in brackets at 99 days incubation are standard deviations (Smolders et al., unpublished)

Cd source	Soil solution Cd (% of Cd-salt treated soil)					
	Sandy pH 4.4			Clayey sand, pH 5.4		
	8 days	33 days	99 days	8 days	33 days	99 days
Untreated	0.3	0.2	0.6(0.1)	0.6	0.5	0.1(< 0.1)
CdO	103	76	71(12)	56	77	86(4)

In the study of Khan and Frankland (1983), a loamy sand soil (pH 4.6) was incubated for 15 days after contaminating with 10, 50, 100 and 500  $\mu\text{g g}^{-1}$  Cd as CdCl<sub>2</sub> or with 100, 500 and 1,000  $\mu\text{g g}^{-1}$  Cd as CdO. Yield of 42-day-old radish plants decreased consistently with increasing Cd rate. From the curves fitted to the shoot yield responses to both Cd compounds, the EC<sub>50</sub> was predicted to be 70  $\mu\text{g g}^{-1}$  for Cd added as CdCl<sub>2</sub> and 190  $\mu\text{g g}^{-1}$  for the Cd added as CdO. Muramoto et al. (1991) measured Cd uptake in unpolished rice after applying various soluble and insoluble Cd forms. Cd application rates were 10 and 50  $\mu\text{g g}^{-1}$ . The yield of rice (16 weeks) was reduced by 17% at the highest rate using CdCl<sub>2</sub> and by 8% using CdO. The Cd concentration in rice was not significantly different between CdCl<sub>2</sub> or CdO treated plants at the highest application rate. Webber (1973) compared Cd uptake in different plants from compost (pH 6.1) treated with various rates (0-500  $\mu\text{g g}^{-1}$ ) of Cd added as CdO or CdSO<sub>4</sub>. The author concluded that CdO was at least as phytotoxic as CdCl<sub>2</sub>. The Cd concentrations in the plant supplied with CdO were even higher than in those treated with CdSO<sub>4</sub>.

Isotopic exchange using <sup>109</sup>Cd<sup>2+</sup> is a method allowing calculating the fraction of the Cd in soils contributing to Cd<sup>2+</sup> sorption /desorption reactions within defined conditions of time, solution composition and pH. A "radiolabile" fraction of 100% of total Cd in soil effectively means that all Cd in soil is equally available as recently added Cd<sup>2+</sup>. In 33 polluted soils from U.K., Nakhone and Young (1993) found that this fraction varies from 6% to 102%. Many of these soils were contaminated by mine spoils and were characterised by a low fraction of "radiolabile" Cd. In the soils where the majority of Cd originated from sludge or from smelter fumes (Cd/CdO), the Cd labile pool varied from 29-102% (average 55%). In 10 Belgian soils with both background as elevated Cd levels, the "radiolabile" Cd pool was found to vary from 62-90% of aqua regia soluble Cd (Smolders et al., 1999). In a sandy soil sampled in the vicinity of a former Zn smelter in northern Belgium and which has been polluted through atmospheric deposition with mainly CdO, all aqua regia soluble Cd (10  $\mu\text{g g}^{-1}$ ) was found to be "radiolabile" (Vlassak V., personal communication).

Equilibrium calculations with MINTEQA2 (Allison et al., 1991) confirm that CdO is labile in soil and that Cd<sup>2+</sup> becomes adsorbed. Effectively this prediction means that all Cd derived from CdO has the same speciation as Cd derived from soluble Cd salts. **Table 3.213** shows that in a soil contaminated with 50  $\mu\text{g g}^{-1}$  Cd, added as CdO, almost all Cd is adsorbed and than all CdO has dissolved. This is surprising since CdO is considered as an insoluble product. In aqueous systems, CdO is indeed insoluble since the pH increases as the product dissolves, thereby reducing the solubility of the product. In soils, however, the pH is buffered and almost unaffected upon the dissolution of CdO.

All evidence gathered above indicates that, in the short term, CdO is less available than soluble Cd<sup>2+</sup> salts but that the differences in availability between both Cd<sup>2+</sup> forms are not very

pronounced. For these reasons, a soil risk assessment for CdO based on soluble salt studies seems to be justified.

Table 3.213 Equilibrium speciation in soil contaminated with 50  $\mu\text{g g}^{-1}$  Cd added as CdO. The speciation is predicted with MINTEQA2 (Allison et al., 1991). The logK value of the reaction  $\text{Cd}^{2+} + \text{H}_2\text{O} \rightarrow \text{CdO} (\text{Monteponite}) + 2\text{H}^+$  is  $-15.12$  (database of MINTEQA2). Input parameters: soil moisture content =  $0.2 \text{ g g}^{-1}$ ; soil solution composition  $\text{Ca}(\text{NO}_3)_2$  5 mM. Sorption of  $\text{Cd}^{2+}$  was assumed to occur on an infinite number of sites. At each soil pH, a solid:liquid concentration ratio  $K_D$  (solution  $\text{Cd}^{2+}$  activity based) was selected that represents a typical value (see Table 3.1.88)

speciation	Soil pH 5 $K_d$ 50L/kg	Soil pH 6 $K_d$ 200L/kg	Soil pH 7 $K_d$ 800L/kg
CdO (% of total)	0.0	0.0	0.0
$\text{Cd}^{2+}$ sorbed on soil solid (% of total)	99.3	99.8	99.9
Cd in soil solution (% of total)	0.7	0.2	< 0.1
Soil solution			
$\text{Cd}^{2+}$ ( $\mu\text{M}$ )	14.4	3.61	0.9
$\text{Cd}(\text{NO}_3)^+$ ( $\mu\text{M}$ )	0.2	0.05	< 0.01

#### Influence of soil properties on Cd toxicity

Soil properties influence Cd toxicity. This is illustrated in this review in several tests that have been performed on a series of different soils. A general trend emerges that toxicity increases in soil when mobility of Cd is higher, i.e. soil toxicity increases as soil pH, or soil organic matter decrease. Exceptions to this rule have also been found (Mahler et al., 1978, see Section 3.2.3.4.).

The toxicity data were not converted to a standard soil in contrast with suggestions of the Technical Guidance Document (TGD, 1996, p.338). The suggested conversion corrects the data to a soil with a standard organic matter content of 3.4%. Whereas this conversion may be relevant for hydrophobic compounds, no information was found that bioavailability of metals in soil is predominantly related to soil organic matter content. Other normalisation equations that are used for defining maximum permissible concentrations in soils in Flanders-Belgium (Vlarebo, 1996) or in the Netherlands (Lexmond et al., 1986) are merely corrections for variance in background concentrations with soil properties. Since most LOEC data are substantially higher than background concentrations, no such normalisation equation can be advocated. We are not aware of any experimentally obtained relationship between soil properties and soil toxicity for Cd. Sauvé et al. (1998) demonstrated that toxicity of Pb and Cu on plants or on microbial processes correlates better with soil solution metal activity than with total concentrations. This indicates that soil solution metal activities represent the toxic dose in the soil. If this is the case, then soil toxicity data could be normalised based on e.g. soil properties that affect solid-liquid distribution of Cd. Crommentuijn et al. (1997b) however demonstrated that variation in Cd  $\text{EC}_{50}$  values for growth of the collembollan *Folsomia candida* increased when effects were expressed as Cd concentrations instead of total concentrations. The collembollan were exposed to Cd in artificial soils varying in pH and organic matter content, and hence, varying in  $\text{Cd}^{2+}$  sorption. It is unclear if the same is true for plants or soil microbial processes.

### 3.2.3.2 Toxicity to soil microflora

Table 3.214 Selected data for Cd toxicity to soil microflora. Fifty tests were reviewed from 18 source documents and 36 tests were selected

	Min	Median	Max	n
NOEC ( $\mu\text{g g}^{-1}$ )	3.6	50	3,000	21
LOEC ( $\mu\text{g g}^{-1}$ )	7.1	100	8,000	21
E(L)C <sub>x50</sub> ( $\mu\text{g g}^{-1}$ )	7.1	283	5,264	20

The soil microflora cycle C, N, P and S compounds in soil. Toxicity to some essential pathways in these cycles may result in plant nutrient deficiencies or unacceptable losses of nutrients to the environment.

*Respiration* is a process which is performed by a suite of soil organisms with varying sensitivities to soil contamination. Bond et al. (1976) measured respiration in a forest soil and litter microcosm for 24 days following soil contamination with 0, 0.01 and 10  $\mu\text{g g}^{-1}$  Cd. The respiration rate between days 6-24 at the highest Cd rate was decreased by 36% compared with the control. No information was given on soil properties. Similar respiration studies with forest soil (0-4.5 cm) microcosms contaminated with 0, 0.6 and 6  $\mu\text{g g}^{-1}$  Cd could not detect significant toxic effects on respiration rates followed over 23 days after contamination (Chaney et al., 1978). Interestingly, respiration rate decreased faster during incubation in control microcosms than in the Cd treated ones, resulting in significant higher respiration rates at 23 days in the Cd treated soils. To overcome the problems with high variability between the replicates, respiration of each microcosm was expressed as a percentage of that rate just prior to the treatment. Expressed this way, respiration was not significantly reduced by Cd up to the highest application rate at either 1.5 or 23 day's incubation. However, in treatments with 47  $\mu\text{g g}^{-1}$  Zn added Cd addition at the highest dose reduced respiration rate faster than in the control soils at 36 hours after contamination. The added amount of Cd was not mixed in the microcosms (applied as a solution on the top layer) and, therefore, this test is not selected for effects assessment. Cornfield (1977) found evidence for increasing Cd toxicity with time on soil respiration. The respiration was followed for 8 weeks after contaminating the acid sandy soil with either 10 or 100  $\mu\text{g g}^{-1}$  Cd. No toxic effects were noted for the 0-2 week's incubation whereas respiration significantly reduced by 17 % at the lowest rate tested for the 0-8 week's incubation. Saviozzi et al. (1997) found no Cd effects up to 50  $\mu\text{g g}^{-1}$  on total respiration (28 days) in an inceptisol. Walter and Stadelman (1979) measured soil respiration for 24 hours in loamy sand previously grown for 14 weeks by maize plants. The soils were contaminated with Cd at 5 rates between 0 and 58  $\mu\text{g g}^{-1}$  before plant growth. The LOEC was found at 29.1  $\mu\text{g g}^{-1}$  at which respiration was 36% lower than in the nil treatment. Doelman and Haanstra (1984) compared toxic effects on respiration between five different soils amended with various Cd rates between 55 and 8,000  $\mu\text{g g}^{-1}$ . Respiration rate was followed during approximately 18 months after contamination. In one soil (sandy soil) toxicity markedly reduced by ageing whereas no such clear trend was found in the other soils. The respiration rates at the end of the incubation period were insignificantly affected by Cd concentrations up to concentrations ranging from 150 to 3,000  $\mu\text{g g}^{-1}$ . Increasing clay content and organic matter content reduced Cd toxicity in soil (Doelman and Haanstra, 1984). It is unclear why NOEC values in this study are much higher than the LOEC values for respiration from the studies cited above. In another study by the same authors (Haanstra and Doelman, 1984) glutamic acid (GLU) induced respiration was followed on the same soils (one soil not included). The time to reach a peak in respiration rate was chosen as the endpoint. The soils were all measured 18 months after Cd addition. Elevated Cd reduced GLU decomposition rate. In the

sandy soil, a small but significant decrease in decomposition rate was already found at  $55 \mu\text{g g}^{-1}$  (lowest concentration tested). In the other 4 soils, an inhibitory effect was only found at higher concentrations or not found (peat soil). A similar study on substrate (glucose and GLU) induced respiration was made on three different soils amended with various Cd rates between 1.8 and  $229 \mu\text{g g}^{-1}$  (Reber 1989). In this study, the respiration rate of the treated soils was measured at the time where respiration rate increased maximally in the control soils. This endpoint proved to be very sensitive and statistically significant toxic effects (6% inhibition) were already found at Cd levels of  $2.7\text{-}7.8 \mu\text{g g}^{-1}$ . More than 10% inhibition was found at  $7\text{-}29 \mu\text{g g}^{-1}$  (LOEC values). It should be stressed that this endpoint should not be compared with, for example, cumulative respiration, an endpoint that is far less sensitive as can be derived from the studies cited above. Khan and Frankland (1984) measured toxic effects of Cd on cellulolytic activity in a loamy sand soil. The cellulolytic activity was measured using the dye release from a dyed cellophane film, encased in a nylon mesh and placed for 30 days in the soil. The soil was contaminated with various Cd rates between 0 and  $100 \mu\text{g Cd}$  and incubated for 15 days prior to the test. The dye release was measured in a pot with or without growing plants. In the uncropped soils, the LOEC was  $50 \mu\text{g g}^{-1}$  at which cellulolytic activity was 17% below that of the control. In the presence of plants, cellulolytic activity was more sensitive to Cd and the LOEC with oat plants was found at  $10 \mu\text{g g}^{-1}$  (lowest concentration tested) where the inhibition was already 34%.

The *N-cycle* provides various pathways on which toxic effects can be monitored. Liang and Tabatabai (1978) measured  $\text{NH}_4^+\text{-N}$  induced nitrification as  $\text{NO}_3^- + \text{NO}_2^-$  accumulation after 10 days of incubation. Three soil types were contaminated with only one Cd application rate ( $560 \mu\text{g g}^{-1}$ ). Nitrification decreased by between 67% and 94% compared with the nil treated soils. Bewley and Stotzky (1983) followed mineralisation and nitrification for 35 days after adding glycine to soils contaminated with 50, 100, 500 and  $1,000 \mu\text{g g}^{-1}$  Cd. Nitrate accumulated at a lower rate in the Cd treated soil columns compared with the control. After 4 days, nitrate accumulation was 23% lower at the lowest Cd concentration tested ( $50 \mu\text{g g}^{-1}$ ). After 35 days incubation, significant effects on nitrate accumulation were only found at the highest concentration tested. The Cd application was not well mixed in the soil columns and, therefore, these data were not selected for the effects assessment. Dušek (1995) measured ammonification and nitrification in two soils with and without  $\text{NH}_4^+$  addition. Both soils were contaminated with 0, 10, 100 and  $500 \mu\text{g g}^{-1}$  Cd. The LOEC's on maximum nitrate production rate were found at  $100 \mu\text{g g}^{-1}$  or above. Walter and Stadelman (1979) measured ammonification on the same soil sample on which respiration was measured (see above). The ammonium accumulated after 50 days incubation was not sensitively affected up to the highest concentration tested ( $58 \mu\text{g g}^{-1}$ ). Denitrification of nitrate in anaerobic conditions in a helium atmosphere was followed for a silt loam soil contaminated with various Cd rates between 0 and  $500 \mu\text{g g}^{-1}$  (Bollag and Barabasz, 1979). Some samples were autoclaved and subsequently inoculated with *Pseudomonas*. Because of unknown effect of autoclaving soils on Cd availability, only the data obtained with the native soil microflora in unautoclaved soils are reported here. The various N forms ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$ ) were followed during 3 weeks of incubation. Removal of nitrate was slower and accumulation of the intermediates ( $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$ ) was higher in the Cd treated soils. The presence of the intermediate  $\text{N}_2\text{O}$  (a greenhouse gas) was already higher at the lowest concentration tested ( $10 \mu\text{g g}^{-1}$ ) after two or three weeks incubation. At a Cd level of  $100 \mu\text{g g}^{-1}$ , the remaining quantities of  $\text{NO}_3^- + \text{N}_2\text{O}$  in the systems were about twice as high as in the control soil after 2 weeks incubation.

Toxic effects on *soil enzymes* are often used in soil toxicology, perhaps because of the ease of measurement. The enzymes reported here, urease, phosphatase and arylsulphatase, represent responsible parts of the N, P and S cycle respectively. Doelman and Haanstra (1986, 1989) and Haanstra and Doelman (1991) reported effects of Cd addition on enzyme activities in the five

soils which were also used for the respiration studies (Doelman and Haanstra, 1984). The enzyme activities were recorded at a saturating substrate concentration in soils either 6 weeks or 18 months after Cd addition. Cd rates varied from 55 to 8,000  $\mu\text{g g}^{-1}$ . The inhibition of the enzyme activity was plotted to the log of the added Cd concentration. A logistic response curve was plotted to the data and an  $\text{EC}_{50}$  was calculated by interpolation where curve fitting was possible. The  $\text{EC}_{50}$  values are given in **Table 3.215**. Toxicity of Cd increased with time (decrease of  $\text{EC}_{50}$ ) for all combinations of soil and type of enzymes where response curves could be fitted. In all soils, except the peat soil, response curves were significant at 18 months after incubation and this incubation time was chosen for discussion below. The toxic effects of Cd were in general terms most pronounced in the sandy soil. Among the three enzymes, the urease activity was generally most sensitive to Cd (lowest  $\text{EC}_{50}$  values) except in the silty loam at pH 7.7. The  $\text{EC}_{50}$  value of urease in the sandy loam was 30  $\mu\text{g g}^{-1}$  and is below the lowest concentration tested. The authors also reported the  $\text{EC}_{10}$  which were calculated with the experimental curves. These  $\text{EC}_{10}$  values range from  $< 1$  to 280  $\mu\text{g g}^{-1}$  for urease, from 16 to 8,000  $\mu\text{g g}^{-1}$  for phosphatase and from 3.4 to 5,880  $\mu\text{g g}^{-1}$  for arylsulphatase. Ten of the 14  $\text{EC}_{10}$  values however fall below the lowest concentration tested (55  $\mu\text{g g}^{-1}$ ) and, hence, their statistical significance is questionable. The LOEC's were unfortunately not given in the original papers.

Biological  $\text{N}_2$  fixation (either by free living cyanobacteria or as symbiotic associations) is very sensitive to soil pollution (Brookes, 1995). Toxic effects are found in soils treated with sewage sludge where, of course, multiple metal contamination is found. The LOEC values on yield of clover or on population of *Rhizobium leguminosarum* biovar *trifolii* are 0.8  $\mu\text{g g}^{-1}$ , 1.0  $\mu\text{g g}^{-1}$  and 6.0  $\mu\text{g g}^{-1}$  Cd in three European long-term sludge treated plots (McGrath et al., 1995). The Zn levels on these sites are 130  $\mu\text{g g}^{-1}$ , 200  $\mu\text{g g}^{-1}$  and 180  $\mu\text{g g}^{-1}$  respectively. All three Zn levels are below current limits of sludge treated soils in the EC. Effects of single metals on survival of *Rhizobium leguminosarum* biovar *trifolii* in soil was reported by Chaudri et al. (1992). This survival study used a farmyard manure treated plot of the Woburn Experimental Farm (U.K.). Two month after  $\text{CdSO}_4$  application, no toxic effects were found on survival of the *Rhizobium* strains. After 18 months, however, the cell number was decreased in all soils and this decrease was most pronounced in the metal applied samples. The Cd NOEC was 4  $\mu\text{g g}^{-1}$  and at 7.1  $\mu\text{g g}^{-1}$  no more cells of the *Rhizobium* strains were detected. The nitrogen content in white clover plants grown on these soils decreased with increasing soil Cd content with a LOEC of 7.1  $\mu\text{g g}^{-1}$ . In N-fertilised samples, no such decrease in plant N-content was found confirming toxicity on  $\text{N}_2$ -fixation. The evidence of metal toxicity on  $\text{N}_2$ -fixation which has been gathered in the last decade is however conflicting. NOEC values on  $\text{N}_2$ -fixation in sludge treated soils are often higher than the LOEC values given above (e.g. Ibekwe et al., 1995)

The toxicity tests for soil microflora lack standardisation that complicates mutual comparison of the tests described above. Toxicity of Cd generally decreases with increasing clay content, pH and organic matter content. The data compilation shows that  $\text{N}_2$ -fixation is probably the most sensitive soil microbial process. Toxic effects on  $\text{N}_2$ -fixation have been found at moderate Cd pollution, both in metal salt applied soils as in sludge treated soils.

Table 3.215 Toxicity to soil microflora. All underlined data are selected to discuss the critical concentrations (Table 3.214). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	pH <sup>a</sup>	%OC <sup>b</sup>	% clay	Equil. Period (d)	Duration (d)	Endpoint	NOEC (µg g <sup>-1</sup> )	Cat.*	LOEC (µg g <sup>-1</sup> ) (%effect)	EC <sub>250</sub> (µg g <sup>-1</sup> ) (%effect)	References	R.I.		
CdOAc.	native soil microflora	phaeosem	6.9	1.3	21	>1 week	84(min.)	substrate induced respiration rate	<u>3.6</u>	1	<u>7.1(15)</u>	<u>60</u>	Reber, 1989	2		
		neutral sandy hortisol	7	1.5	3		84(min.)	substrate induced respiration rate	<u>3.6</u>	1	<u>7.1(15)</u>	<u>70</u>		2		
		acidic cambisol	5.6	1	7		84(min.)	substrate induced respiration rate	<u>14.3</u>	1	<u>28.6(18)</u>	<u>&gt;228(HT)</u>		2		
CdCl <sub>2</sub>	native soil microflora	grassland soil	7.4	5.7	24	0	33	nitrification: NO <sub>3</sub> <sup>-</sup> production rate -NH <sub>4</sub> <sup>+</sup> substrate	<u>50</u>	2	<u>100(19)</u>		Dušek, 1995	2		
			7.6	2.9	19	33	nitrification: NO <sub>3</sub> <sup>-</sup> production rate -NH <sub>4</sub> <sup>+</sup> substrate	<u>50</u>	2	<u>100(12)</u>						
								+NH <sub>4</sub> <sup>+</sup> substrate	<u>100</u>	1	<u>500(45)</u>					
								+NH <sub>4</sub> <sup>+</sup> substrate	<u>100</u>	1	<u>500(45)</u>					
Cd(NO <sub>3</sub> ) <sub>2</sub>	native soil microflora	loamy sand	5.8	2.7	16	>98	1	24h respiration	<u>14.6</u>	1	<u>29.1(36)</u>		Walter and Stadelman, 1979	2		
CdCl <sub>2</sub>	native soil microflora	sand	7	1.1	2	560	1-2	glutamic acid decomposition time				<u>150(56)</u>	Haanstra and Doelman, 1984	2		
		silty loam	7.7	2.6	19	560	1-2	glutamic acid decomposition time	<u>55</u>	1	<u>150(15)</u>			2		
		clay	7.5	3.4	60	560	1-2	glutamic acid decomposition time	<u>150</u>	1	<u>400(10)</u>			2		
CdCl <sub>2</sub>	native soil microflora	sand	7	1.1	2	490	42-70	respiration	<u>150</u>	3	<u>400(23)</u>		Doelman and Haanstra, 1984	3		
		sandy loam	6	6.1	9	301	42-70	respiration	<u>150</u>	1	<u>400(20)</u>			2		
		silty loam	7.7	2.6	19	630	42-70	respiration	<u>150</u>	1	<u>400(17)</u>			2		
		clay	7.5	3.4	60	560	42-70	respiration	<u>3,000</u>	1	<u>8,000(34)</u>			2		
		peat	4.5	13.6	5	574	42-70	respiration	<u>400</u>	1	<u>1,000(19)</u>			2		
CdCl <sub>2</sub>	native soil microflora	sandy soil	7	1.1	2	42	5h	urease activity				340	Haanstra and Doelman, 1991	2		
			560	5h	urease activity				<u>120</u>							
			42	1h	phosphatase activity							840				
			560	1h	phosphatase activity							<u>330</u>				
					42	2h	arylsulphatase activity						2,206			
					560	2h	arylsulphatase activity						<u>121</u>			
				sandy loam	6	6.1	9	42	5h	urease activity				>8,000		
							42	1h	phosphatase activity							
					42	2h	arylsulphatase activity					>8,000				

Table 3.215 continued overleaf

Table 3.215 continued Toxicity to soil microflora. All underlined data are selected to discuss the critical concentrations (Table 3.214). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	pHa	%OCb	% clay	Equil. Period (d)	Duration (d)	Endpoint	NOEC (µg g <sup>-1</sup> )	Cat.*	LOEC (µg g <sup>-1</sup> ) (%effect)	EC <sub>50</sub> (µg g <sup>-1</sup> ) (%effect)	References	R.I.
		silty loam	7.7	2.6	19	560	2h	arylsulphatase activity				<u>1,792</u>		2
						42	5h	urease activity				970		
						560	5h	urease activity				<u>520</u>		
						42	1h	phosphatase activity				5488		
						560	1h	phosphatase activity				<u>235</u>		
						42	2h	arylsulphatase activity				1,882		
						560	2h	arylsulphatase activity				<u>137</u>		
		clay	7.5	3.4	60	42	5h	urease activity				4,460		
						560	5h	urease activity				<u>520</u>		
						42	1h	phosphatase activity				9,744		
						560	1h	phosphatase activity				<u>5,264</u>		
						42	2h	arylsulphatase activity				9,486		
						560	2h	arylsulphatase activity				<u>1,016</u>		
		peat	4.5	13.6	5	42	5h	urease activity				3,260		
						560	5h	urease activity				<u>490</u>		
						42	2h	arylsulphatase activity				3,181		
CdSO <sub>4</sub>	native soil microflora	sandy soil	4.9	2.2	5.2	0	56	respiration	<u>5</u>	2	<u>10(17)</u>		Cornfield 1977	3
CdSO <sub>4</sub>	<i>Rhizobium leguminosarum</i> bv. <i>trifolii</i>	sandy loam	6.5	/	9		540	cell number (survival)	<u>4</u>	3		<u>7.1(100)</u>	Chaudri et al., 1992	3
CdCl <sub>2</sub>	native soil microflora	brown earth loamy sand	4.6	<u>1-20**</u>	<u>0-75**</u>	15	45	cellulolytic activity: unplanted soil	<u>10</u>	1	<u>50(17)</u>		Khan and Frankland, 1984	3
								oat grown soil			<u>10(34)LT</u>			3
								wheat grown soil			<u>50(43)LT</u>			3
CdSO <sub>4</sub>	native soil microflora	organic soil	4.5	47		180	180	respiration rate	<u>60</u>	3		<u>1,574</u>	Frostegård et al., 1993	3
								ATP content	112	3		2,810		3
		sandy-loam	7.8	2.6		180	180	ATP content	<u>112</u>	3		<u>708</u>		3
CdCl <sub>2</sub>	native soil microflora	inceptisol	5.2	1.4	8	0	28	substrate induced respiration	<u>50</u>	3	<u>250(27)</u>		Saviozzi et al., 1997	3
Cd(NO <sub>3</sub> ) <sub>2</sub>	native soil microflora	silt loam	6.7	1.9	28	0	14	denitrification			<u>10LT</u>	<u>100</u>	Bollag and Barabasz, 1979	3

Table 3.215 continued overleaf

Table 3.215 continued Toxicity to soil microflora. All underlined data are selected to discuss the critical concentrations (Table 3.214). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	pHa	%OCb	% clay	Equil. Period (d)	Duration (d)	Endpoint	NOEC (µg g-1)	Cat.*	LOEC (µg g-1) (%effect)	EC <sub>50</sub> (µg g-1) (%effect)	References	R.I.	
<i>Supporting data</i>															
CdSO <sub>4</sub>	native soil microflora	sandy soil	4.9	2.2	5.2	0	14	respiration	100HT				Cornfield 1977	4	
CdCl <sub>2</sub>	native soil microflora	forest soil (0-4.5cm)	4.8	1.1	0-15**	0	1.5	respiration rate:			6.7(28)		Chaney et al., 1978	4	
								47ppm Zn added	1.3			4			
			loamy sand	23	no Zn added	6.7HT			with or without Zn added	6.7HT				4	
Cd(NO <sub>3</sub> ) <sub>2</sub>	native soil microflora	loamy sand	5.8	2.7	16	>98	50	ammonification: NH <sub>4</sub> <sup>+</sup> found after 50 days incubation	58HT				Walter and Stadelman, 1979	4	
CdCl <sub>2</sub>	native soil microflora	Peat	4.5	13.6	5	560	1-2	glutamic acid decomposition time	1,000HT				Haanstra and Doelman, 1984	4	
CdSO <sub>4</sub>	native soil microflora	surface soil	4.8	3.8	9	0	4	nitrification: % NO <sub>3</sub> <sup>-</sup> of total N			50(30)LT	1,000(54)	Bewley and Stotzky, 1983	4	
CdSO <sub>4</sub>	native soil microflora	surface soil	5.8	2.8	23	0	10	nitrification: NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> accumulation after 10 days with addition of NH <sub>4</sub> <sup>+</sup>				560(94)LT		Liang and Tabatabai, 1978	4
			7.8	3.9	30		10	nitrification: NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> accumulation after 10 days with addition of NH <sub>4</sub> <sup>+</sup>				560(70)LT			
			7.4	5.7	34		10	nitrification: NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> accumulation after 10 days with addition of NH <sub>4</sub> <sup>+</sup>				560(67)LT			
CdSO <sub>4</sub>	native soil microflora	Lösslehm	6.10	1.56			30	microbial biomass	30(HT)				Beck, 1981	4	
							52	nitrification	33(HT)			4			
		Lösslehm degr	3.25	3.45			30	microbial biomass	30(HT)					4	
		Lösslehm + kalk	7.25	1.47			30	microbial biomass	30(HT)					4	
							38	nitrification	30(HT)					4	
		Auengleye	7.50	2.91			30	microbial biomass	30(HT)					4	
							37	nitrification	33(HT)					4	
		Auenboden	7.20	1.95			30	microbial biomass	30(HT)					4	
					37	nitrification	33(HT)					4			
CdCl <sub>2</sub>	native soil microflora	forest soil				0	24	respiration	0.01	2	10(36)		Bond et al., 1976	4	

- a) pH-water ;  
 b) %OC= %OM/1.7;  
 LT Lowest Tested concentration;  
 HT Highest Tested concentration;  
 \* NOEC classification (see Section 3.2.1.2);  
 \*\* estimated OC - clay content..

### 3.2.3.3 Toxicity to soil fauna

Table 3.216 Selected data for Cd toxicity to soil fauna. Forty tests were reviewed from 22 source documents and 37 tests were selected

	Min	Median	Max	n
NOEC ( $\mu\text{g g}^{-1}$ )	5	32	320	13
LOEC ( $\mu\text{g g}^{-1}$ )	5	59	326	12
E(L)C <sub>x&gt;50</sub> ( $\mu\text{g g}^{-1}$ )	27	102	3,680	28

The potential hazards of environmental pollutants to soil invertebrates have been assessed in acute and chronic toxicity tests. The toxicity of Cd ( $\text{Cd}^{2+}$  salts) has been tested with standard tests: the 14-day LC<sub>50</sub> test using the earthworm *Eisenia fetida* (OECD 1984, EEC 1985) and the ISO test (ISO, 1994) with the collembolan *Folsomia candida*.

**Table 3.216** summarises the reviewed literature data. Reproduction parameters are generally more sensitive to Cd than growth or survival. Spurgeon et al. (1994) grew adult *E. fetida* in contaminated OECD artificial soil (pH 6.3) for 8 weeks to test the effects of Cd [as  $\text{Cd}(\text{NO}_3)_2$ ] on survival and cocoon production. Soil contamination ranged from 10 to 300  $\mu\text{g g}^{-1}$ . The calculated LC<sub>50</sub> was greater than 300  $\mu\text{g Cd/g soil}$  (highest concentration tested). Cocoon production was unaffected at 5  $\mu\text{g g}^{-1}$  but was reduced by 80% at 20  $\mu\text{g g}^{-1}$ . The NOEC value for cocoon production in this soil is the lowest NOEC value for soil fauna found in this literature review. It was however noted by the authors (Spurgeon et al., 1994) that worms in all treatments lost weight after two weeks in the experiment. Using the same artificial soil, the EC<sub>50</sub> of the growth of *E. fetida* was 33  $\mu\text{g Cd/g soil}$  and there was no observed effect at 18  $\mu\text{g Cd/g soil}$  (Van Gestel et al., 1991). Sexual development of *E. fetida* was inhibited at 10  $\mu\text{g Cd/g soil}$  (lowest concentration tested) and a 50% effect was found at 27  $\mu\text{g Cd/g soil}$ . The LC<sub>50</sub> was 253  $\mu\text{g Cd/g soil}$ . In studies by van Gestel et al. (1993) it was found that reproduction of *Eisenia* was more sensitive than growth. Khalil et al. (1996b) reported a LOEC of 10  $\mu\text{g Cd/g soil}$ , the lowest concentration tested, and an EC<sub>50</sub> of 35  $\mu\text{g Cd/g soil}$  for cocoon production of the earthworm *Aporrectodea caliginosa* in natural soil 56 days after Cd addition. The LC<sub>50</sub> was found at 540  $\mu\text{g Cd/g}$ . Growth of this earthworm in that soil was reduced by 50% at 68  $\mu\text{g Cd/g}$  (Khalil et al., 1996a).

Increasing exposure time generally increases toxicity in the laboratory tests. Van Gestel and van Dis (1988) recorded an increase in mortality with increasing exposure time, using the 14-day OECD test. Khalil et al. (1996b) and van Gestel et al. (1991) extended the exposure time of the earthworm to 8 and 12 weeks respectively. Both authors found a significant decrease of more than 50% of the LC<sub>50</sub> during the exposure period. A short exposure time may therefore explain the higher LC<sub>50</sub> values found by Neuhauser et al. (1985) in an artificial soil. An LC<sub>50</sub> value of 1,843  $\mu\text{g g}^{-1}$  was recorded in 2 weeks of exposure.

Fitzpatrick et al. (1996) compared the sensitivity to Cd in an artificial OECD-soil between two earthworm species. The LC<sub>50</sub> of *Lumbricus terrestris* was lower than that of *Eisenia fetida* (256 versus 374  $\mu\text{g g}^{-1}$  soil).

Soil characteristics influence Cd sorption and therefore its bioavailability and toxicity. Van Gestel and van Dis (1988) investigated the influence of pH on the toxicity of Cd to earthworms. Toxicity was assessed in a sandy soil limed from pH 4.1 to pH 7.0. The LC<sub>50</sub> value at pH 4.1 was at least 3 to 4-fold lower than at pH 7.0. Bengtsson et al. (1986) studied the combined effects of Cd pollution and acidification of the soil on the earthworm *Dendrobaena rubida*. Tests were

performed at pH 4.5, 5.5 and 6.5 in the C horizon of a sandy coniferous forest soil mixed with well decomposed cattle dung. Cocoon production was lower at pH 4.5 than at higher pH values in the nil treated soils. Cadmium significantly reduced cocoon production at pH 4.5. At pH 5.5 and 6.5 however, 10  $\mu\text{g Cd/g}$  increased cocoon production whereas 100  $\mu\text{g Cd/g}$  significantly decreased this productions at pH 5.5 only. Similar conclusions were made about effects of pH and Cd on success of hatching of the cocoons. No toxic effects of Cd on growth were found. At pH 6.5, growth was even increased by 100  $\mu\text{g Cd/g}$  compared to control. Crommentuijn et al. (1997b) investigated the effects of pH and organic matter content on toxicity of Cd on growth and reproduction of the springtail *Folsomia candida*. The difference in soil properties affected the performance of the test organisms. Soluble Cd concentrations increased when pH or organic matter decreased in soil. The variation in Cd EC<sub>50</sub> values for growth increased when effects were expressed as soluble Cd concentrations instead of total concentrations.

Kammenga et al. (1996), Korthals et al. (1996) and Parmelee et al. (1997) studied the effect of Cd pollution on nematodes. Korthals et al. (1996) recorded a NOEC value of 160  $\mu\text{g Cd/g}$  (highest concentration tested) for survival of the natural nematode community in a sandy soil. Parmelee et al. (1997) found a comparable NOEC value of 200  $\mu\text{g g}^{-1}$  (highest concentration tested) for survival in a forest topsoil. Kammenga et al. (1996) found a NOEC value for the juvenile/adult ratio of the nematode *Plectus acuminatus* of 32  $\mu\text{g g}^{-1}$  in an artificial OECD-soil.

This data compilation seems to indicate that soil fauna are less sensitive to Cd than soil microflora. The LOEC values obtained with soil fauna are all higher than or equal to 5  $\mu\text{g g}^{-1}$  whereas Cd toxicity to soil microbial processes or plants has been shown at lower Cd concentrations (see Section 3.2.3.2 and 3.2.3.4). Soil fauna could indeed be more resistant to Cd but it is striking to note that sensitive endpoints (e.g. reproduction) have rarely been tested in the 1-10  $\mu\text{g g}^{-1}$  range. Some LOEC values of 10  $\mu\text{g g}^{-1}$  are found at the lowest concentration tested for reproduction parameters of *Eisenia andrei* (van Gestel et al., 1991 and 1993). Three tests were found where Cd toxicity was measured below 10  $\mu\text{g g}^{-1}$  (Khalil et al., 1996a, Spurgeon et al., 1994 and Parmelee et al., 1997). One of these tests showed Cd toxicity at 5  $\mu\text{g g}^{-1}$  (Khalil et al., 1996a).

Table 3.217 Toxicity to soil fauna. All underlined data are selected to discuss the critical concentrations (Table 3.216). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	pH <sup>a</sup>	%OC <sup>b</sup>	Clay	Equil. Period (d)	Duration (d)	Endpoint	NOEC (µg <sup>-1</sup> )	Cat.*	LOEC (µg g <sup>-1</sup> ) (%effect)	EC <sub>250</sub> (µg g <sup>-1</sup> ) (%effect)	LC <sub>250</sub> (µg g <sup>-1</sup> ) (%effect)	References	R.I.
CdCl <sub>2</sub>	<i>Folsomia candida</i>	OECD-soil	6.1 <sup>s</sup>	5.9	20		42	fresh weight reproduction	50 <u>22</u>	1 5		322 <u>51</u>		van Gestel and Hensbergen, 1997	1
CdCl <sub>2</sub>	<i>Eisenia felida</i>	OECD soil	7 <sup>s</sup>	5.9	10.4	0		mortality				> <u>1,000</u> HT	Van Gestel and van Dis, 1988	1	
CdCl <sub>2</sub>	<i>Folsomia candida</i>	OECD soil	6.6	5.9	20	0	35	mortality growth number of juveniles population increase				633 <u>153</u> 152	972 Crommentuijn et al., 1995	1	
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Eisenia felida</i>	OECD-soil	6.5	5.8	20	0	14	mortality				374	Fitzpatrick et al., 1996	1	
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Dendrobaena rubida</i>	C-horizon of sandy coniferous forest soil+well decomposed cattle dung	4.5 5.5 6.5 5.5	4.5-6.9		4 weeks	110 270	cocoon production cocoon production hatching success embryonic development	<u>10</u> <u>10</u>	1 1		<u>100</u> (72%) <u>100</u> (78%) <u>100</u> (47) <u>10</u> LT	Bengtsson et al., 1986	2 2 2 2	
CdCl <sub>2</sub>	<i>Lumbricus rubellus</i>	sandy loam soil	7.3	4.7	17	0	42	mortality weight	150 <u>150</u>	3 3			<u>1,000</u> (100)	Ma, 1982	3
CdCl <sub>2</sub>	<i>Folsomia candida</i>	OECD-soil	6.3 <sup>s</sup>	5.9	20	0	42	mortality at 25% MC 45%MC 55%MC fresh weight at 25%MC 35%MC 45%MC 55%MC reproduction at 25%MC 35%MC 45%MC 55%MC	<u>160</u> <u>320</u> <u>80</u> <u>160</u>	3 1 3 3	<u>320</u> (72) <u>160</u> (43) <u>320</u> (29)	523 640(73) 253 481 <u>80</u> (56)LT <u>80</u> (57)LT <u>80</u> (46)LT <u>80</u> (43)LT	1,275 868 617 van Gestel and van Diepen, 1997	3 3 2 3 3 3	
CdCl <sub>2</sub>	<i>Eisenia felida</i>	sandy soil	4.1 <sup>s</sup>	1	4.3	0	14	mortality					<u>320</u> -560	Van Gestel & van Dis, 1988	2

Table 3.217 continued overleaf

Table 3.217 continued Toxicity to soil fauna. All underlined data are selected to discuss the critical concentrations (Table 3.216). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225).  
Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	pHa	%OCb	Clay	Equil. Period (d)	Duration (d)	Endpoint	NOEC (µg-1)	Cat.*	LOEC (µg g-1) (%effect)	ECx≥50 (µg g-1) (%effect)	LCx≥50 (µg g-1) (%effect)	References	R.I.	
CdCl <sub>2</sub>	<i>Folsomia candida</i>	OECD soil; T 20; 50% WHC	5.4-5.9 <sup>§</sup>	1.2	20	0	35	growth				246		Crommentuijn et al., 1997b	2	
								reproduction				<u>125</u>				
			5.4 <sup>§</sup>						mortality				356			323
				2.1					growth				<u>44</u>			
									reproduction				389			
			5.7 <sup>§</sup>						mortality				<u>82</u>			684
				3.1					growth				651			
									reproduction				<u>193</u>			
			5.9 <sup>§</sup>						mortality				615			758
				4					growth				615			
									reproduction				<u>130</u>			
			5.9 <sup>§</sup>						mortality				615			758
				4.9					growth				615			
									reproduction				<u>130</u>			
			5.8 <sup>§</sup>						mortality				824			940
				5.9					growth				<u>193</u>			
									reproduction				824			940
			3.1 <sup>§</sup>						mortality				<u>193</u>			
				5.9					growth				302			
									reproduction				<u>102</u>			890
3.7 <sup>§</sup>						mortality				316						
	5.9					growth				<u>102</u>						
						reproduction				316						
4.3 <sup>§</sup>						mortality				<u>102</u>						
	5.9					growth				542	1261					
						reproduction				<u>164</u>						
5.7 <sup>§</sup>						mortality				542						
	5.9					growth				697	743					
						reproduction				<u>177</u>						
7 <sup>§</sup>						growth				583						
	5.9					reproduction				<u>113</u>						
						growth				601	1276					
	7.3					reproduction				<u>306</u>						
	5.9					growth				601	1276					
						reproduction				<u>306</u>						
CdCl <sub>2</sub>	<i>Folsomia candida</i>	OECD soil	6	5.9	20	0	19	mortality	326	1	707		917	Crommentuijn et al., 1993	2	
								number of offspring				/				
								growth	148	1	326	448				

Table 3.217 continued overleaf

Table 3.217 continued Toxicity to soil fauna. All underlined data are selected to discuss the critical concentrations (Table 3.216). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225).  
Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	pHa	%OCb	Clay	Equil. Period (d)	Duration (d)	Endpoint	NOEC (µg-1)	Cat.*	LOEC (µg g-1) (%effect)	ECx≥50 (µg g-1) (%effect)	LCx≥50 (µg g-1) (%effect)	References	R.I.
							23	mortality	326	1	707		778		2
								number of offspring	71	1	148	159			2
								growth	148	1	326	376			2
							26	mortality	326	1	707		822		2
								number of offspring	71	1	148	204			2
								growth	326	1		707			2
							30	mortality	326	1	707		893		2
								number of offspring	71	1	148	227			2
								growth	148	1	326	541			2
							35	mortality	326	1			854		2
								number of offspring	<u>148</u>	1	<u>326</u>	807			2
								growth	326	1	707				2
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Eisenia fetida</i>	OECD soil	6	5.9	20	0	14	mortality					1843	Neuhauser et al., 1985	2
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Eisenia fetida</i>	OECD soil	6.3	5.9	20		56	cocoon production	<u>5</u>	1		<u>46</u>		Spurgeon et al., 1994	3
CdCl <sub>2</sub>	<i>Eisenia andrei</i>	OECD soil	6.3	5.9	20	7	21	cocoon production			<u>10(LT)</u>			Van Gestel et al., 1993	3
								juvenile/adult ratio	<u>10</u>	3	<u>18(38)</u>				3
CdSO <sub>4</sub>	<i>Aporrectodea caliginosa</i>	natural forest soil	7.05	12.5		0	42	growth			<u>5(40)LT</u>	<u>68</u>		Khalil et al., 1996a	3
CdSO <sub>4</sub>	<i>Aporrectodea caliginosa</i>	natural forest soil	7.05	12.7		0	56	mortality					540	Khalil et al., 1996b	3
								cocoon production			<u>10(28)LT</u>	<u>35</u>			3
CdCl <sub>2</sub>	<i>Eisenia andrei</i>	OECD soil	6.7	5.9	20		84	growth	<u>18</u>	1		33		van Gestel et al., 1991	3
								mortality					253		3
								sexual development			<u>10(37)LT</u>	<u>27</u>			3
CdCl <sub>2</sub>	<i>Plectus acuminatus</i>	OECD soil	5.5	5.9	20	5h	21	juvenile/adult ratio	<u>32</u>	1	<u>100(24)</u>	321		Kammenga et al., 1996	3
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Lumbricus terrestris</i>	OECD-soil	6.5	5.8	20	0	14	mortality					<u>256</u>	Fitzpatrick et al., 1996	3
CdCl <sub>2</sub>	<i>Enchytraeus albidus</i>	OECD-soil	6.5	5.9	20	0	28	mortality					<u>3,680</u>	Römbke, 1989	3

Table 3.217 continued overleaf

Table 3.217 continued Toxicity to soil fauna. All underlined data are selected to discuss the critical concentrations (Table 3.216). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225).  
Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Organism	Medium	pHa	%OCb	Clay	Equil. Period (d)	Duration (d)	Endpoint	NOEC (µg-1)	Cat.*	LOEC (µg g-1) (%effect)	ECx≥50 (µg g-1) (%effect)	LCx≥50 (µg g-1) (%effect)	References	R.I.
Supporting data															
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Eisenia fetida</i>	OECD soil	6.3	5.9	20		56	mortality	300HT					Spurgeon et al., 1994	4
CdCl <sub>2</sub>	<i>Eisenia andrei</i>	OECD soil	6.3	5.9	20	7	21	growth	100HT					Van Gestel et al., 1993	4
CdSO <sub>4</sub>	nematode community	top 10cm of an arable field on a sandy soil	4.1	1.9	4		14	mortality	160HT					Korthals et al., 1996	4
CdSO <sub>4</sub>	trophic groups of nematode and microarthropod communities	top 10cm of A-horizon of mature oak-beech forest soil	3.8 <sup>§</sup>	3.4	11	0	7	mortality	200HT					Parmelee et al., 1997	4
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Lumbricus terrestris</i>	artificial-soil				0	16	sperm-count				100		Cikutovic et al., 1993	4

- a) pH-water;
- \$ pH-KCl;
- b) OM = OC\*1.7;
- LT Lowest Tested concentration;
- HT Highest Tested concentration;
- MC Moisture content;
- \* NOEC classification (see Section 3.2.1.2)

### 3.2.3.4 Toxicity to higher plants

Table 3.218 Selected data for Cd toxicity to higher plants. Seventy-six tests were reviewed from 15 source documents and 54 tests were selected

	Min	Median	Max	n
NOEC ( $\mu\text{g g}^{-1}$ )	1.8	10	80	41
LOEC ( $\mu\text{g g}^{-1}$ )	2.5	40	160	44
E(L)C <sub>x&gt;50</sub> ( $\mu\text{g g}^{-1}$ )	2.8	100	320	34

Many studies report effects of Cd salts on plant development in potted soil. Only few studies were found in recent literature. There is currently a consensus that toxicity to plants due to single Cd pollution seldom occurs in the environment. In most cases, Cd pollution is associated with Zn pollution. Zinc is known to be more toxic to plants and plant growth effects in metal polluted areas are often attributed to Zn and not to Cd (Tiller, 1989). As stated above, we only report data that were obtained with single Cd pollution.

A summary of the literature review is given in **Table 3.218**. All data have been obtained using pot trials in greenhouse conditions. In most pot trials, Cd is homogeneously mixed in the whole soil prior to plant growth. In the experiments reported by Miles and Parker (1979) and by Kelly et al. (1979) however, the Cd<sup>2+</sup> salts were incorporated by top dressing. These data are reported here but they were not selected for the effects assessment. Miles and Parker (1979) found that soil Cd in the top 2.5 cm of the pots was about twice as high as the intended average Cd level in soil. Near background Cd concentrations (< 1  $\mu\text{g/g}$ ) were recorded in the base 2.5 cm of the pots. The strong toxic effects on growth of 3 of the 6 natural species tested at the lowest average concentration tested (10  $\mu\text{g g}^{-1}$ ) should therefore be treated with caution. Many threshold levels for Cd toxicity were obtained by Bingham et al. (1975) and by Mahler et al. (1978) using soils to which 1% sludge was incorporated. Sludge Cd was not the source for increasing Cd rates in soils (all soils obtained equal sludge rate). Bingham et al. (1975) report that the sludge was low in heavy metals without supplying the data. Mahler et al. (1978), from the same group of Bingham, report that 1% sludge application is equivalent to a metal application rate of 0.1  $\mu\text{g Cd/g}$ , 6  $\mu\text{g Cu/g}$ , 0.4  $\mu\text{g Ni/g}$  and 20  $\mu\text{g Zn/g}$ . These metal concentrations are all low and should not strongly increase the plant sensitivity to Cd. The data obtained by these two reports are interesting as they allow comparing differences in Cd toxicity between plant types (Bingham et al., 1975) and between soil types (Mahler et al., 1978). The data of Bingham et al. (1975) show that EC<sub>25</sub> values vary from 4  $\mu\text{g g}^{-1}$  to 170  $\mu\text{g g}^{-1}$  between plant types. The EC<sub>25</sub> values of rice were over 640  $\mu\text{g g}^{-1}$ , the highest concentration tested. Mahler et al. (1978) showed that EC<sub>50</sub> values vary from 105-320  $\mu\text{g g}^{-1}$  for chard and from 18-270  $\mu\text{g g}^{-1}$  for lettuce between the 8 soils. Among these 8 soils, 4 are acid (pH < 5.7), and 4 are calcareous (pH > 7.4). The Cd toxicity to chard is generally higher in acid soils (lower EC<sub>50</sub>) than in calcareous soils, as expected based on the effect of pH on Cd sorption. However, Cd toxicity to lettuce is surprisingly generally higher in calcareous soils than in acid soils. Cd uptake in both plants is lower in the calcareous soils than in the acid soils. Why growth sensitivity of lettuce to absorbed Cd is so much higher in lettuce at higher soil pH is unknown. The other tests where Cd toxicity is compared between soil types support the general idea that Cd toxicity in soil is higher if the Cd sorption capacity of the soil is lower, i.e. at low pH, clay content and organic C content (Reber et al., 1989; Miller et al., 1976).

The low values of some LOEC values call for attention. The reliable LOEC values lower or equal to  $4 \mu\text{g g}^{-1}$  are found by Miller et al. (1977), Reber (1989), Haghiri (1973) and by Bingham et al. (1975-with spinach only). These data generally relate to added Cd concentrations and Cd concentrations of the control soils were not given (generally below  $1 \mu\text{g g}^{-1}$ ). The LOEC values from the tests of Haghiri (1973) are derived as  $\text{EC}_{>20}$  values without statistical information.

Two more source documents can be quoted here, which show Cd toxicity below  $4 \mu\text{g g}^{-1}$  but of which data are not included in the table. The first report (Bingham et al., 1986) shows a significant yield reduction of 9 week-old Swiss chard upon adding 1 or  $2.5 \mu\text{g Cd/g}$  to an unlimed sandy loam at pH 4. The yield reduction was 33% and 42% compared with the 'control' soil which was not a nil treatment but a soil supplied with  $0.25 \mu\text{g Cd/g}$ . Because the 'control' soil was contaminated, no LOEC could be derived. The second report (Strickland et al., 1979) shows that yield of soybeans is reduced by over 30% upon adding Cd at  $2.5 \mu\text{g g}^{-1}$ . The soil in which this effect was observed is, however an artificial substrate (quartz sand with 0.5% peat moss) wetted with dilute nutrient solution. Since this substrate represents an extreme example of a soil low in Cd sorption properties, we chose not to incorporate it in the table.

Table 3.219 Toxicity to higher plants. All underlined data are selected to discuss the critical concentrations (Table 3.218). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Plant	Medium	pH <sup>a</sup>	%OC <sup>b</sup>	% clay	Equil. time prior to plant growth (d)	Growing period (d)	Pot (P) or field (F) trial	Endpoint	NOEC (µg g <sup>-1</sup> )	Cat.*	LOEC (µg g <sup>-1</sup> ) (%effect)	EC <sub>250</sub> (µg g <sup>-1</sup> ) (%effect)	References	R.I.
CdCl <sub>2</sub>	<i>Picea sitchensis</i>	peaty gley	3.3	45	<u>40-100</u> **	2	100	P	root length	<u>1.8</u>	1		<u>2.8(59)</u>	Burton et al., 1984	2
CdOAc	<i>Triticum aestivum</i>	phaeosem	6.9	1.3	21	>84	28	P	shoot dry weight	<u>7.1</u>	1	<u>14.3(15)</u>		Reber, 1989	2
		neutral sandy hortisol	7.0	1.4	3					<u>29</u>	1	<u>57(15)</u>			2
		acidic cambisol	5.6	0.9	7							<u>3.6(11)</u>			2
CdCl <sub>2</sub>	<i>Glycine max</i>	silt loam	7.9	<u>1-20</u> **	<u>0-28</u> **	4 drying and rewetting cycles	28	P	shoot dry weight	<u>10</u>	3	<u>100(22)</u>		Miller et al., 1976	3
			6.0		<u>0-28</u> **					<u>10</u>	3	<u>100(69)</u>			3
			5.5		<u>0-28</u> **							<u>10(26)</u>			3
			6.5		<u>0-28</u> **					<u>5</u>	4	<u>10(12)</u>	<u>100(47)</u>		3
			6.1		<u>28-40</u> **					<u>10</u>	3	<u>100(66)</u>			3
CdCl <sub>2</sub>	<i>Zea mays</i>	loamy sand	6			4 drying and rewetting cycles	24	P	shoot dry weight			<u>2.5(47)LT</u>		Miller et. al, 1977	3
CdCl <sub>2</sub>	<i>Raphanus sativus</i>	loamy sand	5.4	<u>1-20</u> **	<u>0-15</u> **	15	42	P	shoot dry weight	<u>10</u>	1	<u>50(30)</u>	<u>70</u>	Khan and Frankland, 1983	3
CdO												<u>100(29)LT</u>	<u>190</u>		3
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Lactuca sativa</i>	soil	3.9	1.2	8		42	P	shoot dry weight	<u>2</u>	2	<u>32(30)</u>		Jasiewicz,1994	3
CdCl <sub>2</sub>	<i>Avena sativa</i>	loamy sand	5.4	<u>1-20</u> **	<u>0-15</u> **	15	42	P	root dry weight			<u>10(24)LT</u>		Khan and Frankland, 1984	3
	<i>Triticum aestivum</i>					15	42	P	root dry weight				<u>50(61)LT</u>		
CdO	<i>Triticum aestivum</i>					15	42	P	root dry weight			<u>100(47)LT</u>			
CdCl <sub>2</sub>	<i>Lactuca sativa</i>	humic sand	5.1	2.2			14	P	shoot fresh weight	<u>32</u>	1		<u>136(50)</u>	Adema and Henzen, 1989	3
		loam	7.5	0.8						<u>3.2</u>	1		<u>33(50)</u>		3
	<i>Lycopersicon esculentum</i>	humic sand	5.1	2.2									<u>16(50)</u>		3
		loam	7.5	0.8						<u>32</u>	1		<u>171(50)</u>		3
	<i>Avena sativa</i>	humic sand	5.1	2.2						<u>10</u>	1		<u>97(50)</u>		3
		loam	7.5	0.8						<u>10</u>	1		<u>159(50)</u>		3

Table 3.219 continued overleaf

Table 3.219 continued Toxicity to higher plants. All underlined data are selected to discuss the critical concentrations (Table 3.218). Bold data are used to estimate the HC<sub>5</sub> (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Plant	Medium	pH <sup>a</sup>	%OC <sup>b</sup>	% clay	Equil. time prior to plant growth (d)	Growing period (d)	Pot (P) or field (F) trial	Endpoint	NOEC (µg g <sup>-1</sup> )	Cat.*	LOEC (µg g <sup>-1</sup> ) (%effect)	EC <sub>25</sub> <sup>50</sup> (µg g <sup>-1</sup> ) (%effect)	References	R.I.
CdSO <sub>4</sub>	<i>Phaseolus vulgaris</i>	silt-loam soil amended with 1% clean sludge	7.5		0-28**		up to maturity	P	bean dry weight	<u>20</u>	3	<u>40 (25)</u>		Bingham et al., 1975	3
	<i>Glycine max</i>								bean dry weight	<u>2.5</u>	3	<u>5 (25)</u>			3
	<i>Triticum aestivum</i>								grain weight	<u>20</u>	3	<u>50 (25)</u>			3
	<i>Zea mays</i>								kernel weight	<u>10</u>	3	<u>18 (25)</u>			3
	<i>Lycopersicon esculentum</i>								ripe fruit weight	<u>80</u>		<u>16(25)</u>			3
	<i>Cucurbita pepo</i>								fruit weight	<u>80</u>	3	<u>160 (25)</u>			3
	<i>Brassica oleracea</i>								head weight	160(HT)	3				4
	<i>Lactuca sativa</i>								head weight	<u>5</u>	3	<u>13 (25)</u>			3
	<i>Lepidium sativum</i>								shoot weight	<u>5</u>	3	<u>8 (25)</u>			3
	<i>Spinacia oleracea</i>								shoot weight	1.25	3	<u>4 (25)</u>			4/3
	<i>Brassica rapa</i>								tuber weight	<u>10</u>	3	<u>28 (25)</u>			3
	<i>Raphanus sativus</i>								tuber weight	<u>40</u>	3	<u>96 (25)</u>			3
	<i>Daucus carota</i>								tuber weight	<u>10</u>		<u>20 (25)</u>			3
	<i>Oryza sativa</i>								grain weight	640(HT)					4
	CdSO <sub>4</sub>								<i>Lactuca sativa</i>	surface soils amended with 1% clean sludge	4.8	2.6			8.3
<i>Beta vulgaris</i>		shoot dry weight	<u>20</u>	3	<u>80(35)</u>	<u>110</u>									
<i>Lactuca sativa</i>		shoot dry weight	<u>40</u>	3	<u>160(22)</u>	<u>270</u>									
<i>Beta vulgaris</i>		shoot dry weight	<u>20</u>	3	<u>80(30)</u>	<u>135</u>									
<i>Lactuca sativa</i>		shoot dry weight	5.0	3.3	14.6	14		<u>10</u>	3		<u>40(35)</u>	<u>100</u>			
<i>Beta vulgaris</i>		shoot dry weight	<u>40</u>	3	<u>80(25)</u>	<u>110</u>									
<i>Lactuca sativa</i>		shoot dry weight	5.3	0.9	8.9	14		<u>20</u>	3		<u>80(25)</u>	<u>160</u>			
<i>Beta vulgaris</i>		shoot dry weight	<u>40</u>	3	<u>160(40)</u>	<u>185</u>									
<i>Lactuca sativa</i>		shoot dry weight	5.7	3.0	37.5	14		<u>20</u>	3		<u>80(35)</u>	<u>195</u>			
<i>Beta vulgaris</i>		shoot dry weight	<u>40</u>	3	<u>160(25)</u>	<u>320</u>									
<i>Lactuca sativa</i>		shoot dry weight	7.4	1.4	18.7	14		<u>40</u>	4		<u>10(25)</u>	<u>80</u>			
<i>Beta vulgaris</i>		shoot dry weight	<u>2.5</u>	4	<u>10(25)</u>	<u>80</u>									
<i>Lactuca sativa</i>		shoot dry weight	7.5	0.6	4.4	14		<u>20</u>	3		<u>80(25)</u>	<u>105</u>			
<i>Beta vulgaris</i>		shoot dry weight	<u>40</u>	3	<u>160(30)</u>	<u>18</u>									
<i>Lactuca sativa</i>		shoot dry weight	7.7	0.9	40.6	14		<u>5</u>	3		<u>10(30)</u>	<u>18</u>			
<i>Beta vulgaris</i>	shoot dry weight	<u>40</u>	3	<u>160(35)</u>	<u>195</u>										
<i>Lactuca sativa</i>	shoot dry weight	7.8	0.7	15.2	14		<u>10</u>	3	<u>40(38)</u>	<u>58</u>					
<i>Beta vulgaris</i>	shoot dry weight	<u>80</u>	3	<u>320</u>											

Table 3.219 continued overleaf

Table 3.219 continued Toxicity to higher plants. All underlined data are selected to discuss the critical concentrations (Table 3.218). Bold data are used to estimate the HC5 (Table 3.225). Data with reliability index 4 are given as supporting information but they are not used in the effects assessment

Test substance	Plant	Medium	pH <sup>a</sup>	%OC <sup>b</sup>	% clay	Equil. time prior to plant growth (d)	Growing period (d)	Pot (P) or field (F) trial	Endpoint	NOEC (µg g <sup>-1</sup> )	Cat.*	LOEC (µg g <sup>-1</sup> ) (%effect)	EC <sub>25</sub> 50 (µg g <sup>-1</sup> ) (%effect)	References	R.I.	
CdCl <sub>2</sub>	<i>Glycine max</i>	silty clay loam	6.7	2.5	<u>28-40**</u>		35	P	shoot dry weight				<u>10(50)</u>	Haghiri, 1973	3	
	35						P	shoot dry weight			<u>2.5(21)LT</u>	3				
	26						P	root dry weight			<u>2.5(36)LT</u>	3				
	37						P	shoot dry weight			<u>2.5(40)LT</u>	3				
	112						P	pepper dry weight	10HT			4				
	117						P	leaf dry weight	10HT			4				
Supporting data																
CdCl <sub>2</sub>	<i>Poa pratensis</i>	sandy	4.8	1.1	<u>0-15**</u>	7-10	42	P	shoot dry weight	10	3		30(90)	Miles and Parker, 1979	4	
	shoot dry weight										10(30)					
	shoot dry weight								10	3		30(63)				
	shoot dry weight										10(21)					
	shoot dry weight										10(79)					
	shoot dry weight								10	3		30(68)				
CdCl <sub>2</sub>	<i>Glycine max</i>	silt loam	4.5	<u>1-20**</u>	<u>0-28**</u>	4 drying and rewetting cycles	28	P	shoot dry weight	1	3		<u>10(52)</u>	Miller et al., 1976	4/3	
			6.1		<u>0-28**</u>						1	3	<u>10(33)</u>		<u>100(66)</u>	4/3
			7.0		<u>0-2**8</u>						1	3	<u>10(33)</u>		<u>100(50)</u>	4/3
		loamy sand	5.7		<u>0-28**</u>						0.5	4			<u>10(77)</u>	4/3
CdCl <sub>2</sub>	<i>Pinus strobus</i>	forest soil	4.8	1.1	<u>0-15**</u>	several weeks	120	P	shoot dry weight	15	1		100(57)	Kelly et al., 1979	4	
	<i>Pinus taeda</i>	0-14cm							shoot dry weight	15	3		100(55)			
	<i>Liriodendron tulipifera</i>	sandy							shoot dry weight	15	3		100(78)			
	<i>Betula alleghaniensis</i>								shoot dry weight	15	1		100(82)			
	<i>Prunus virginiana</i>								shoot dry weight	15	1		100(62)			
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Nicotinia tabacum</i>	sandy clay	5.3	0.9	9.4	21	60	P	total plant dry weight	5.4(HT)				Mench et al., 1989	4	
	<i>Nicotinia rustica</i>								total plant dry weight	5.4(HT)						
	<i>Zea mays</i>								total plant dry weight	0.4		5.4(21)				

- a) pH-water;  
 \$ pH-KCl;  
 b) OM = OC\*1.7;  
 LT Lowest Tested concentration;  
 HT Highest Tested concentration;  
 \* NOEC classification (see Section 3.2.1.2);  
 \*\* estimated OC - clay content.

### 3.2.3.5 Discussion

**Table 3.220** lists all selected toxicity data of soil microflora, soil fauna and higher plants. This data set contains all data that were underlined in **Tables 3.215, 3.217 and 3.219**. This selection is based on data quality, i.e. data with RI 1-3 only, and on an attempt to avoid overrepresentation of data from the same test or the same organism (see introduction of effects assessment section). The selected data are retrieved from 167 different tests. This selection of results is used in this section to identify the factors that affect Cd toxicity, i.e. type of organism and environmental conditions. The data with RI 1-3 are considered to be reliable (no critical information is missing).

Table 3.220 Summary of selected Cd toxicity data for the terrestrial environment ( $\mu\text{g g}^{-1}$ ). All data have  $\text{RI} \leq 3$  and a data selection was made to avoid overrepresentation of data from the same test or the same organism (see introduction of effects assessment section)

	NOEC				
	min	5 <sup>th</sup> perc.	median	max	n
microflora	3.6	3.6	50	3,000	21
higher plants	1.8	2.5	10	80	41
soil fauna	5	8.0	32	320	13
	LOEC				
	min	5 <sup>th</sup> perc.	median	max	n
microflora	7.1	7	100	8,000	21
higher plants	2.5	2.5	40	160	44
soil fauna	5	7.8	59	326	12
	E-LC <sub>x≥50</sub>				
	min	5 <sup>th</sup> perc.	median	max	n
microflora	7.1	57	283	5,264	20
higher plants	2.8	10	100	320	34
soil fauna	27	38	102	3,680	28

The median and 5<sup>th</sup> percentiles of the NOEC, LOEC and  $\text{EC}_{x \geq 50}$  values of tests with higher plants are lower than corresponding values for microflora and soil fauna. This may indicate that Cd more sensitively affects higher plants than microbial processes or soil fauna. It must be stressed, however, that the low Cd concentration range ( $1\text{-}10 \mu\text{g g}^{-1}$ ) has been tested in more detail with higher plants than with the other organisms.

### 3.2.3.6 The $\text{PNEC}_{\text{soil}}$

#### 3.2.3.6.1 Species sensitivity distributions at different levels of data quality

The  $\text{PNEC}_{\text{soil}}$  is calculated from the selected NOEC values. Different SSD's can be calculated for different selections of the data since the NOEC values have attached information such as data quality (the Reliability Index, RI) and properties of the test (species, soil characteristics and endpoint). The statistical properties of the NOEC data as a function of data quality is given in

**Table 3.221.** All data with RI=4 (unreliable) were not included because critical information of the test was lacking. The selected NOEC data are summarised in **Table 3.2.22**.

Table 3.221 The NOEC values ( $\mu\text{g g}^{-1}$ ) of the terrestrial compartment for various levels of reliability (RI, defined in the introduction of effects assessment section). The selected data are underlined in preceding Tables 3.215, 3.217 and 3.219

NOEC					
	Min	5 <sup>th</sup> perc. of the NOEC data	Median	Max	n
RI 1-3	1.8	3.0	20	3,000	75
RI 1-2	1.8	3.6	40	3,000	22
RI 1			22		1

To evaluate the toxicity data, the statistical extrapolation method is used (Aldenberg and Slob, 1993). The fifth percentile ( $\text{HC}_5$ ), with 50% confidence, of a species sensitivity distribution is calculated using the software package ETX 1.3a (RIVM, Bilthoven, The Netherlands). The  $\text{HC}_5$  is calculated for three different approaches of data selection. The first approach is by using all the data (see **Table 3.222**), without calculation of species geometric mean values. The second approach is by calculating ‘geometric mean’ NOEC values for each species, resulting in one NOEC per species (see **Table 3.223**). The third approach is by calculating ‘geometric mean’ NOEC’s on a case-by-case basis (see **Table 3.224**). Geometric mean NOEC’s are calculated for the same species and the same endpoint, tested in similar<sup>¶</sup> soils. This approach does not result in one NOEC per species. NOEC’s of soil microbial assays have never been averaged across soils because of the intrinsic variability of the microbial population between soils.

<sup>¶</sup> Soils are considered similar if their pH differs by maximum 0.2 units, and if the %OC and %clay difference is less than or equal to 1 and 8%.

Table 3.222 Selected data of effects of Cd in soil. Data derived from Tables 3.215, 3.217 and 3.219 within quality class RI 1-3

Organism	Phylum/class	Order	Family	Medium	pH <sup>a</sup>	Duration (d)	Endpoint	NOEC (µg g <sup>-1</sup> )	References	R.I.
native soil microflora				phaeosem	6.9	84(min.)	substrate induced respiration rate	3.6	Reber, 1989	2
				neutral sandy hortisol	7	84(min.)	substrate induced respiration rate	3.6		2
				acidic cambisol	5.6	84(min.)	substrate induced respiration rate	14.3		2
native soil microflora				grassland soil	7.4	33	nitrification: NO <sub>3</sub> <sup>-</sup> production rate -NH <sub>4</sub> <sup>+</sup> substrate	50	Dušek, 1995	2
							+NH <sub>4</sub> <sup>+</sup> substrate	10		
					7.6	33	nitrification: NO <sub>3</sub> <sup>-</sup> production rate -NH <sub>4</sub> <sup>+</sup> substrate	50		
							+NH <sub>4</sub> <sup>+</sup> substrate	100		
native soil microflora				loamy sand	5.8	1	24h respiration	14.6	Walter and Stadelman, 1979	2
native soil microflora				silty loam	7.7	1-2	glutamic acid decomposition time	55	Haanstra and Doelman, 1984	2
				clay	7.5	1-2	glutamic acid decomposition time	150		2
native soil microflora				sand	7	42-70	respiration	150	Doelman and Haanstra, 1984	3
				sandy loam	6	42-70	respiration	150		2
				silty loam	7.7	42-70	respiration	150		2
				clay	7.5	42-70	respiration	3,000		2
				peat	4.5	42-70	respiration	400		2
native soil microflora				sandy soil	4.9	56	respiration	5	Cornfield 1977	3
<i>Rhizobium leguminosorum</i> bv. <i>trifolii</i>				sandy loam	6.5	540	cell number (survival)	4	Chaudri et al., 1992	3
native soil microflora				brown earth loamy sand	4.6	45	cellulolytic activity: unplanted soil	10	Khan and Frankland, 1984	3
native soil microflora				organic soil	4.5	180	respiration rate	60	Frostegård et al., 1993	3
				sandy-loam	7.8	180	ATP content	112		3
native soil microflora				inceptisol	5.2	28	substrate induced respiration	50	Saviozzi et al., 1997	3
<i>Folsomia candida</i>	Arthropoda	Collembola	Isotomidae	OECD-soil	6.1 <sup>s</sup>	42	reproduction	22	van Gestel and Hensbergen, 1997	1
<i>Dendrobaena rubida</i>	Annelida	Haplotaxida	Lumbricidae	C-horizon of sandy coniferous forest soil+well decomposed cattle dung	4.5	110	cocoon production	10	Bengtsson et al., 1986	2
					6.5	270	hatching success	10		2

Table 3.222 continued overleaf

Table 3.222 continued Selected data of effects of Cd in soil. Data derived from Tables 3.215, 3.217 and 3.219 within quality class RI 1-3.

Organism	Phylum/class	Order	Family	Medium	pH <sup>a</sup>	Duration (d)	Endpoint	NOEC (µg g <sup>-1</sup> )	References	R.I.
<i>Lumbricus rubellus</i>	Annelida	Haplotaxida	Lumbricidae	sandy loam soil	7.3	42	weight	150	Ma, 1982	3
<i>Folsomia candida</i>	Arthropoda	Collembola	Isotomidae	OECD-soil	6.3 <sup>s</sup>	42	fresh weight at 25%MC	160	van Gestel and van Diepen, 1997	3
							35%MC	320		2
							45%MC	80		3
							55%MC	160		3
<i>Folsomia candida</i>	Arthropoda	Collembola	Isotomidae	OECD soil	6	35	number of offspring	148	Crommentuijn et al., 1993	2
<i>Eisenia fetida</i>	Annelida	Haplotaxida	Lumbricidae	OECD soil	6.3	56	cocoon production	5	Spurgeon et al., 1994	3
<i>Eisenia andrei</i>	Annelida	Haplotaxida	Lumbricidae	OECD soil	6.3	21	juvenile/adult ratio	10	Van Gestel et al., 1993	3
<i>Eisenia andrei</i>	Annelida	Haplotaxida	Lumbricidae	OECD soil	6.7	84	growth	18	Van Gestel et al., 1991	3
<i>Plectus acuminatus</i>	Nemata	Araeolaimida	Plectidae	OECD soil	5.5	21	juvenile/adult ratio	32	Kammenga et al., 1996	3
<i>Picea sitchensis</i>	Pinopsida	Pinales	Pinaceae	peaty gley	3.3	100	root length	1.8	Burton et al., 1984	2
<i>Triticum aestivum</i>	Lillopsida	Cyperales	Poaceae	phaeosem	6.9	28	shoot dry weight	7.1	Reber, 1989	2
				neutral sandy hortisol	7.0			29		2
<i>Glycine max</i>	Mafholiopsida	Fabales	Fabaceae	silt loam	7.9	28	shoot dry weight	10	Miller et al., 1976	3
					6.0			10		3
					6.5			5		3
				clay loam	6.1			10		3
<i>Raphanus sativus</i>	Mafholiopsida	Capparales	Brassicaceae	loamy sand	5.4	42	shoot dry weight	10	Khan and Frankland, 1983	3
<i>Lactuca saliva</i>	Mafholiopsida	Asterales	Asteraceae	soil	3.9	42	shoot dry weight	2	Jasiewicz, 1994	3
<i>Lactuca saliva</i>	Mafholiopsida	Asterales	Asteraceae	humic sand	5.1	14	shoot fresh weight	32	Adema and Henzen, 1989	3
				loam	7.5			3.2		3
<i>Lycopersicon esculentum</i>	Mafholiopsida	Solanales	Solanaceae	loam	7.5			32		3
<i>Avena sativa</i>	Lillopsida	Cyperales	Poaceae	humic sand	5.1			10		3
				loam	7.5			10	3	

Table 3.222 continued overleaf

Table 3.222 continued Selected data of effects of Cd in soil. Data derived from Tables 3.215, 3.217 and 3.219 within quality class RI 1-3

Organism	Phylum/class	Order	Family	Medium	pH <sup>a</sup>	Duration (d)	Endpoint	NOEC (µg g <sup>-1</sup> )	References	R.I.
<i>Phaseolus vulgaris</i>	Mafnoliopsida	Fabales	Fabaceae	silt-loam soil amended with 1% clean sludge	7.5	up to maturity	bean dry weight	20	Bingham et al., 1975	3
<i>Glycine max</i>	Mafnoliopsida	Fabales	Fabaceae				bean dry weight	2.5		3
<i>Triticum aestivum</i>	Lillopsida	Cyperales	Poaceae				grain weight	20		3
<i>Zea mays</i>	Lillopsida	Cyperales	Poaceae				kernel weight	10		3
<i>Lycopersicon esculentum</i>	Mafnoliopsida	Solanales	Solanaceae				ripe fruit weight	80		3
<i>Cucurbita pepo</i>										
<i>Lactuca sativa</i>	Mafnoliopsida	Violales	Cucurbitaceae				fruit weight	80		3
<i>Lepidium sativum</i>	Mafnoliopsida	Asterales	Asteraceae				head weight	5		3
<i>Brassica rapa</i>	Mafnoliopsida	Capparales	Brassicaceae				shoot weight	5		3
<i>Raphanus sativus</i>	Mafnoliopsida	Capparales	Brassicaceae				tuber weight	10		3
<i>Daucus carota</i>	Mafnoliopsida	Capparales	Brassicaceae				tuber weight	40		3
	Mafnoliopsida	Apiales	Apiaceae	tuber weight	10	3				
<i>Lactuca sativa</i>	Mafnoliopsida	Asterales	Asteraceae	surface soils amended with 1% clean sludge	4.8	63	shoot dry weight	40	Mahler et al., 1978	3
<i>Beta vulgaris</i>	Mafnoliopsida	Caryophyllales	Chenopodiaceae		shoot dry weight			20		
<i>Lactuca sativa</i>					5.0		40			
<i>Beta vulgaris</i>							20			
<i>Lactuca sativa</i>					5.3		10	3		
<i>Beta vulgaris</i>							40			
<i>Lactuca sativa</i>					5.7		20			
<i>Beta vulgaris</i>							40			
<i>Lactuca sativa</i>					7.4		20			
<i>Beta vulgaris</i>							40			
<i>Lactuca sativa</i>					7.5		2.5			
<i>Beta vulgaris</i>							20			
<i>Lactuca sativa</i>					7.7		5			
<i>Beta vulgaris</i>							40			
<i>Lactuca sativa</i>					7.8		10			
<i>Beta vulgaris</i>							80			

a pH-water;

\$ pH-KCl;

MC Moisture content.

Table 3.223 'One species, one NOEC': selected NOEC data of effects of Cd in soil on fauna and higher plants, and calculation of "geometric mean" NOEC's. Data derived from Table 3.222

Organism	Phylum/class	Order	Family	Endpoint	NOEC (µg g <sup>-1</sup> )	
<i>Dendrobaena rubida</i>	Annelida	Haplotaxida	Lumbricidae		10	geometric mean of 10 and 10
<i>Lumbricus rubellus</i>	Annelida	Haplotaxida	Lumbricidae		150	
<i>Folsomia candida</i>	Arthropoda	Collembola	Isotomidae		113	geometric mean of 22, 80, 148, 160, 160, 320
<i>Eisenia fetida</i>	Annelida	Haplotaxida	Lumbricidae		5	
<i>Eisenia andrei</i>	Annelida	Haplotaxida	Lumbricidae		13	geometric mean of 10 and 18
<i>Plectus acuminatus</i>	Nemata	Araeolaimida	Plectidae		32	
<i>Avena sativa</i>	<i>Avena sativa</i>	Cyperales	Poaceae		10	geometric mean of 10 and 10
<i>Picea sitchensis</i>	Pinopsida	Pinales	Pinaceae		1.8	
<i>Triticum aestivum</i>	Lillopsida	Cyperales	Poaceae		16	geometric mean of 7.1, 20, 29
<i>Glycine max</i>	Mafnolopsida	Fabales	Fabaceae		7	geometric mean of 2.5, 5, 10, 10, 10
<i>Raphanus sativus</i>	Mafnolopsida	Capparales	Brassicaceae		20	geometric mean of 10 and 40
<i>Lactuca sativa</i>	Mafnolopsida	Asterales	Asteraceae		10	geometric mean of 2, 2.5, 3.2, 5, 5, 10, 10, 20, 20, 32, 40, 40
<i>Lycopersicon esculentum</i>	Mafnolopsida	Solanales	Solanaceae		51	geometric mean of 32 and 80
<i>Phaseolus vulgaris</i>	Mafnolopsida	Fabales	Fabaceae		20	
<i>Zea mays</i>	Lillopsida	Cyperales	Poaceae		10	
<i>Cucurbita pepo</i>	Mafnolopsida	Violales	Cucurbitaceae		80	
<i>Lepidium sativum</i>	Mafnolopsida	Capparales	Brassicaceae		5	
<i>Brassica rapa</i>	Mafnolopsida	Capparales	Brassicaceae		10	
<i>Daucus carota</i>	Mafnolopsida	Apiales	Apiaceae		10	
<i>Beta vulgaris</i>	Mafnolopsida	Caryophyllales	Chenopodiaceae		34	geometric mean of 20, 20, 20, 40, 40, 40, 40, 80

Table 3.224 'Case-by-case selection': selected NOEC data of effects of Cd in soil on fauna and higher plants, and case-by-case calculation of "geometric mean" NOEC's. Bold, underlined data are selected for the HC<sub>5</sub> calculation. Data derived from Table 3.222

Organism	Medium	pH	%OC	%clay	Endpoint	NOEC (µg g <sup>-1</sup> )	
<i>Dendrobaena rubida</i>	C-horizon of sandy coniferous forest soil+well decomposed cattle dung	4.5	4.5-6.9		cocoon production	<u>10</u>	no geometric mean: different endpoints
		6.5	4.5-6.9		hatching success	<u>10</u>	
<i>Lumbricus rubellus</i>	sandy loam soil	7.3	4.7	17	weight	<u>150</u>	
<i>Folsomia candida</i>	OECD soil	6	5.9	20	reproduction	148	geometric mean: similar soil, same endpoint, same species

Table 3.224 continued overleaf

Table 3.224 continued 'Case-by-case selection': selected NOEC data of effects of Cd in soil on fauna and higher plants, and case-by-case calculation of "geometric mean" NOEC's. Bold, underlined data are selected for the HC<sub>5</sub> calculation. Data derived from Table 3.222

Organism	Medium	pH	%OC	%clay	Endpoint	NOEC (µg g <sup>-1</sup> )	
<i>Folsomia candida</i>	OECD-soil	6.1	5.9	20	reproduction	22	geometric mean = <u>57</u>
<i>Folsomia candida</i>	OECD-soil	6.3	5.9	20	fresh weight	160	geometric mean: similar soil, same endpoint, same species geometric mean = <u>160</u>
					fresh weight	320	
					fresh weight	80	
					fresh weight	160	
<i>Eisenia fetida</i>	OECD soil	6.3	5.9	20	cocoon production	<u>5</u>	
<i>Eisenia andrei</i>	OECD soil	6.3	5.9	20	juvenile/adult ratio	<u>10</u>	no geometric mean: different endpoints
<i>Eisenia andrei</i>	OECD soil	6.7	5.9	20	growth	<u>18</u>	
<i>Plectus acuminatus</i>	OECD soil	5.5	5.9	20	juvenile/adult ratio	<u>32</u>	
<i>Picea sitchensis</i>	peaty gley	3.3	45		root length	<u>1.8</u>	
<i>Triticum aestivum</i>	phaeosem	6.9	1.3	21	shoot dry weight	<u>7.1</u>	no geometric mean: different endpoints, different soils
<i>Triticum aestivum</i>	neutral sandy hortisol	7.0	1.4	3	shoot dry weight	<u>29</u>	
<i>Triticum aestivum</i>	silt-loam soil amended with 1% clean sludge	7.5			grain weight	<u>20</u>	
<i>Glycine max</i>	silt loam	7.9			shoot dry weight	<u>10</u>	no geometric mean: different endpoints, different soils
<i>Glycine max</i>	silt loam	6.0			shoot dry weight	<u>10</u>	
<i>Glycine max</i>	silt loam	6.5			shoot dry weight	<u>5</u>	
<i>Glycine max</i>	clay loam	6.1			shoot dry weight	<u>10</u>	
<i>Glycine max</i>	silt-loam soil amended with 1% clean sludge	7.5			bean dry weight	<u>2.5</u>	
<i>Raphanus sativus</i>	loamy sand	5.4			shoot dry weight	<u>10</u>	no geometric mean: different soils
<i>Raphanus sativus</i>	silt-loam soil amended with 1% clean sludge	7.5			tuber weight	<u>40</u>	
<i>Lycopersicon esculentum</i>	Loam	7.5			shoot fresh weight	<u>32</u>	no geometric mean: different soils
<i>Lycopersicon esculentum</i>	silt-loam soil amended with 1% clean sludge	7.5			ripe fruit weight	<u>80</u>	
<i>Avena sativa</i>	humic sand	5.1			shoot fresh weight	<u>10</u>	no geometric mean: different soils
<i>Avena sativa</i>	loam	7.5				<u>10</u>	
<i>Phaseolus vulgaris</i>	silt-loam soil amended with 1% clean sludge	7.5			bean dry weight	<u>20</u>	
<i>Zea mays</i>					kernel weight	<u>10</u>	
<i>Cucurbita pepo</i>					fruit weight	<u>80</u>	
<i>Lepidium sativum</i>					shoot weight	<u>5</u>	
<i>Brassica rapa</i>					tuber weight	<u>10</u>	
<i>Daucus carota</i>					tuber weight	<u>10</u>	

Table 3.224 continued overleaf

Table 3.224 continued 'Case-by-case selection': selected NOEC data of effects of Cd in soil on fauna and higher plants, and case-by-case calculation of "geometric mean" NOEC's. Bold, underlined data are selected for the HC<sub>5</sub> calculation. Data derived from Table 3.222

Organism	Medium	pH	%OC	%clay	Endpoint	NOEC (µg g <sup>-1</sup> )	
<i>Lactuca sativa</i>	humic sand	5.1	2.2		shoot fresh weight	<u>32</u>	no geometric mean: different soils
	loam	7.5	0.8		shoot fresh weight	<u>3.2</u>	
<i>Lactuca sativa</i>	Soil	3.9	1.2	8	shoot dry weight	<u>2</u>	
<i>Lactuca sativa</i>	surface soils amended with 1% clean sludge	4.8	2.6	8.3	shoot dry weight	40	geometric mean: same endpoint, same species, similar soils
<i>Lactuca sativa</i>		5.0	3.3	14.6	shoot dry weight	40	geometric mean = <u>40</u>
<i>Lactuca sativa</i>	surface soils amended with 1% clean sludge	5.3	0.9	8.9	shoot dry weight	<u>10</u>	
<i>Lactuca sativa</i>		5.7	3.0	37.5	shoot dry weight	<u>20</u>	
<i>Lactuca sativa</i>	surface soils amended with 1% clean sludge	7.4	1.4	18.7	shoot dry weight	20	geometric mean: same endpoint, same species, similar soils
<i>Lactuca sativa</i>	silt-loam soil amended with 1% clean sludge	7.5		14	shoot weight	5	geometric mean = <u>10</u>
<i>Lactuca sativa</i>	surface soils amended with 1% clean sludge	7.5	0.6	4.4	shoot dry weight	<u>2.5</u>	no geometric mean: different soils
<i>Lactuca sativa</i>	surface soils amended with 1% clean sludge	7.7	0.9	40.6	shoot dry weight	<u>5</u>	
<i>Lactuca sativa</i>		7.8	0.7	15.2	shoot dry weight	<u>10</u>	
<i>Beta vulgaris</i>	surface soils amended with 1% clean sludge	4.8	2.6	8.3	shoot dry weight	20	geometric mean: same endpoint, same species, similar soils
<i>Beta vulgaris</i>		5.0	3.3	14.6	shoot dry weight	20	geometric mean = <u>20</u>
<i>Beta vulgaris</i>	surface soils amended with 1% clean sludge	4.8	2.6	8.3	shoot dry weight	<u>20</u>	no geometric mean: different soils
<i>Beta vulgaris</i>		5.0	3.3	14.6	shoot dry weight	<u>20</u>	
<i>Beta vulgaris</i>		5.3	0.9	8.9	shoot dry weight	<u>40</u>	
<i>Beta vulgaris</i>		5.7	3.0	37.5	shoot dry weight	<u>40</u>	
<i>Beta vulgaris</i>		7.4	1.4	18.7	shoot dry weight	<u>40</u>	
<i>Beta vulgaris</i>		7.5	0.6	4.4	shoot dry weight	<u>20</u>	
<i>Beta vulgaris</i>		7.7	0.9	40.6	shoot dry weight	<u>40</u>	
<i>Beta vulgaris</i>		7.8	0.7	15.2	shoot dry weight	<u>80</u>	

There are enough data from all three trophic levels to calculate the  $PNEC_{soil}$  by the assessment factor method (AFM) using the lowest assessment factor 10 (TGD, 1996, p. 339). The lowest NOEC value with a  $RI \leq 3$  is  $1.8 \mu\text{g g}^{-1}$ . This yields a  $PNEC_{soil} = 1.8/10 \mu\text{g g}^{-1}$  or  $0.18 \mu\text{g g}^{-1}$ . That value is within the range of Cd background concentrations in soil. Rather than making a risk assessment based on one single NOEC value, it is possible to use the statistical extrapolation method (TGD, 1996, p. 469) if enough NOEC data are available. This condition is certainly met in the case of Cd and is preferred because it is based on information from a wide range of species and soil microbial processes. The need for additional assessment factors in that assessment will be discussed in the next section.

The statistical extrapolation method (SEM) was applied to the NOEC data (some geometric mean values, see above), calculating the median 5<sup>th</sup> percentile ( $HC_5$ ) of both the log-logistic and the log-normal distribution with the software package ETX 1.3a (RIVM, Bilthoven, The Netherlands) (see **Table 3.225**).

Table 3.225 Calculation of critical concentrations ( $\mu\text{g g}^{-1}$ ) using the assessment factor method (AFM) or the statistical extrapolation method (SEM; Aldenberg and Slob, 1993) for Various levels of data quality

Data quality group	AFM: NOEC/AF	
	$\mu\text{g g}^{-1}$	
	AF = 10	
RI 1-2: whole data set (n=22)	0.18	
RI 1-3: whole data set (n=75)	0.18	
RI 1-3: microflora (n=21)	0.36	
RI 1-3: plants+invertebrates (n=54)	0.18	
	SEM: $HC_5$ at 50% (and 95%) confidence	
	$\mu\text{g g}^{-1}$	
	Logistic distribution	Normal distribution
RI 1-2: whole data set (n=22)	1.8 (0.5)	1.9 (0.5)
RI 1-3: whole data set (n=75)	2.3 (1.3)	2.2 (1.4)
<i>RI 1-3 microflora</i>		
Selection of NOEC's, RI 1-3 (Table 3.222); n = 21	2.3 (0.6)	2.3 (0.7)
<i>RI 1-3 higher plants + invertebrates</i>		
Selection of all NOEC's, RI 1-3 (Table 3.222); n = 54	2.5 (1.5)	2.5 (1.5)
One species, one value: geometric mean NOEC's (Table 3.222); n = 20	2.5 (1.0)	2.6 (1.1)
Case-by-case geometric mean calculation (Table 3.222); n = 49	2.7 (1.6)	2.6 (1.7)

Selection on data quality slightly affects the value of  $HC_5$  between groups RI 1-3 and RI 1-2 (see **Table 3.225**; whole data set), illustrating that the frequency distributions of both data sets overlap ( $2.3$  versus  $1.8 \mu\text{g Cd g}^{-1}$ ). The median NOEC is distinctly higher for RI 1-2 than for RI 1-3 (see **Table 3.221**), but the higher variance in the former data set results in a larger difference between the 5th percentile and the median. Many plant data are excluded from the group RI 1-2 (only 3 NOEC values of plants in that group) whereas plants seem to be the most sensitive group (see Section 3.2.3.5). Several Cd toxicity tests on higher plants are selected from older source

documents (1970-1980) and the information on the test, such as statistical treatment, is often not complete in these documents. Statistical data analysis is a prerequisite for a test to enter class RI 2.

The HC<sub>5</sub> value of tests with RI 1-2 is based on 14 NOEC's from 3 different soil microbial processes, 5 NOEC's from 2 different invertebrate families (2 species), and 3 NOEC's from 2 different plant families (2 species; **Table 3.226**). The RI 1-3 database consists of 24 NOEC's from 7 soil microbial processes, 12 NOEC's from 3 invertebrate families (5 species), and 41 NOEC's from 9 plant families (16 species). The data with RI 1-2 have a higher quality label, but are derived from a limited number of species (only 4 different species and 3 different soil microbial processes). The majority of data within group RI 3 lack statistical data analysis to classify them as RI 2 (details not shown). In consequence, the choice for which data group is based on a preference for either a large diversity in species or for data supplied with statistical analysis of the test result (class 1 and 2 NOEC's). The underlying assumption in the statistical extrapolation technique is that the logistic frequency distribution reflects species sensitivity distribution. Since the class RI 1-2 has limited species, it is proposed to use the class RI 1-3 as the basis for deriving the PNEC.

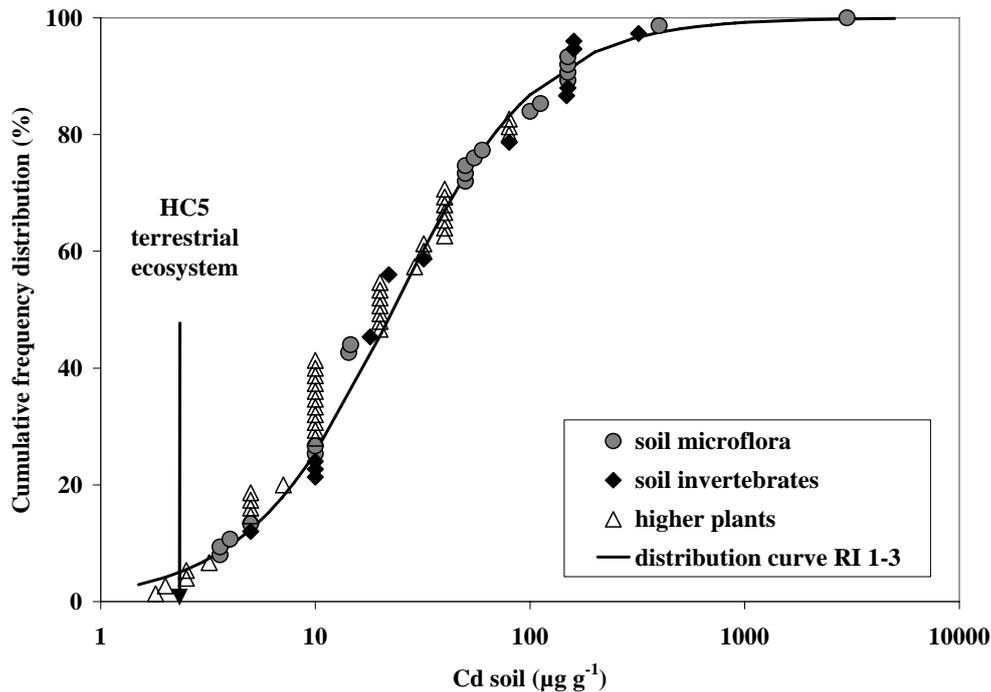
The terrestrial data set is split in two groups: microbial processes and soil invertebrates + higher plants. The endpoints for microbial processes are relevant at the ecosystem functioning level, while the endpoints for soil fauna and plants are relevant at the species level. The principle of splitting the terrestrial data in two groups is open to criticism: there is no scientific argument (e.g. field validation) for either option. For both groups, the choice of SSD does not affect the HC<sub>5</sub>, nor does the choice of data selection (geometric mean calculation or not) for soil invertebrates and higher plants. However, the statistical uncertainty surrounding the HC<sub>5</sub> is smaller using the combined dataset. In contrast to the procedure used to derive a PNEC<sub>water</sub>, the lowest NOEC selection approach was not performed because such a selection would not yield a representative data set for the terrestrial ecosystem (e.g. all clay soils would be excluded). The HC<sub>5</sub> for the microflora furthermore equals the HC<sub>5</sub> for soil fauna and plants.

Concluding we propose to use the HC<sub>5</sub> based on all NOEC's of the microflora data set, which is the lowest of all HC<sub>5</sub> values is, i.e.

$$HC_5 = 2.3 \mu\text{g Cd/g}$$

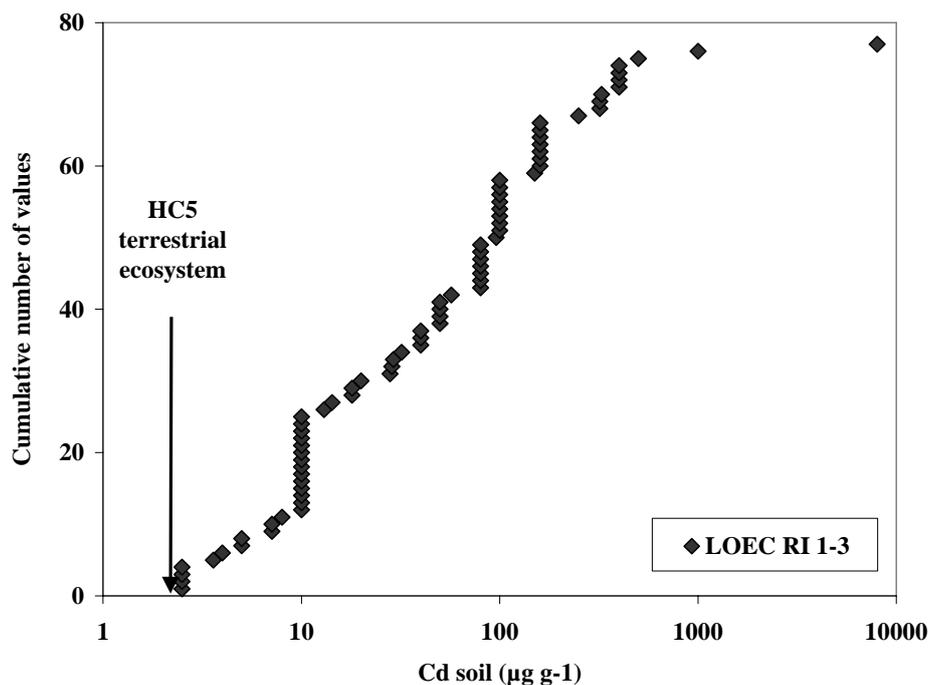
The frequency distribution and HC<sub>5</sub> are illustrated in **Figure 3.17**.

Figure 3.17 The cumulative frequency distribution of the selected NOEC values of Cd toxicity tests of soil microflora, invertebrates and higher plants. Observed data and logistic distribution curve for the whole RI 1-3 data set fitted on the data



The HC<sub>5</sub> for the terrestrial ecosystem, based on all NOEC's of the microflora group and on a logistic distribution, is 2.3  $\mu\text{g g}^{-1}$ . The whole data set of terrestrial tests (including tests with RI = 4) contains no observations where toxicity was found below 2.3  $\mu\text{g g}^{-1}$  (see **Figure 3.18**). The lowest toxicity data (2.5  $\mu\text{g Cd/g}$ ; 4 values) are classified as RI = 3 and were found on plant growth.

Figure 3.18 The cumulative number of LOEC values of selected tests of data quality group RI 1-3



### 3.2.3.6.2 Calculation of the generic PNEC<sub>soil</sub>

The EU workshop on statistical extrapolation (17-18 January, 2001) proposed that the statistical extrapolation technique can be applied to derive a PNEC, but that an additional assessment factor should be applied to the HC<sub>5</sub>, which is estimated as a median 5<sup>th</sup> percentile of the NOEC distribution. This assessment factor may be chosen between 5 and 1 and should remove uncertainty in extrapolating the PNEC to the field situation. The uncertainty is related to the limited number of taxa included in the species sensitivity distribution, the unknown long term effects in the field and the possibility that mixed pollution renders cadmium more readily toxic.

#### *Species diversity*

The HC<sub>5</sub> value of the terrestrial ecosystem is derived from 5 different microbial processes. This HC<sub>5</sub> almost equals the HC<sub>5</sub> values based on the fauna and plant data (49 different tests) and the HC<sub>5</sub> of the whole RI 1-3 data set (derived from 65 different tests with 20 different species and 5 different soil microbial processes). The plants belong to 9 different families and 9 different orders and the invertebrates belong to 3 different families and 3 different orders. This diversity certainly meets the recommendation of the EU workshop (17-18 January, 2001) on statistical extrapolation that the data set should contain at least 8 different taxa for applying the statistical extrapolation technique. The entire database does, however, not contain community system data and is biased towards agricultural species.

Along the same lines, it can be argued that the data should be based on a diversity of soil properties. The tests on which the HC<sub>5</sub> value is based are performed in soils with pH 3.1-7.9% carbon 0.6-47 and % clay 2-70. This range in soil properties covers most of the European topsoils.

#### *Lab to field extrapolation*

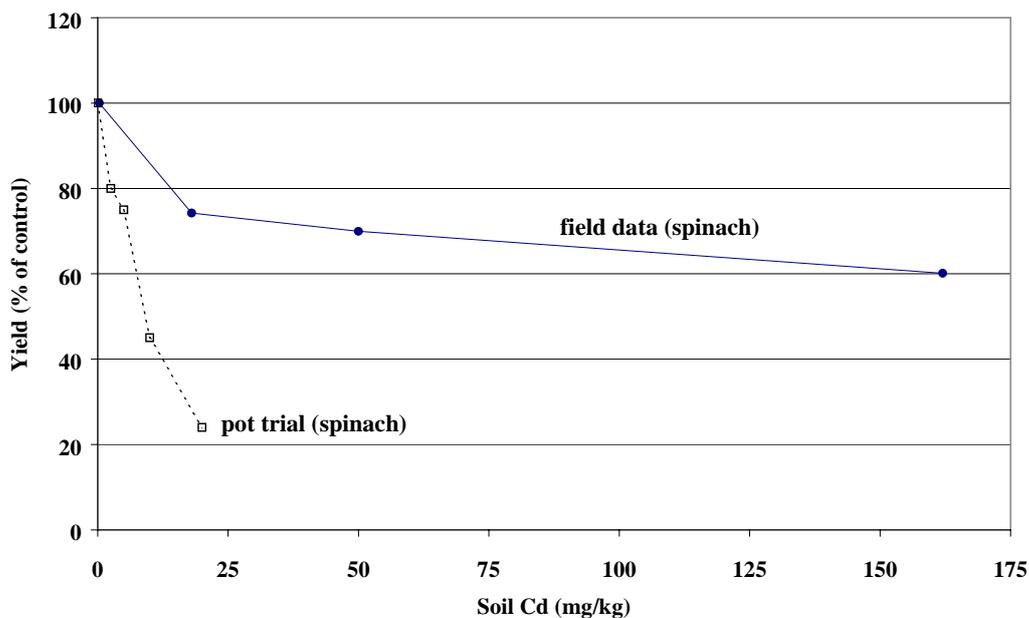
There are only limited field data that allow deriving threshold concentrations of Cd in soil at the field scale. Cadmium is usually associated with other metals in the field and these other metals are more readily toxic than Cd itself. In most cases, Cd pollution is associated with Zn pollution. Effects of smelter contamination on plants or on earthworms are often attributed to Zn and not to Cd (Tiller, 1989; Spurgeon and Hopkin, 1995).

Few toxic effects of Cd-salts were found in the field observations (Sajwan et al., 1995, Kádár, 1995). In the former test, the top 7.5 cm of loamy sand microplots were contaminated with Cd up to 6.7 µg Cd/g (measured concentration) along with small doses of Ni (11 µg g<sup>-1</sup>) and Se (0.2 µg g<sup>-1</sup>). There were no growth effects observed in bush beans compared with the nil treatment where soil Cd was at 0.6 µg Cd/g (Sajwan et al., 1995).

A field trial on the effects of metal salts was started in Nagyhörösök (Hungary) in 1991 by Dr. I. Kádár. Cadmium (as CdSO<sub>4</sub>) was applied to the soil at 4 rates above control with threefold replication (see **Table 3.226**). The soil is a calcareous chernozem, characterised by a high cation exchange capacity, high pH and high base saturation. More details on this field trial are described elsewhere (Kádár, 1995; Kádár et al., 1998). This type of soil is certainly *not* a worst case scenario for cationic metals, which are strongly sorbed in that type of soil. No toxic effect of Cd on plant growth was detected up to the highest rate during the first 4 years. Toxic effects were very pronounced in 1995 and 1996 in spinach and red beet, both plants belonging to the same family, and, to a lesser extent, in 1997 in wheat grain. Pot trial studies confirm that spinach is far more sensitive to Cd than corn, wheat or carrots (Bingham et al., 1975, see also **Table 3.219**). The NOEC's for spinach and red beet in the field were both 50 µg Cd/g, i.e. well

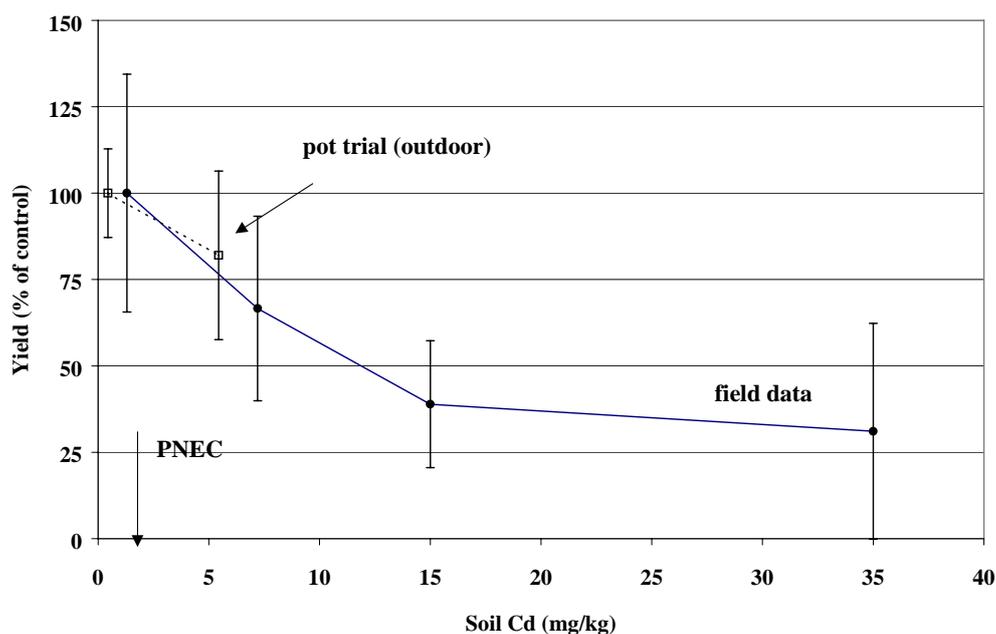
above the  $HC_5$  as derived from the laboratory tests. The average yield data (see **Table 3.226**) show that the average plant yield is already considerably reduced at this NOEC, but that this reduction is not large enough to yield a statistically significant effect. The intrinsically higher variability in field data biases the comparison of field NOEC's with laboratory NOEC's. Effect concentrations may, therefore, be a better basis for a lab-field comparison for plant growth. The response of spinach growth to Cd shows that yield is reduced with about 25% at 18  $\mu\text{g Cd/g}$  (see **Table 3.226**). The  $EC_{25}$  of spinach grown in a pot trial was 4  $\mu\text{g Cd/g}$ , i.e. more than 4-fold lower in than in the field (Bingham et al., 1975; see also **Table 3.219** and **Figure 3.19**). The soil in that pot trial (pH 7.5) has a similar pH as in the field trial (7.3). No pot trial studies were found with red beet. The Bingham et al. study also reports the  $EC_{25}$  of Cd on wheat grain as 50  $\mu\text{g Cd/g}$  (same soil as with spinach) whereas the highest Cd rate in the field did not even result in 25% reduction in wheat grain yield. The highest Cd rate in the field was 810 kg Cd/ha, equivalent to 456  $\mu\text{g Cd/g}$  EDTA extractable Cd (Kádár, 1995). The total Cd in that soil is most likely similar to EDTA extractable Cd. Concluding, the phytotoxic effect of Cd in the field trials in the Hungarian calcareous chernozem are found at higher concentration than in the pot trials of Bingham et al. (1975) with a calcareous silt loam.

Figure 3.19 Yield of spinach: field data (Hungary; Kádár et al., 1998) and pot trial data (Bingham et al., 1975). The soil pH was 7.3 in the field experiment and 7.5 in the pot trial



Another long-term field trial was started in 1988-1990 in Bordeaux (France) by Dr. M. Mench of the INRA Bordeaux. By 1990, there were 3 nominal Cd rates above control: 10, 20 and 40  $\mu\text{g Cd/g}$ . The field has plots with pH 5.3-5.6 and plots with pH 6.7-7.0. The corn shoot yield data of 2000 are given in **Table 3.226**. Cadmium was more toxic in the most acid plots and had no significant effect on corn shoot yield up to 7-8  $\mu\text{g Cd/g}$ . The LOEC's at 15  $\mu\text{g Cd/g}$  are associated with a 50% (high pH) and 61% (low pH) lower shoot yield than the control. One pot trial with corn is reported in a similar soil as in the acid plots. Leaf and stem dry weight was reduced by 18% at 5.4  $\mu\text{g Cd/g}$ , the highest concentrations tested (Mench et al., 1989; **Figure 3.20**). The field data suggest a similar inhibition of growth of corn by Cd as in the pot trials if the field data between control and the first Cd rate are interpolated.

Figure 3.20 Yield of corn: field data and pot trial data (pot trials with 17 kg soil; Mench et al., 1989)



Concluding, the few field data yield NOEC's that are well above the HC<sub>5</sub> of 2.3 µg Cd/g. Toxicity of Cd on plants grown in pot trials is equally or more pronounced than in the field. There is currently no indication of higher toxicity of Cd salts in the field than in the laboratory.

#### *Goodness-of-fit*

The goodness-of-fit of the SSD's is tested with the Kolmogorov-Smirnov test. The log-logistic and the log-normal distribution are accepted at the 1-10% significance levels when applied on the microbial data set on which the HC<sub>5</sub> is based. The lower 95% confidence level is 0.6 (log-logistic distribution) and 0.7 (log-normal distribution), which is considerably lower than the HC<sub>5</sub>. The lower 95% confidence level in the combined dataset is 1.5 showing that the statistical uncertainty strongly reduces when combining all terrestrial data.

All these arguments given above suggest that an assessment factor ranging from 1 to 2 might be appropriate to derive a PNEC<sub>soil</sub> from the HC<sub>5</sub>. Therefore we propose

HC <sub>5</sub>	Assessment factor	PNEC <sub>soil</sub>
2.3 µg g <sup>-1</sup>	1	2.3 µg g <sup>-1</sup>
2.3 µg g <sup>-1</sup>	2	1.15 µg g <sup>-1</sup>

It must be recalled that there is no single test in the entire database (including tests with RI 4) at which a toxic effect of Cd was found at or below the PNEC<sub>soil</sub> = 2.3 µg Cd /g. Furthermore, the PNEC<sub>soil</sub> based on secondary poisoning is below 1.15 µg Cd/g (see Section 3.2.7.3), and therefore a single value for the PNEC<sub>soil</sub> based on microbial processes is of no importance on the overall outcome of the risk characterisation for the soil compartment.

Table 3.226 Phytotoxicity of Cd salts in field trials

Test substance	Soil properties	Results*						
CdSO <sub>4</sub>	Nagyhörcsök (Hungary): calcareous Chernozem; pH (CaCl <sub>2</sub> ) = 7.3; 3% org. matter; 5%CaCO <sub>3</sub> ; CEC 22 cmol <sub>e</sub> /kg	1991: 1 single Cd application (kg Cd/ha)	0	30	90	270	810	Kádár et al., 1998
		1994: soil Cd (µg)	0.3	18	50	162	not meas.	
		yield (tonnes FW/ha)						
		1991: corn		n.s.	n.s.	n.s.	n.s.	
		1992: carrot		n.s.	n.s.	n.s.	n.s.	
		1993: potato		n.s.	n.s.	n.s.	n.s.	
		1994: pea		n.s.	n.s.	n.s.	n.s.	
		1995: red beet	14.6 <sup>a</sup>	7.4 <sup>a</sup>	9.5 <sup>a</sup>	3.7 <sup>b</sup>	0.7 <sup>b</sup>	
		1996: spinach	16.3 <sup>a</sup>	12.1 <sup>a</sup>	11.4 <sup>a</sup>	9.8 <sup>b</sup>	3.7 <sup>b</sup>	
		1997: wheat grain	6.8 <sup>a</sup>	n.d.	7.3 <sup>a</sup>	6.4 <sup>a</sup>	5.4 <sup>a</sup>	
Cd(NO <sub>3</sub> ) <sub>2</sub>	Borde aux (France) pH (CaCl <sub>2</sub> ) = 5.3-5.6; CEC 10 cmol <sub>e</sub> /kg	1988-1990 Cd applications						Mench, pers. com. (2000)
		2000:soil Cd (mg Cd/kg)	1.3	7.2	15	35		
		2000: corn (g FW/plant)	59.9 <sup>a</sup>	39.9 <sup>a</sup>	23.3 <sup>b</sup>	18.6 <sup>b</sup>		
Cd(NO <sub>3</sub> ) <sub>2</sub>	Bordeaux (France) pH (CaCl <sub>2</sub> ) = 6.7-7.0; CEC 15 cmol <sub>e</sub> /kg	1988-1990 Cd applications						Mench, pers. com. (2000)
		2000:soil Cd (mg Cd/kg)	1.2	8.3	15	32		
		2000: corn (g FW/plant)	35.6 <sup>a</sup>	44.0 <sup>a</sup>	17.9 <sup>b</sup>	16.4 <sup>b</sup>		

\* Values in the same row with the same superscript do not differ significantly.

n.s. Not specified

n.d. Not determined

### 3.2.3.6.3 PNEC<sub>soil</sub> in relation to soil properties

Toxicity is well known to vary with soil properties, which justifies deriving PNEC values per soil type. As an example, a very low EC<sub>x≥50</sub> value (2.8 µg g<sup>-1</sup>) was found for root growth in a forest soil with pH 3.3 (Burton et al., 1984). Clearly, such soil should not be compared with arable soils at higher pH values for which EC<sub>x≥50</sub> values are almost one order of magnitude higher. As discussed above, no empirical equation has been developed for Cd to normalise toxicity to a standard soil. In this section, an attempt will be made to calculate the PNEC for different soil classes. All selected NOEC data with RI ≤ 3 are used in this calculation. The number of classes is restricted to maintain a sufficient number of degrees of freedom. Two selection methods are tested: one is by pH and one is by soil texture.

The pH of the soil dominates the solid-liquid distribution of Cd in soil (see **Table 3.10**). It is often assumed that the metal concentration in soil solution represents the toxic dose for the ecosystem and, therefore, a correlation between metal toxicity and pH is to be expected. At higher pH, metal solubility is low and the HC<sub>5</sub> could be higher than at low pH where metals are more soluble. A significant correlation between the log NOEC values and soil pH was, however, not found ( $P > 0.05$ ) for the data collated here (see **Figure 3.21**). A positive trend between log NOEC and soil pH emerges up to about pH 6 beyond which there seems to be no further trend.

The data were classified in two groups, data obtained at soil pH lower or equal to 6.0 and data obtained at soil pH above 6.0. Statistical properties of the data are given in **Table 3.227**. The HC<sub>5</sub> was calculated by statistical extrapolation of the log logistic distribution of the NOEC values (ETX 1.3a, RIVM, Bilthoven, The Netherlands). The HC<sub>5</sub> value is lower in the group pH > 6.0 (see **Table 3.227**). The mean log NOEC value is identical for both groups but the standard deviation of the log NOEC values is largest in the group pH > 6.0. Therefore, the extrapolated HC<sub>5</sub> value is smaller for the group pH > 6.0.

No correlation was found between log NOEC values and % clay in soil (details not shown). The NOEC values found in soils with less than 10% clay are somewhat lower than in soils with more than 10% clay. The lowest HC<sub>5</sub> value is found in soils with less than 10% clay. The median log NOEC is also lowest in this group, while the standard deviation is identical in both groups.

Figure 3.21 Semi log plot of the selected Cd NOEC values in soil (n=72) as a function of soil pH

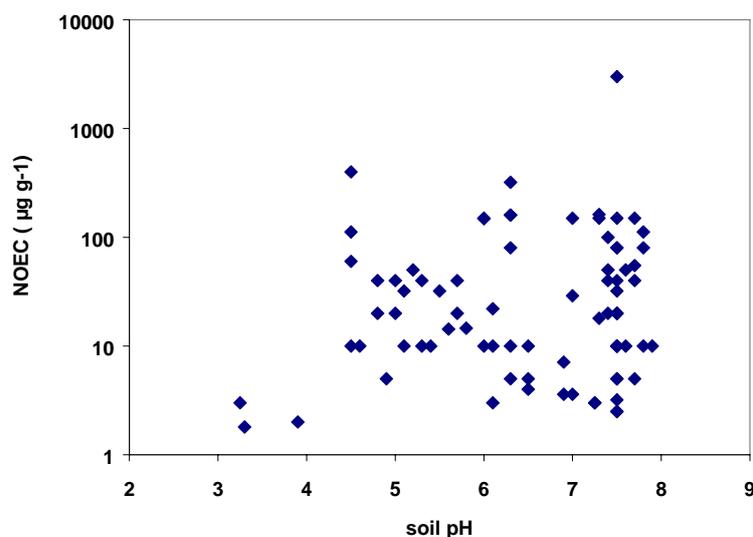


Table 3.227 The  $PNEC_{soil}$  ( $\mu\text{g Cd/g}$ ) calculated as the  $HC_5$  value using the statistical extrapolation method (Aldenberg and Slob, 1993) on the NOEC data sorted by soil characteristics. The NOEC data were sorted either by soil texture or by soil pH

	n	Min. NOEC	Median NOEC	$HC_5$ ( $\mu\text{g Cd/g}$ )
classified by pH				
pH $\leq$ 6.0	25	1.8	20	2.7
pH $>$ 6.0	50	2.5	20	2.0
classified by %clay				
% clay $\leq$ 10	18	2.0	17	1.5
% clay $>$ 10	48	1.8	20	2.4

It is striking that the  $HC_5$  values vary only slightly with soil properties whereas higher variability in toxicity between soil types is often found in comparative experiments (see e.g. plant data of Miller et al., 1976). That variability is reduced here for several reasons. Firstly, the effect of soil factors on the NOEC data is obscured by all other sources of variance, e.g. variance in sensitivity among species and endpoints. Secondly, a NOEC value relates to the *lack* of toxicity. Soil properties may, for example, have a more pronounced effect on the concentrations at which toxicity is found (LOEC and  $EC_{x \geq 50}$  values).

An attempt was made to unravel the effect of soil type on Cd toxicity using the effect data (LOEC and  $EC_{x \geq 50}$  values). The % effect was related to neither total soil Cd nor to soluble Cd concentrations. The soluble Cd concentrations are calculated from total concentrations based on a model relating soil properties with the solid-liquid distribution coefficient  $K_D$ . The model proposed by Römken and Salomons, 1998 was used (see **Table 3.10**). This model estimates the  $K_D$  based on soil pH only. Few LOEC data were found for which the % effect was not clear from the data. The % inhibition for these data was assumed to be 30%.

The correlation coefficient between % inhibition and soluble Cd concentrations ( $R^2 = 0.02$ ) is similar as between % inhibition and total soil Cd ( $R^2 = 0.04$ ) and  $EC_{50}$  values seem to span an almost equal order of magnitude variability whether expressed as solubles or totals (see **Figure 3.22**). Other  $K_D$  models were tested (see **Table 3.10**) but none of these models yielded better correlations (details not shown). It is concluded that normalisation of terrestrial Cd toxicity data based on the solubility of Cd in soil is still not justified pending experimentally proven models.

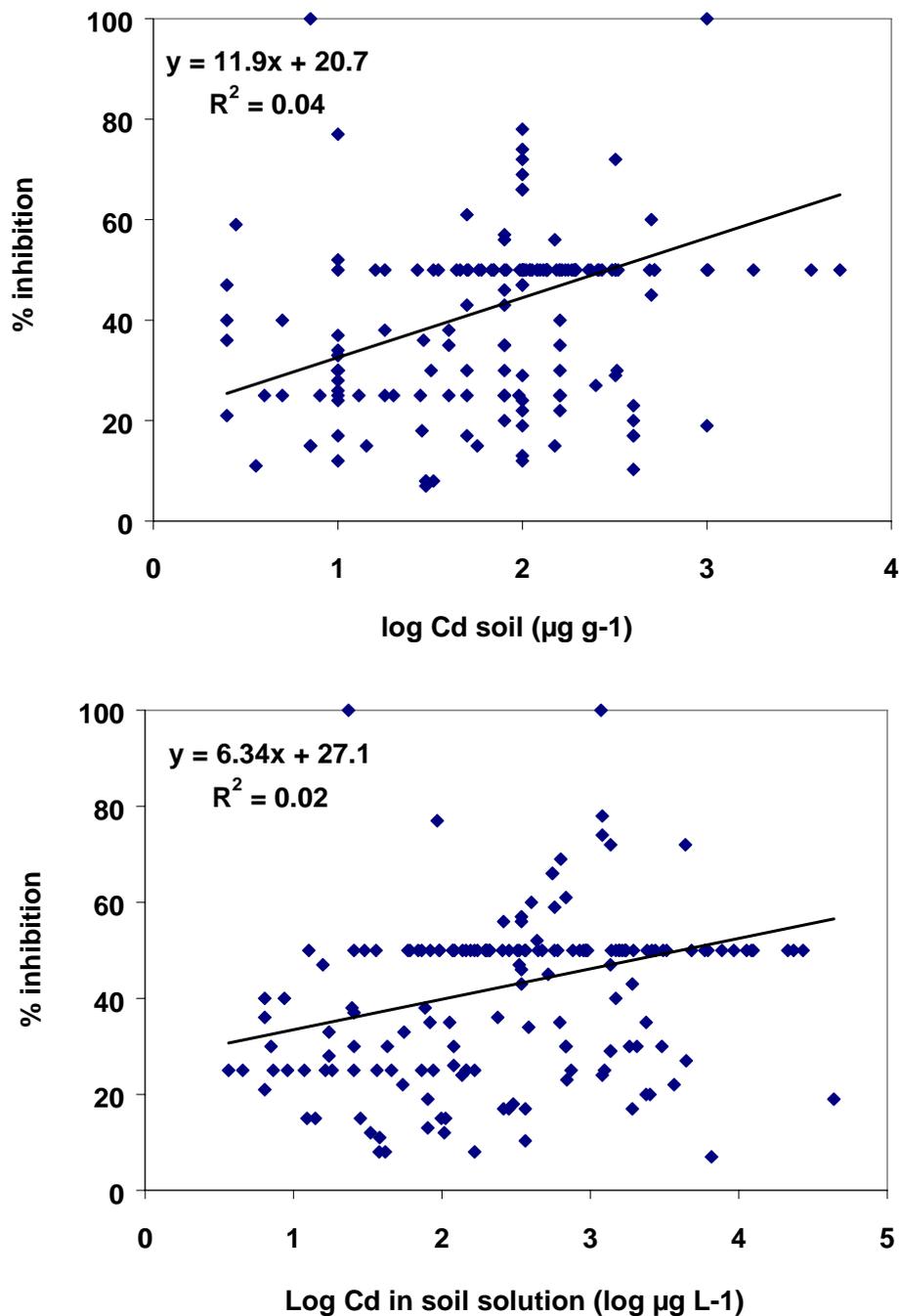
### 3.2.3.7 Conclusion

The  $PNEC_{soil}$  of CdO is based on the 5<sup>th</sup> percentile ( $HC_5$ ) of a log-logistic distribution fitted to 21 NOEC's of microbial processes (5 different processes). The  $HC_5$  of the microbial processes almost equals the  $HC_5$  values based on the fauna and plant data (54 different tests) and the  $HC_5$  of the whole data set of reliable tests (derived from 75 different tests with 20 different species and 5 different soil microbial processes). The NOEC data are derived from terrestrial toxicity tests with  $Cd^{2+}$  salts. The  $HC_5$  is  $2.3 \mu\text{g g}^{-1}$ . There is currently no justification for higher toxicity of Cd salts in the field than in the laboratory. Therefore, a PNEC can be proposed as the median  $HC_5$  with an additional assessment factor ranging from 1 to 2. This yields:

$$PNEC_{soil} = 1.15\text{-}2.3 \mu\text{g Cd/g}_{dw}$$

No adverse effects of Cd were found below  $2.3 \mu\text{g g}^{-1}$  in the entire data set (including data that were considered unreliable). Soils with less than 10% clay have a slightly lower  $\text{PNEC}_{\text{soil}}$  ( $1.5 \mu\text{g g}^{-1}$ ) than soils with more than 10% clay ( $2.0 \mu\text{g g}^{-1}$ ). Normalising the Cd toxicity data to soil solution Cd concentrations does not reduce the variance of toxic Cd concentrations between the tests.

Figure 3.22 The % inhibition of Cd in soil related to the soil total Cd concentrations (top) or to soil solution Cd concentrations (bottom). The soil solution concentrations are estimated from soil Cd concentrations based on soil pH (see main text for details)



### 3.2.4 Toxicity to benthic organisms

The fate of CdO powder in sediments is not documented. In the absence of this information, it is hypothesised that the metal behaves as the  $\text{Cd}^{2+}$  salt after equilibration. Only limited relevant data on the toxicity of  $\text{Cd}^{2+}$  to freshwater benthic organisms were found. These data refer to tests where uncontaminated sediment was spiked with  $\text{Cd}^{2+}$  salts. Several tests with field-contaminated sediments were found. These tests cannot be used for dose-response analysis because the sediments are contaminated with various other metals and with organic compounds. Some of these tests are nevertheless included as supportive information in the review given below. Tests with marine sediments were not included.

#### 3.2.4.1 Influence of sediment properties on toxicity of Cd

There are 3 potential pathways for contaminants to reach benthic organisms: the sediment (e.g. ingestion), the overlying water and the interstitial (pore) water (e.g. across respiratory surfaces and body walls). The relative importance of each route depends on a number of factors - sediment characteristics such as type of organisms and feeding habitat (Power and Chapman, 1996).

The Cd mobility in anaerobic sediments is controlled by the concentration of acid-volatile sulphides (AVS) by the particulate organic carbon (POC) and by the dissolved organic carbon (DOC). In aerobic conditions, in which the AVS are virtually absent, Cd mobility depends on the content of the POC and of Fe and Mn-hydroxides. The toxicity of Cd most likely depends on its mobility in the sediment. Since the beginning of the 90's the role of AVS on metal toxicity in sediments has been studied intensively (Van den Berg et al., 1998, Pesch et al., 1995, Allen et al., 1993, Zhuang et al., 1994, Di Toro et al., 1992, Carlson et al., 1991). A relationship was found between cadmium toxicity and the AVS normalised Cd content. In general, toxicity was expected to be absent when the ratio of the simultaneously extractable metals (SEM) to the AVS  $< 1$  (molar ratio) and to increase drastically from SEM/AVS  $\geq 1$ . Metal toxicity above this value furthermore depend on water hardness, pH and solid phase properties. However, the molar ratio did not seem to be a good predictor of potential effects, because the ratio gives no indication about the absolute amount of SEM present in excess of AVS. Therefore, the molar difference was introduced as a better predictor. At a molar SEM-AVS difference  $< 0$  no toxic effects are expected while at molar SEM-AVS difference  $> 0$  toxic effects may occur. Recently, Di Toro et al. (2000) suggested another modification to the SEM-AVS procedure that significantly improves the prediction of organism mortality. The indicator of risk is the ratio of [SEM-AVS] to the organic carbon content (oc) of the sediment. The SEM-AVS relationships can, however, only be applied in anaerobic conditions and ignores spatial and temporal variations (Van den Berg et al., 1998, Zhuang et al., 1994).

There are exceptions to the AVS based normalisation for bioavailability of Cd in sediments. Lee et al. (2000) did not find a correlation between metal concentrations in animal tissue of four benthic organisms and metal concentrations in pore water. The metal concentrations in the animal tissue were correlated with the metal concentrations extracted from the sediment, indicating that exposure of these organisms principally occurred through ingestion of particles. Therefore, the AVS-based approach may be appropriate for protecting some, but not all, benthic organisms. One study furthermore identified Cd toxicity at SEM concentrations below the AVS (Hansen et al., 1996b). A marine sediment with an AVS level of about  $17 \text{ mmol kg}^{-1}_{\text{dw}}$  was spiked with  $\text{CdCl}_2$ . Effects were found at  $12 \text{ mmol SEM kg}^{-1}_{\text{dw}}$  on the abundances of *Nematoda* and *Annelida*. Although this effect concentration is found at rather high total metal

concentration, it reveals that the AVS normalisation may not be applicable in all cases. The study was, however, carried out in marine sediments, and is therefore not used in our calculation of the  $PNEC_{\text{sediment}}$ .

### 3.2.4.2 Acute and prolonged toxicity to benthic organisms

Table 3.228 Selected data with RI 1-3 for Cd toxicity to benthic organisms. Seventeen tests were reviewed from 5 source documents and 14 tests were selected

	Min	Median	Max	n
NOEC ( $\mu\text{g g}_{\text{dw}}^{-1}$ )	115	680	3,390	15
LOEC ( $\mu\text{g g}_{\text{dw}}^{-1}$ )	334		1,079	2
E(L) $C_{x\geq 50}$ ( $\mu\text{g g}_{\text{dw}}^{-1}$ )	563	1,400	6,200	13

A summary of the literature review is given in **Table 3.228**. The Cd concentrations in the sediment/water systems are either expressed per unit sediment dry weight ( $\mu\text{g g}_{\text{dw}}^{-1}$ ) or as the dissolved fraction in the liquid phase ( $\mu\text{g L}^{-1}$ ). The main factors influencing toxicity results are physico-chemical characteristics of the test medium, test species (physiological behaviour), life stage of the test organisms, test design and preparation of the test medium. The criteria for defining reliability indices are explained for each source document in the IUCLID document. Data obtained from mixed polluted sediments were considered unreliable (RI 4).

Carlson et al. (1991) and Di Toro et al. (1992) studied the influence of the type of sediment on toxicity of Cd. Carlson et al. (1991) studied toxicity to *Lumbricus variegatus* in two lake sediments and one river sediment. The sediments were contaminated with Cd (40-16,000  $\mu\text{g g}_{\text{dw}}^{-1}$ ) by equilibrating the sediment with Cd spiked Lake Superior water. The  $LC_{50}$  values varied from 700-6,000  $\mu\text{g g}_{\text{dw}}^{-1}$ . The  $LC_{50}$  values were positively related with the AVS—content, i.e. more AVS reduces Cd toxicity. Similar dose-response curves were obtained for the three sediments if the sediment Cd concentration was normalised per unit AVS. Cadmium was extracted with cold hydrochloric acid ( $[\text{Cd}]_{\text{SE}}$ ), simultaneous with AVS. No toxicity was recorded when  $[\text{Cd}]_{\text{SE}}/\text{AVS} < 1$  (molar concentration ratio). Mortality increased sharply to 100% when  $[\text{Cd}]_{\text{SE}}/\text{AVS} \geq 1$ . Di Toro et al. (1992) performed similar tests with the same test species and sediments of the same three locations. They found no unique relationship between  $[\text{Cd}]_{\text{SE}}$  ( $\text{mg kg}_{\text{dw}}^{-1}$ ) and mortality of the test organisms for the different freshwater sediments. By contrast, a clear mortality-concentration relationship was observed when relating mortality to the  $[\text{Cd}]_{\text{SE}}/\text{AVS}$  molar ratio. No mortality in excess of 20% was observed for sediments with  $[\text{Cd}]_{\text{SE}}/\text{AVS} < 1$ . For sediments with  $[\text{Cd}]_{\text{SE}}/\text{AVS} > 1-3$ , mortality increased significantly. Similar results were found by Hansen et al. (1996a) for mixed polluted sediments. The simultaneously extractable metals (SEM) however included Cd+Cu+Ni+Zn+Pb. The authors conclude that the AVS is a reactive pool that binds heavy metals and render them unavailable to biota. Hare et al. (1994) studied the in situ colonisation of Cd-spiked freshwater sediments by macroinvertebrates in a chronic field study. Lake sediments below the top 10 cm layer was sampled, spiked with Cd, transferred to 8-L test trays and then installed in the lake bottom at 15 m depth. The mean total abundance for all taxa in the test trays was not significantly related to Cd exposure. Taken individually (at species level), the abundances of most species also did not appear to be related to exposure up to the highest Cd exposure level (563  $\mu\text{g Cd/g}_{\text{dw}}$ ). Only the number of *Chironomus (salinarius) gp* sp., which is one of the most abundant *Chironomidae* species, was strongly

reduced at  $563 \mu\text{g Cd/g}_{\text{dw}}$ . Larvae of this species burrow deep in the sediment and have their guts filled with sediment, indicating a high exposure via sediment intake.

The physiological behaviour of the test species affects their sensitivity to Cd (Carlson et al. (1991), Di Toro et al. (1992) and Francis et al. (1984)). The sensitivity of the worm *Lumbricus variegatus* and the snail *Helisoma* sp. was measured in spiked sediments (Carlson et al., 1991, Di Toro et al., 1992). *Lumbricus* was found to be the most sensitive to Cd in 4 out of the 6 different freshwater sediments. The higher sensitivity of the worms was attributed to the extended exposure of the worms due their life strategy. *Lumbricus* is usually half buried in the sediment while the other half remains in the overlying water for respiration. The snails however remain on the surface of the sediment, decreasing their contact with Cd in the sediment. Francis et al. (1984) investigated the effect of Cd-enriched sediment on goldfish, leopard frog and largemouth bass in the embryonic and larvae stages. The sediment was contaminated between 1 and  $1,000 \text{ mg kg}^{-1}_{\text{dw}}$ . No effects on survival were found up to the highest level for goldfish and frog. There was, however, 14% mortality at hatching of the bass larvae at the highest Cd level. The authors attribute the higher sensitivity of bass to the extended contact time of embryos and larvae with the contaminated sediment. Eggs of largemouth bass are settled onto the sediment and larvae remain there after hatching. Embryos and larvae of goldfish and leopard frog however remain in the overlying water and are less exposed to Cd in the sediment.

Nebeker et al. (1986b) studied survival of *Hyalella azteca* in Cd-spiked water and in sediment. Tests were performed in static and flow through conditions. The Cd concentrations in the solutions of the flow through systems were far below those in the static system. In the flow-through test, Cd had no effect on mortality of *Hyalella azteca* whereas in the static test, effects are found in sediment/water systems containing  $20 \mu\text{g Cd L}^{-1}$ . The gradient between the pore water and bottom water Cd concentrations is disturbed in flow-through systems. Therefore the pore water and bottom water concentrations decrease and the sediment appears to be less toxic.

Table 3.229 Toxicity to benthic organisms. All underlined data are selected for the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Equilibration period (d)	Duration (d)	Endpoint	NOEC		Cat*	LOEC		EC <sub>50</sub>		references	R.I.							
								$\mu\text{-g}^{-1}\text{dw}$	$\mu\text{g L}^{-1}$		$\mu\text{g g}^{-1}\text{dw}$	$\mu\text{g L}^{-1}$	$\mu\text{g g}^{-1}\text{dw}$	$\mu\text{g L}^{-1}$									
<i>Hellsoma sp.</i>  <i>Lumbricus variegatus</i>	uncontaminated freshwater sediment from:  Pequaywan Lake East River West Bearskin Lake Pequaywan Lake East River West Bearskin Lake	semi-static; sed./water:1:3 (vol)	M-total	/	10	mortality									Di Toro et al., 1992								
																	<u>3390</u>	1		<u>4520</u>			3
																	<u>2260</u>	1		<u>3340</u>			3
																	<u>340</u>	1		<u>790</u>			3
																	<u>3390</u>	1		<u>4520</u>			3
																	<u>680</u>	1		<u>1130</u>			3
																	<u>340</u>	1		<u>680</u>			3
CdCl <sub>2</sub>	<i>Hyalella azteca</i>	n-tural sediment (Soap Creek Pond - Oregon State University); 200 ml spiked natural sediment + 800 ml well water	static; T 19°C; sediment characteristics: 3% organic carbon, 15% sand, 29% silt, 56% clay; water characteristics: pH 7.1, H 54 mg L <sup>-1</sup> CaCO <sub>3</sub> , BC < 0.5 µg L <sup>-1</sup> , AVS unknown	M (diss.)	0.5	4	mortality	<u>167</u>	1.1	2	<u>334</u> (26)	3.2		6.6	Nebeker et al., 1986b	3							
CdCl <sub>2</sub>	<i>Micropterus salmoides</i>	natural stream sediment; 250 g <sub>dw</sub> sediment ;approach:ld-solution or distilled deionized water (control) +350 ml reconstituted water	DO 6.6-8.1 mg L <sup>-1</sup> , T 22.1-22.5 °C, pH 7.9-8-4; sed: OM 2.3%, Cd. 1.02 mg kg <sup>-1</sup> , Zn <sub>T</sub> 108.2 mg kg <sup>-1</sup> , Fe <sub>T</sub> 5.52%; 5.52% sand, 35.4% silt, 12% clay	M	0.42	7	mortality	<u>540</u>	22	2	<u>1079</u> (14)	44 (14)			Francis et al., 1984	3							
CdNO <sub>2</sub>	<i>Chironomus (salinaris) sp.</i>	natural lake sediment (Lake Tantaré, Canada), sampled below the top 1-10 cm; spiked sediments in test trays replaced in the test location in the lake	field test; water characteristics: pH 5.5-5.6, H 3; sediment characteristics: AVS: 0.5 µmol/g <sub>dw</sub>	N	/	14 months	abundance	<u>115</u>		1			<u>563</u> (80)		Hare et al., 1994	2							

Table 3.229 continued overleaf

Table 3.229 continued Toxicity to benthic organisms. All underlined data are selected for the effect assessment

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Equilibration period (d)	Duration (d)	Endpoint	NOEC		Cat*	LOEC		EC <sub>20</sub> <sub>50</sub>		references	R.I.											
								µg g <sup>-1</sup> <sub>dw</sub>	µg L <sup>-1</sup>		µg g <sup>-1</sup> <sub>dw</sub>	µg L <sup>-1</sup>	µg g <sup>-1</sup> <sub>dw</sub>	µg L <sup>-1</sup>													
CdCl <sub>2</sub>	<i>Lumbricus variegatus</i>	Pequaywan Lake	sediment AVS content: 38-32 µmol/g	M	4	10	mortality			1			<u>6000</u>	Carlson et al., 1991	2												
		East River sediment	6.8-7.3 µmol/g													<u>800</u>	<u>1400</u>										
		West Bearskin Lake	2.8-3.2 µmol/g													<u>380</u>	<u>700</u>										
	<i>Hellsoma</i> sp.	Pequaywan Lake	38-32 µmol/g																								
		East River sediment	6.8-7.3 µmol/g													<u>3000</u>	<u>6200</u>										
		West Be arskin Lake	2.8-3.2 µmol/g													<u>2300</u>	<u>4100</u>										
																test water: sand filtered Lake Superior water; T-21-22 °C, alkalinity 45-46 mg L <sup>-1</sup> , hardness 44-45 mg L <sup>-1</sup> , pH 7.9-8, dissolved oxygen concentration >6 mg L <sup>-1</sup> , continuous flow; T 23°C; 1.5L Cd sol. + 1L sed.									<u>380</u>	<u>810</u>	
Supporting data																											
CdCl <sub>2</sub>	<i>Hyalella azteca</i>	contaminated freshwater sediment from Foundry cove	semi -static; sed./w ater:1:3 (vol) AVS: 0.1-47 µmol/g; SEM (Ni+Cd) 0.3-1000 µmol/g	M-total	/		mortality						17 (100)	Di Toro et al., 1992	4												
CdCl <sub>2</sub>	<i>Rana pipiens</i>	natural stream sediment; 250 g <sub>av</sub> sediment	DO 6.6-8.1 mg L <sup>-1</sup> , T 22.1-22.5 °C, pH 7.9-8-4; sed: OM 2.3%, Cd: 1.02 mg kg <sup>-1</sup> , Zn <sub>T</sub> 108.2 mg kg <sup>-1</sup> , Fe <sub>T</sub> 5.52%; 5.52% sand, 35.4% silt, 12% clay	M	0.42	7	mortality	1074(HT)	77					Francis et al., 1984	4												
	<i>Carassius auratus</i>	approachid-solution or distilled deionized water (control) +350 ml reconstituted water						1008(HT)	69							4											
Cd <sup>2+</sup>	<i>Hyalella azteca</i>	natural sediment: Foundry cove	% total organic carbon: 0.55-16.4 µg/g, total Cd: 0.4-38900 µg/g, total Cu: 18-143 µg/g, total Ni: 18-31500 µg/g, total Pb: 6.1-357 µg/g, total Zn: 65-403 µg/g, sum metals: 2.9-893, SEM: 0.2-779 µmol/g, AVS: 0.4-64.6 µmol/g, SEM/AVS: 0.02-139	M-total	/	10	mortality	72			363(20)		Hansen et al., 1996a	4													

TOC Total organic carbon;  
 AVS Acid volatile sulphides;  
 SEM Simultaneously extractable metals  
 HT Highest Tested concentration;  
 H Water hardness (mg CaCO<sub>3</sub> L<sup>-1</sup>);  
 \* NOEC classification (see section 3.2.1.2).

### 3.2.4.3 The $PNEC_{\text{sediment}}$

There is only one sediment toxicity test available within the data set that can be considered as a real chronic test (test duration of other tests are 4-10 days and use mortality as endpoint). The statistical extrapolation technique will therefore not be used on the NOEC data and two alternative methods will be proposed.

According to the TGD (TGD 1996, p.335), the  $PNEC_{\text{sediment}}$  may be calculated using the equilibrium partitioning (EP) method in the absence of ecotoxicological data for sediment-dwelling organisms. Based on the equilibrium partitioning, the following formula is applied to calculate  $PNEC_{\text{sediment}}$  ( $\text{mg kg}^{-1}_{\text{ww}}$ ):

$$PNEC_{\text{sediment}} = \frac{K_{\text{sed-water}}}{RHO_{\text{sediment}}} \cdot PNEC_{\text{water}} \cdot 1000 \quad \text{Equation 3.3}$$

with  $PNEC_{\text{water}}$  expressed in  $\text{mg L}^{-1}$ ,  $RHO_{\text{sediment}}$  the bulk density of wet sediment ( $\text{kg}_{\text{ww}} \text{m}^{-3}$ ),  $K_{\text{sed-water}}$  the water-sediment partition coefficient ( $\text{m}^3 \text{m}^{-3}$ ).

This equation can be transformed to a dry weight based  $PNEC_{\text{sediment}}$  as

$$PNEC_{\text{sediment}} = K_p \cdot PNEC_{\text{water}} \cdot 10^{-3} \quad \text{Equation 3.4}$$

in which  $K_p$  equals the solid-water partition coefficient of suspended matter, expressed in  $\text{L kg}^{-1}$ , and  $PNEC_{\text{water}}$  expressed in  $\mu\text{g L}^{-1}$ . This transformation has assumed that the fraction Cd in the pore water can be neglected compared to the total amount of Cd in the sediment. Even at the lowest  $K_p$  assumed in the table below, this fraction is less than 0.01%. The  $PNEC_{\text{water}}$  equals  $0.19 \mu\text{g L}^{-1}$  (see Section 3.2.2.7). The  $K_p$  ranges  $17 \cdot 10^3 \text{ L kg}^{-1}$ -  $224 \cdot 10^3 \text{ L kg}^{-1}$  (typical value,  $130 \cdot 10^3 \text{ L kg}^{-1}$  see Section 3.1.2.3.1, **Table 3.82**). The TGD stipulates an upper limit of  $K_p$  beyond which an additional safety factor of 10 should be included (either in  $PNEC$  or in  $PEC$ ) to take the risk of direct ingestion into account. This upper limit is at  $K_p$  of about  $2,000 \text{ L kg}^{-1}$ . This situation is certainly the case for Cd, therefore the  $PNEC$  should be lowered by a factor of 10 in all cases, i.e. the  $PNEC_{\text{sediment}}$  should be calculated in this case as

$$PNEC_{\text{sediment}} = K_p \cdot PNEC_{\text{water}} \cdot 10^{-4} \quad \text{Equation 3.5}$$

This results in:

$K_p$ ( $\text{L kg}^{-1}$ )	$PNEC_{\text{sediment}}$ ( $\text{mg Cd/kg}_{\text{dw}}$ )
17,000	0.32
130,000	2.5
224,000	4.3

The 'generic'  $PNEC_{\text{sediment}}$  derived with the EP method using the typical  $K_p$  values of suspended matter is, therefore,  $2.5 \text{ mg Cd/kg}_{\text{dw}}$

Another approach to calculate the  $PNEC_{\text{sediment}}$  is using the assessment factor (AF) method. The NOEC of the chronic test ( $115 \text{ mg kg}^{-1}$ ) is divided by an AF of 50. The choice of an AF of 50 instead of 100 is justified by the number of acute toxicity data, showing no differences between species. This results in

$$PNEC_{\text{sediment}} = 115 \text{ mg kg}^{-1}/50 = 2.3 \text{ mg Cd/kg}_{\text{dw}}$$

The AF method yields a PNEC that is almost identical as the ‘generic’  $PNEC_{\text{sediment}}$  derived with the EP method. The AF method however predicts a PNEC which is even below the background value of the sediment in which the lowest chronic NOEC was found (2.8 mg Cd/kg<sub>dw</sub>, Hare et al., 1994). The separation between the PNEC and effect concentrations (n=15) is higher than 100-fold, and this is large for natural elements. Additional chronic toxicity data (currently not found) could remove this concern by reducing the AF to 10 or below. However, it should be recalled that sediment toxicity tests spiked with Cd have little field relevance because Cd availability can remain low as long as the capacity of free sulphides (AVS) in the sediment is not exceeded. Mixed metal pollution is the rule rather than the exception in the field and the Cd availability in metal polluted sediment is larger than in clean sediment. The AVS normalisation method proposed by DiToro et al. (2000) for predicting chronic effects can be a useful alternative, but can hardly be used to set generic sediment criteria (see below).

The rapporteur of the present document has clear reservations against the AF method (see above) but has no other choice than selecting the AF above the EP method for a pragmatical reason: the EP method that includes the safety factor 10 leads to an enigma that risk is predicted in all local scenarios, even if emissions are zero and the Cd concentrations in water are within the *natural* background range. This enigma remains whatever the choice of Kp as will be demonstrated in the next paragraph.

The local risk characterisation method of the TGD uses the risk factor for sediment, defined as  $PEC_{\text{local}_{\text{sed}}}/PNEC_{\text{sediment}}$ . The  $PEC_{\text{local}_{\text{sed}}}$  is calculated from the local water concentrations and the suspended matter-water partitioning coefficient (Eqn. 50 in the TGD). It can be shown that  $PEC_{\text{local}_{\text{sed}}}/PNEC_{\text{sediment}}$  effectively eliminates the Kp factor in the nominator and denominator, leading to  $PEC_{\text{local}_{\text{sed}}}/PNEC_{\text{sediment}}=10 \cdot PEC_{\text{local}_{\text{water}}}/PNEC_{\text{water}}$ . In simple terms, this means that the risk is predicted (risk factor above 1.0) when the local water concentration is larger than the  $PNEC_{\text{water}}/10$ , i.e. risk for the sediment compartments is predicted when the Cd concentrations in the overlying water are above 0.019  $\mu\text{g L}^{-1}$ . The natural background Cd concentration is estimated as 0.050  $\mu\text{g Cd/L}$  (see Section 3.2.2.1.1) which means that risk is predicted even when emissions are zero and where the Cd concentrations in water are background. Different hypothesis can be forwarded to explain this enigma (i) the benthic organisms may be less sensitive to Cd than aquatic organisms; (ii) exposure via the pore water is the dominant route and the safety factor 10 is overly protective; (iii) the Cd concentrations in the pore water of sediment are lower than that in the overlying water in contrast with the TGD method that assumes equal concentrations in local scenarios (formation of metal sulphides that reduce  $\text{Cd}^{2+}$  activity in sediments compared to the overlying water can explain such reductions). The safety factor 10 could be disregarded to avoid the enigma with the EP method, however no consensus was reached at the Technical Meetings and it is proposed to use the AF method.

Concluding, it is proposed to select a PNEC derived with an AF as:

$$PNEC_{\text{sediment}} = 2.3 \text{ mg Cd/kg}_{\text{dw}}$$

There seems to be many studies that indicate that the SEM/AVS concept (see Section 3.2.4.1) may be used for evaluating site-specific toxicity of metals. There are, however, a number of comments on the SEM/AVS concept, which limits its use for a generic approach. Firstly, Ankley (1996) showed that in some cases there appeared to be a linear accumulation of metals with increasing sediment metal concentration irrespective of the SEM/AVS content. This questions the validity of the assumption that when the SEM/AVS < 1, the metals would not be bioavailable.

Secondly, both the qualities of the SEM-data and the AVS-data are under recent discussion. The experimentally determined SEM values may underestimate the actual concentration of metals (Cooper and Morse, 1998), while the AVS values from pooled sediment samples may overestimate the actual AVS concentration in the top, aerobic sediment layer (Van den Berg et al., 1998).

Thirdly, relative to the SEM/AVS concentrations, sediment guidelines based upon dry weight-normalised concentrations were equally or slightly more accurate in predicting both non-toxic and toxic results in laboratory tests (Long et al., 1998). These latter findings currently limit the value of the SEM/AVS ratio for risk assessment.

Fourthly, further research is required to the proposed SEM/AVS concept to better implement its significance (Ankley et al., 1996; Ankley, 1996; Mayer et al., 1996)

- for benthic organisms that have a habitat at or slightly above the sediment surface where aerobic conditions prevail, and the AVS-content will be very low;
- to protect aquatic systems from metal release associated with sediment suspension;
- for the transport of metals into the food web either from sediment ingestion or the ingestion of contaminated benthos; and
- for organisms that are capable of actively extracting substances from sediments, such as polychaetes, that may produce ligands for (essential) metals, to accelerate uptake.

Due to the several comments on the SEM/AVS concept, its use for a generic approach is not adopted in the present RAR. However, taking into account AVS in assessing the risk of Cd for site-specific purposes might be possible.

The two-tiered approach as proposed in the Zn RAR (draft version, June 2001; Annex 3.3.2.C) could be followed.

To apply the AVS-approach, the worst case approach should be followed, i.e. the highest SEM concentration, the lowest AVS concentration and the lowest  $f_{oc}$  value. Furthermore, before applying the AVS-approach, some answers should be found on questions about the representativeness of the studies used to develop the AVS approach, the cut off value of  $100 \mu\text{mol g}^{-1}_{oc}$ , seasonal variations in SEM, AVS and  $f_{oc}$  and the presence of other metals.

In conclusion, the  $\text{PNEC}_{\text{sediment}}$  is derived by the assessment factor method, i.e.

$$\text{PNEC}_{\text{sediment}} = 2.3 \text{ mg Cd/kg}_{\text{dw}}$$

will be used for risk characterisation.

Remark: After the TMIV'02 last visit discussion on cadmium in sediment a number of MSs (UK, F, DE) and Industry commented on the sediment assessment (see Risk Characterisation and Conclusions).

For UK and DE comments see Risk Characterisation (see Section 3.3.2).

F expressed it cannot accept a final **conclusion (iii)** based on PNEC derived from an assessment factor of 50. An additional test for the sediment compartment should be requested, in order to reduce the uncertainty of the hazard assessment of the sediment compartment. So, F suggests a general **conclusion (i)** for the sediment compartment (long-term assay on sediment spiked with cadmium). In addition F supports the proposal made by Industry (French CA, 21.01.03).

Industry proposes a stepwise approach (IZA Europe, ICdA CollectNiCad letter, 6 February, 2003). The first step is related to the incorporation of the results of the studies dealing with bioavailability of metals performed in the frame of the zinc risk assessment. If needed, a second step, an additional long-term assay on sediment could be performed.

### 3.2.5 Atmospheric compartment

No toxicity data of CdO in the atmospheric compartment were found.

### 3.2.6 Toxicity for micro-organisms in a sewage treatment plant (STP)

Toxicity data of Cd to micro-organisms are presented in **Table 3.230**. Two tests on the effect of Cd on sludge respiration were found. Both tests were performed according to the OECD 209-guidelines (respiration inhibition test). The tests were performed using metallic Cd powder and CdO powder. Accounting for the variability of the test results, it seems that both Cd and CdO have a similar toxic action (similar NOEC and LOEC values) when based on the soluble fraction. Cd only affects sludge respiration at about 1 mg Cd/L in the dissolved fraction. This concentration was found at a loading of 100 mg metallic Cd powder or 100 mg CdO powder per litre of sludge suspension.

The LOEC values in the dissolved fraction (~1 mg Cd/L) are high compared with LOEC values for aquatic species (mostly in the 10-100 µg Cd/L range). This may indicate a high tolerance of bacteria to Cd. Some toxicity tests were found with bacterial cultures. These bacteria are tested in artificial media and a high tolerance to Cd was found for *Pseudomonas putida*, *Zoogloea ramigera* and *Escherichia coli* (Bringman and Kuhn, 1980; Norberg and Molin, 1983; Zwarum 1973). The threshold toxic Cd concentration for *Pseudomonas putida* is 80 µg L<sup>-1</sup> (Bringman and Kuhn, 1980), but this concentration refers to 3% inhibition and can be considered as a NOEC. Cd only affects the other species above 1 mg L<sup>-1</sup> range. It is unknown to what extent the components of the media, in which the bacteria are tested, can reduce Cd toxicity through metal complexation. Therefore, none of the tests with bacterial cultures have been selected for deriving the PNEC<sub>micro-organisms</sub>.

A PNEC<sub>micro-organisms</sub> is derived by dividing the lowest NOEC value of a respiration inhibition by an assessment factor of 10 (TGD, 1996, p.334).

This yields:

$$\text{PNEC}_{\text{micro-organisms}} = 20 \text{ } \mu\text{g Cd/L}$$

This concentration refers to the Cd in the dissolved fraction.

Table 3.230 Toxicity for micro-organisms in a sewage treatment plant or in artificial media

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Duration (d)	Endpoint	NOEC ( $\mu\text{g Cd L}^{-1}$ )	LOEC ( $\mu\text{g Cd L}^{-1}$ )	EC <sub>50</sub> ( $\mu\text{g Cd L}^{-1}$ )	References	R.I.
Cd	0.5 mm sieved activated domestic sludge	activated domestic sludge (1.6g L <sup>-1</sup> ) fed with synthetic sewage	pH 7.7-7.8; T 18.5-19.2	M-total (Cd)	0.125	respiration rate	32,600	100,000(11)		LISEC, 1998c	1
				M-dissolved							
CdO	0.5 mm sieved activated domestic sludge	activated domestic sludge (1.6g L <sup>-1</sup> ) fed with synthetic sewage	pH 7.59-7.79; T 18.5-19.3	M-total (Cd)	0.125	respiration rate	27,300	77,800(26)		LISEC, 1998d	1
				M-dissolved							
CdCl <sub>2</sub>	<i>Escherichia coli</i>	artificial medium; pH 6	soy pepton 0.01%	N	1-6h	respiration	600	6,000		Zwarum, 1973	4
Cd(NO <sub>3</sub> ) <sub>2</sub>	<i>Pseudomonas putida</i>	artificial medium; pH 7	static; T 25; H 80	N	0.67	biomass (OD)	80			Bringmann and Kühn, 1980	4
CdCl <sub>2</sub>	<i>Zoogloea ramigera</i>	artificial medium; pH 7; H 81; T 26	static	N	0.87	cell number	1,000		3,000	Norberg and Molin, 1983	4

H Water hardness (mg CaCO<sub>3</sub>/L);

OD Optical density.

### 3.2.7 Assessment of secondary poisoning

#### 3.2.7.1 Source of data and limitations for risk assessment

Toxicity of Cd through secondary poisoning is assessed based on laboratory studies where organisms are exposed to variable Cd concentrations in their prey. A  $PNEC_{oral}$  can be calculated from such studies. This  $PNEC_{oral}$  can be combined with the bioconcentration factors (BCF's) or bioaccumulation factors (BAF's) of the prey to assess risks of secondary poisoning of the predator by Cd originating from soil, freshwater or sediment. This protocol is suggested by the TGD (TGD, 1996) and will be discussed together with an alternative approach for mammals and birds in Section 3.2.7.4).

The risk of secondary poisoning is focussed on mammals and birds and not on lower organisms. No or little data were found to calculate the  $PNEC_{oral}$  for fish or aquatic invertebrates, benthic organisms or lower terrestrial organisms. A short discussion will, however, be given about secondary poisoning in fish or lower terrestrial organisms (see Sections 3.2.7.2.3 and 3.2.7.3.2).

A wealth of data is available on bioconcentration factors or bioaccumulation factors. Only a selection of the data is given here, merely as an illustration rather than to serve as a complete survey. The bioconcentration factors soil-plant (the soil-plant transfer factors) are reported separately in the human health part of this Risk Assessment Report, as this pathway is important for Cd exposure to the general population.

Some BCF and BAF values are derived from systems with mixed metal pollution. Mixed pollution is an additional factor that affects the Cd availability and, hence, the BCF or BAF. No reliability indices were given to the studies from which the BCF's or BAF's are calculated.

#### 3.2.7.2 The aquatic compartment

##### 3.2.7.2.1 The bioconcentration factor in water

The ability of an organism to concentrate a substance from the aquatic environment is expressed as the bioconcentration factor (BCF).

BCF-values calculated on the basis of steady-state uptake and depuration rate constants are indicated with an asterisk in the Tables. Most of the BCF values were, however simply calculated from the concentration ratio between water and biota. Many of the BCF's are calculated on a dry weight basis. The BCF's on dry weight basis are transformed to the wet weight basis if the dry weight percentage of the organism was given in the source document.

Results of Cd bioconcentration studies in water are presented in **Table 3.231**.

Table 3.231 The bioconcentration factor (BCF) of Cd in freshwater organisms. The Cd concentrations in the organisms are the product of BCF and Cd concentration in water

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Cd in water $\mu\text{g L}^{-1}$	BCF ( $\text{L kg}^{-1}_{\text{ww}}$ or $\text{L kg}^{-1}_{\text{dw}}$ )	References	Remark
Primary producers									
CdCl <sub>2</sub>	periphyton (assembly of algae and detritus on rocks)	natural sediment and water of oligotrophic soft water lakes (Ontario)	field study; alkalinity 98 mg L <sup>-1</sup> ; DOC 601 $\mu\text{m L}^{-1}$ ; H 8.3 mg L <sup>-1</sup>	M-total	116	0.09	130,000* <sup>a</sup>		
CdCl <sub>2</sub>	<i>Elodea</i> sp.	tap + deionized water (50/50); T 20°C; DOC 0.9 mg L <sup>-1</sup> ; H 88 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Cd 0.14 $\mu\text{g L}^{-1}$ ; Cu 4 $\mu\text{g L}^{-1}$ ; Zn 4 $\mu\text{g L}^{-1}$ ; Pb 0.2 $\mu\text{g L}^{-1}$	semi-static; pH 6; no aeration	M	16	0.5	60,600-151,500 <sup>(a)</sup> 4,560-11,400 89,000-300,000 <sup>(a)</sup> 6,700-22,333 100,232-310,000 <sup>(a)</sup> 7,535-23,143	Van Hattum et al., 1989	
CdSO <sub>4</sub>	<i>Chlorella vulgaris</i>	algae medium: H 6.2 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Zn 48 $\mu\text{g L}^{-1}$ ; Cu 2.54 $\mu\text{g L}^{-1}$ ; Co 5.9 $\mu\text{g L}^{-1}$ ; Mn 91 $\mu\text{g L}^{-1}$ ; T 25°C; aerated with 5% CO <sub>2</sub>		M	2.08	0.18	2,222 <sup>(a)</sup>	Khummongkol et al., 1982	
CdCl <sub>2</sub>	<i>Phytium</i> sp. <i>Dictyuchus sterile</i> <i>Scytalidium lignicola</i> <i>Phytium</i> sp. <i>Dictyuchus sterile</i> <i>Scytalidium lignicola</i>	bal Medium A     basal Medium B	5 g glucoseL-1, 4 g casamino acidL-1; pH 6.5; T 25°C    2 g glucoseL-1, 1.8 g casamino acidL-1; pH 6.5; T 25°C	M	5    7	5	44,000 <sup>(a)</sup> 89,000 <sup>(a)</sup>  50,000 <sup>(a)</sup>  38,000 <sup>(a)</sup> 90,000 <sup>(a)</sup>  48,000 <sup>(a)</sup>	Duddridge and Wainwright, 1980	
Primary consumers									
CdCl <sub>2</sub>	<i>Daphnia magna</i>	Lake Louhijampi (Finland)   Artificial humic-free water	DOC 14.2 mg L <sup>-1</sup> ; pH 6.5; H 6 mg CaCO <sub>3</sub> L <sup>-1</sup>  DOC < 0.2 mg L <sup>-1</sup> ; pH 6.5; H 30 mg CaCO <sub>3</sub> L <sup>-1</sup>	N	1 3 1	20 20 20	994*  625 510*	Penttinen et al., 1995	

Table 3.231 continued overleaf



Table 3.231 continued The bioconcentration factor (BCF) of Cd in freshwater organisms. the Cd concentrations in the organisms are the product of BCF and Cd concentration in water

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Cd in water $\mu\text{g L}^{-1}$	BCF ( $\text{L kg}^{-1}_{\text{ww}}$ or $\text{L kg}^{-1}_{\text{dw}}$ )	References	Remark
CdCl <sub>2</sub>	<i>Gasterosteus aculeatus</i>	Water; T 14.6 °C; pH 8.09; DO 94%; Alk 99.7 mg CaCO <sub>3</sub> L <sup>-1</sup> ; H 120.6 mg CaCO <sub>3</sub> L <sup>-1</sup>	Semi-static	M	33.3	0.8	511	Pascoe and Matthey, 1977	no gut clearance
					16	2.6	172.5		
					15.3	4.5	216.3		
					16.3	9	101.3		
					30	29	34.03		
					22.2	50	23.14		
					7.6	90	14.36		
					21.5	290	14.77		
					13.3	910	5.24		
					36.8	2970	2.78		
					15.3	5180	2.04		
					2	8670	1.27		
					0.3	97500	0.51		
CdCl <sub>2</sub>	<i>Cyprinus carpio</i>	tap water; T 18-19; pH 6.8; Al 14.8; H 18, BC 0.001 mg L <sup>-1</sup> ; food < 0.05 $\mu\text{g L}^{-1}$	semi-static; viscera gills vertebrae viscera gills vertebrae viscera gills vertebrae viscera gills vertebrae	N	100	1	221 <sup>(a)</sup>	Muramoto, 1981	
							286 <sup>(a)</sup>		
							122 <sup>(a)</sup>		
						10	1,620 <sup>(a)</sup>		
							1,300 <sup>(a)</sup>		
							418 <sup>(a)</sup>		
						50	892 <sup>(a)</sup>		
							236 <sup>(a)</sup>		
							11,500 <sup>(a)</sup>		
						100	613 <sup>(a)</sup>		
							158 <sup>(a)</sup>		
							59 <sup>(a)</sup>		

Table 3.231 continued overleaf

Table 3.231 continued The bioconcentration factor (BCF) of Cd in freshwater organisms. The Cd concentrations in the organisms are the product of BCF and Cd concentration in water

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Cd in water $\mu\text{g L}^{-1}$	BCF ( $\text{L kg}^{-1}_{\text{ww}}$ or $\text{L kg}^{-1}_{\text{dw}}$ )	References	Remark	
CdSO <sub>4</sub>	<i>Lepomis macrochirus</i>	Water; H 207 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Ac 11 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Alk 152 mg CaCO <sub>3</sub> L <sup>-1</sup> ; pH 7.7; DO 6.6 mg L <sup>-1</sup> ; T 16-29 °C	gill	M	330	2.3	< 2,174	Eaton, 1974		
			intestine and caecum				< 2,174			
			liver				< 4,348			
			kidney				< 4,348			
			gill				31			1,097
			intestine and caecum							2,355
			liver							6,484
			kidney							6,065
			gill				80			363
			intestine and caecum							2,188
			liver							4,175
			kidney							2,313
			gill				239			142
			intestine and caecum							1,364
			liver							1,826
			kidney							634
			gill				757			53
			intestine and caecum							229
			liver							363
			kidney							165
			gill				2140			37
intestine and caecum			176							
liver			206							
kidney			68							

Table 3.231 continued overleaf

Table 3.231 continued The bioconcentration factor (BCF) of Cd in freshwater organisms. The Cd concentrations in the organisms are the product of BCF and Cd concentration in water

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Cd in water $\mu\text{g L}^{-1}$	BCF ( $\text{L kg}^{-1}_{\text{ww}}$ or $\text{L kg}^{-1}_{\text{dw}}$ )	References	Remark			
CdCl <sub>2</sub>	<i>Salvelinus fontinalis</i>	sterilised Lake Superior water; H 42-47; pH 7-8; Al 38-46; Ac 1-10; DO 4-12; T 9-15	continuous flow; first generation:	M	266			Benoit et al., 1976				
			kidney							0.06	33,333 <sup>(a)</sup>	
			gill								11,666 <sup>(a)</sup>	
			liver								6,666 <sup>(a)</sup>	
			kidney							0.5	24,000 <sup>(a)</sup>	
			gill								11,000 <sup>(a)</sup>	
			liver								9,000 <sup>(a)</sup>	
			kidney							3.4	14,118 <sup>(a)</sup>	
			gill								2,206 <sup>(a)</sup>	
			liver								2,941 <sup>(a)</sup>	
			gonad								1,912 <sup>(a)</sup>	
			spleen								882 <sup>(a)</sup>	
			muscle								29,4 <sup>(a)</sup>	
			red blood cells								29,4 <sup>(a)</sup>	
			second generation:							735	3.4	
			kidney								1,2647 <sup>(a)</sup>	
											2,647	
gill		1,765 <sup>(a)</sup>										
		1,471										
liver		4,412 <sup>(a)</sup>										
		2,294										

HA Humic acids;

\* BCF-value calculated on the basis of steady-state uptake and depuration rate constants;

DOC Dissolved organic carbon;

H Water hardness (as mg CaCO<sub>3</sub>/L).

The BCF's of Cd are highest for the primary producers and lowest for fish (see **Table 3.232**). The BCF's of algae are obtained by measuring Cd concentration in water and algae. The high BCF's do not necessarily reflect high Cd intake in algae because a significant proportion of Cd is sorbed to the cell wall. Several BCF values of the invertebrates might overestimate true intake if the analysis of the Cd content in the organisms was performed without gut clearance. The kidney and liver of fish concentrate most Cd within the fish total body.

Table 3.232 Comparison of freshwater BCF ( $L\ kg^{-1}$ ) found in this study with data found by Taylor (1983)

	This review			Taylor (1983)	
	Min	Max	Median	Min	Max
algae wet weight	1,636	23,143	7,535	10	10,000
dry weight	2,222	310,000	11,5116		
invertebrates wet weight	396	17,560	994	10	2,000
dry weight	546	33,333	5,000		
vertebrates wet weight	0.51	6–84	229		
dry weight	5	33,333	233		
vertebrates -total body content- wet weight	0.51	5'1	15	1	3,000
dry weight	5	1,385	80		

The BCF's of algae, which were selected in this review, are higher than the BCF's that were reviewed from 40 laboratory studies by Taylor (1983). The reviewed BCF values for freshwater algae range between 10 and 10,000  $L\ kg^{-1}_{ww}$  (Taylor, 1983). This report finds BCF values ranging between 222-31,000  $L\ kg^{-1}_{ww}$  if all dry weigh based data are converted to wet weight data. For this conversion it was assumed that the average dry matter content is 10%. The BCF's for algae, which were collated here, were generally found in soft water. Low water hardness is known to increase availability of soluble metals such as  $Cd^{2+}$ . The range in fresh weight based BCF's of invertebrates is also somewhat above the range found by Taylor (1983). The whole-body fish BCF's cover a similar range in both studies.

Most important factors affecting the bioconcentration of Cd by aquatic organisms are the Cd concentration of the water, the hardness, pH, and the presence of complexing agents such as humic acid.

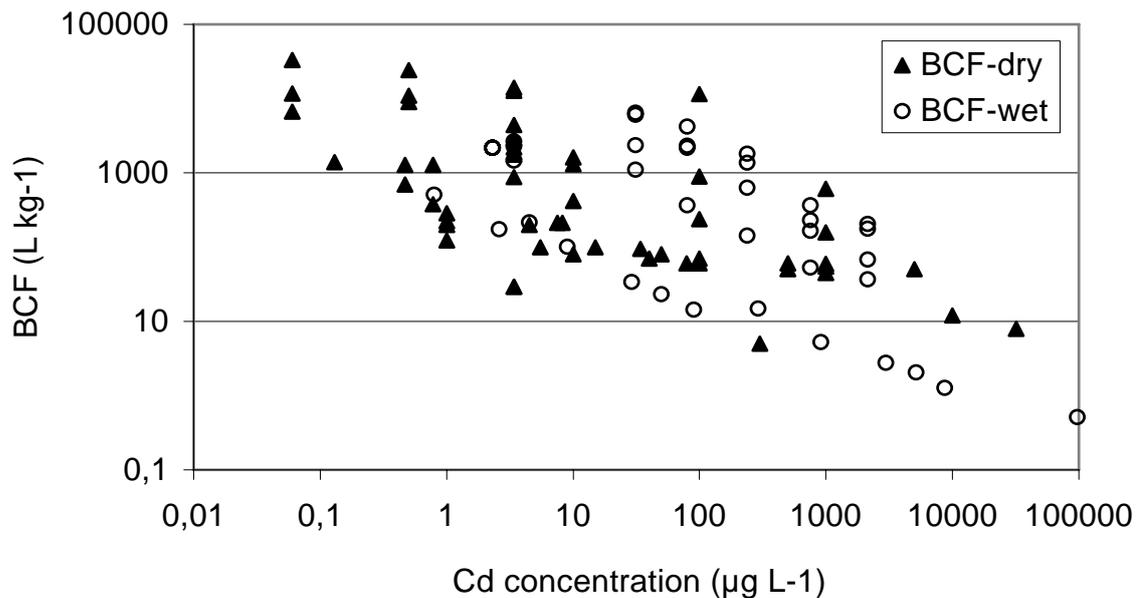
The influence of pH on the bioconcentration of Cd is illustrated by experiments of Lithner et al. (1995). A field study was performed in Swedish brooks. The bryophyte *Fontinalis antipyretica* was transplanted from a pristine brook to various polluted brooks, in the Rönnskär area, containing 0.12 to 0.29  $\mu g\ Cd/L$ . After an exposure period of 14 days the BCF of the top shoots of the bryophytes was determined. An increase in BCF with increasing pH was observed. In acidified brooks ( $pH < 6$ ) BCF values up to 10,000  $L\ kg^{-1}_{dw}$  were found. In neutral brooks ( $pH > 6$ ) BCF values of more than 30,000  $L\ kg^{-1}_{dw}$  were recorded.

Increasing water hardness reduces the BCF of Cd. Penttinen et al. (1995) found a significant effect of hardness on bioconcentration of Cd by *Daphnia magna*. After an exposure period of 1 day in artificial water, the uptake rate constant was 5 times smaller in water with hardness of 30  $mg\ CaCO_3/L$  than in water with hardness 6  $mg\ CaCO_3/L$ . However, Winner and Gauss (1986) found no significant change in Cd bioconcentration by *Selenastrum capricornutum* at water hardness values ranging from 57 to 230  $mg\ CaCO_3/L$ .

Humic acids (HA) associate with Cd and reduce the bioavailability and accumulation of Cd by aquatic organisms. The Cd in *Daphnia magna* decreased from 66 to 50  $\mu\text{g Cd/g}_{\text{dw}}$  when 5 mg HA  $\text{L}^{-1}$  was added to the artificial water (Stackhouse and Benson, 1989). Increasing the HA content to 50 mg HA  $\text{L}^{-1}$  further decreased the Cd uptake by 65%.

Increasing Cd concentration in water reduce the BCF. Tissue Cd concentrations increase with increasing solution Cd but level off at high Cd concentrations (i.e.  $> 10 \mu\text{g L}^{-1}$ ). As a result, the BCF's decrease at high Cd concentrations. This is well illustrated by the BCF values of fish presented in **Figure 3.23**. The decreasing trend was observed in all tissues.

Figure 3.23 The BCF values ( $\text{L kg}^{-1}$ ) of fish or fish tissues as a function of the Cd concentration in water ( $\mu\text{g L}^{-1}$ ). Data collated from experiments where solution Cd was artificially increased (see Table 3.231)



This trend was also observed in aquatic invertebrates (Poldoski, 1979) Cadmium content of *Daphnia magna* increased from 0.08 to 4 mg  $\text{kg}^{-1}_{\text{ww}}$  with increasing solution Cd between 0.023 and 10  $\mu\text{g Cd L}^{-1}$ . The bioconcentration factor however decreased from 3,555 to 396  $\text{L kg}^{-1}_{\text{ww}}$ . The BCF's of the insects *Pteronarcys dorsata*, *Hydropsyche betteni* and the snail *P. integra*. increased up to Cd concentrations of 10  $\mu\text{g Cd/L}$ . Further increasing the Cd concentration in water resulted in a decrease of the BCF's. Van Hattum et al. (1989), however, found increasing BCF values of the isopod *Asellus aquaticus* with increasing solution Cd concentrations between 0.5 and 4.3  $\mu\text{g Cd/L}$ .

In conclusion, the restricted survey of BCF's of aquatic organisms demonstrates that the BCF's are highest in primary producers and lowest in secondary consumers. Factors affecting the BCF are the water hardness, pH, the Cd concentration and the presence of  $\text{Cd}^{2+}$  complexing agents.

### 3.2.7.2.2 The bioaccumulation factor in water

Whereas bioconcentration is the net uptake due to water exposure only, bioaccumulation includes all routes (air, water, soil and food) (TGD, 1996). Several field studies and one laboratory experiment were found in which the BAF ( $\text{L kg}_{\text{ww}}^{-1}$ ) was calculated for organisms, mainly invertebrates, exposed by both water and food. Bioaccumulation factors range from 4 to 170,000  $\text{L kg}^{-1}_{\text{dw}}$ . Comparison of bioaccumulation factors and bioconcentration factors of aquatic invertebrates reveals the latter to be significantly lower.

Lithner et al. (1995) calculated BAF values ranging from 24,000 to 65,000 ( $L\ kg^{-1}_{dw}$ ) for 4 invertebrates living in Swedish lakes (heavy metal contaminated Rönnskär area). In the same area two fish species were captured to determine the Cd concentration of the liver. A BAF of 27,000  $L\ kg^{-1}_{dw}$  was found for liver of *Esox lucius* and of 164,000  $L\ kg^{-1}_{dw}$  for liver of *Perca fluviatilis*. These values are remarkably high but liver is known to concentrate Cd compared to the other tissues (see previous section). The dry weight based BCF values of whole fish (see **Table 3.332**: 5-1385  $L\ kg^{-1}$ ) seem to span a similar range as field derived BAF values of whole fish (4-2492  $L\ kg^{-1}$ , see **Table 3.232** and **3.233**). A similar comment applies to the wet weight based BAF values (see **Table 3.232** and **3.233**).

Table 3.233 The BAF values for whole body vertebrates ( $L\ kg^{-1}$ )

	Min	Max	Median
vertebrates -total body-content- dry weight	4	2,492	167
vertebrates -total body content- wet weight*	1	623	42

\* Calculated assuming a mean dry weight:wet weight ratio of 0.25 for whole fish.

Stephenson and Turner (1993) calculated a BAF of 170,000  $L\ kg^{-1}_{dw}$  for the amphipod *Hyaella azteca* in an oligotrophic Canadian lake containing 0.09  $\mu g\ Cd/L$ . The fraction of body burden Cd derived from food (algae) was calculated to be 58%. This fraction was calculated based on the difference in Cd uptake rate from food only and from food and water. Munger and Hare (1997) found a BAF of 1,345  $L\ kg^{-1}_{dw}$  for the insect *Chaoborus punctipennis* in a laboratory test. They also studied the relative importance of water and food as Cd sources to the insect. In artificial lake water, a food chain was simulated, composed of the larvae of the insect, its crustacean prey (*Ceriodaphnia dubia*), and the prey's algae food (*Selenastrum capricornutum*). Animals were exposed to a Cd concentration of 1.1  $\mu g\ Cd^{2+}/L$ . *Chaoborus punctipennis* was exposed to both food and water and to food alone during a 14 day exposure period. Cadmium concentration in food, the crustacean prey, was 77  $\mu g\ Cd/g_{dw}$  and remained stable throughout the experimental period. No significant difference in Cd content of the insect between both scenarios was found. This suggests that Cd uptake via the water is negligible for *Chaoborus punctipennis*.

From the same test it was possible to study the biomagnification. *Selenastrum capricornutum* exposed to 1.1  $\mu g\ Cd^{2+}/L$  had a Cd content of 1,110  $\mu g\ g^{-1}_{dw}$  and was the food for *Ceriodaphnia dubia*. Exposure of the latter to the same  $Cd^{2+}$  concentration in the water and to Cd-enriched algae resulted in a body burden of 77  $\mu g\ g^{-1}_{dw}$ . *Chaoborus punctipennis* contained 16  $\mu g\ Cd/g_{dw}$  when fed by Cd-enriched *Ceriodaphnia* in water containing 1.1  $\mu g\ Cd/L$ . These results suggest no biomagnification of Cd in the lower aquatic food chain.

### 3.2.7.2.3 Secondary poisoning within the aquatic compartment

The freshwater shrimp *Gammarus pulex* was exposed to Cd contaminated mycelium as a sole nutrient source (Duddridge and Wainwright, 1980). The mycelium was grown in a medium containing 1,000  $\mu g\ Cd/L$  for 4 days prior to the feeding experiment. The shrimps were maintained in a solution containing background Cd or in a solution containing 7  $\mu g\ Cd/L$ . In the latter case, the mycelium fed to the shrimps was not previously contaminated by Cd. A 4-day  $LC_{50}$  value was recorded when feeding the contaminated mycelium (150-170  $mg\ Cd/kg_{dw}$ ) to the shrimp and all shrimps died after 13 days in that treatment. The shrimps exposed to Cd in solution only, survived the treatment better and 50% mortality was observed at 12 days. The

most toxic pathway (water or food) cannot be derived from this study as the food was contaminated at a higher Cd concentration ( $1,000 \mu\text{g L}^{-1}$ ) than that in the solution of the shrimp feeding experiments ( $7 \mu\text{g Cd/L}$ ). Another study with Cd in water only revealed a 4-day  $\text{LC}_{50}$  of  $20 \mu\text{g Cd/L}$  for *Gammarus pulex* (Williams et al., 1985).

No  $\text{PNEC}_{\text{oral}}$  can be calculated for secondary or primary consumers in the aquatic compartment since no  $\text{NOEC}$ 's were found from feeding studies. Cd uptake through food intake may be more important than uptake from water for some organisms, such as amphipods and insects (Stephenson and Turner 1993, Munger and Hare 1997).

Table 3.234 The bioaccumulation factor (BAF) of Cd in freshwater: the Cd concentrations in the organisms are the product of BAF and Cd concentration in water

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Cd water $\mu\text{g L}^{-1}$	BAF ( $\text{L kg}^{-1}\text{ww}$ or $\text{L kg}^{-1}\text{dw}^2$ )	References	Remark
Primary consumers									
CdCl <sub>2</sub>	<i>Hyalella azteca</i>	natural sediment and water of oligotrophic soft water lakes (Ontario)	field study; uptake via water + (periphyton) food; alkalinity 98 mg L <sup>-1</sup> ; DOC 601 $\mu\text{mL}^{-1}$ ; H 8.3 mg L <sup>-1</sup>	M-total	116	0.09	170,000 <sup>(a)*</sup>	Stephenson and Turner., 1993	field study
Cd-water	<i>Asellus aquaticus</i> <i>Libellulidae Stalis lutaria</i>	Surface water of lakes (Sweden)	Lakes neutral: pH 6.5; H 19 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Zn 15.2 $\mu\text{g L}^{-1}$ , Cu 4.6 $\mu\text{g L}^{-1}$ , Cd 0.14 $\mu\text{g L}^{-1}$ , Pb 1.8 $\mu\text{g L}^{-1}$ , As 7 $\mu\text{g L}^{-1}$ ; Acidified: pH 5.6; H 14 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Zn 14.4 $\mu\text{g L}^{-1}$ , Cu 2.4 $\mu\text{g L}^{-1}$ , Cd 0.1 $\mu\text{g L}^{-1}$ , Pb 1.4 $\mu\text{g L}^{-1}$ , As 2.6 $\mu\text{g L}^{-1}$	M	whole-life	0.10-0.14	65,000 <sup>(a)</sup> 41,000 <sup>(a)</sup> 27,000 <sup>(a)</sup>	Lithner et al., 1995	field study/BAF's are arrhythmic means
Cd-water	<i>Chaeroborus punctipennis</i>	Canadian lakes	pH 4.62-7.27; H 7.1-74 mg CaCO <sub>3</sub> L <sup>-1</sup> ; OC 1.29-14.6 mg L <sup>-1</sup> ; Cd 0.017-0.802 $\mu\text{g L}^{-1}$ ; Zn 0.523-2.4 $\mu\text{g L}^{-1}$	M	whole life	dissolved	87,272 <sup>(a)</sup> 11,429 <sup>(a)</sup> 23,483 <sup>(a)</sup> 21,860 <sup>(a)</sup> 25,113 <sup>(a)</sup> 53,889 <sup>(a)</sup> 7,228 <sup>(a)</sup> 1,783 <sup>(a)</sup> 54,065 <sup>(a)</sup> 31,714 <sup>(a)</sup> 48,889 <sup>(a)</sup> 25,067 <sup>(a)</sup> 14,118 <sup>(a)</sup> 20,475 <sup>(a)</sup> 29,814 <sup>(a)</sup> 21,967 <sup>(a)</sup> 13,913 <sup>(a)</sup> 38,235 <sup>(a)</sup> 25,714 <sup>(a)</sup> 7,778 <sup>(a)</sup> 35,806 <sup>(a)</sup> 42,687 <sup>(a)</sup> 9,841 <sup>(a)</sup>	Hare and Tessier, 1996	field study
<sup>109</sup> Cd	<i>Chaeroborus punctipennis</i>	Artificial lake water;	T 10°C, H 11.6 mg CaCO <sub>3</sub> L <sup>-1</sup> ; food: <i>Ceriodaphnia dubia</i> ; Cd background concentration < 0.023 $\mu\text{g L}^{-1}$	M	14	1.1	1,345 <sup>(b)</sup>	Munger and Hare, 1997	laboratory experiment
Secondary consumers									
Cd-water	<i>Perca fluviatilis</i> <i>Esox lucius</i>	Surface water of lakes (Sweden)	Lakes circumneutral: pH 6.5; H 19 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Zn 15.2 $\mu\text{g L}^{-1}$ , Cu 4.6 $\mu\text{g L}^{-1}$ , Cd 0.14 $\mu\text{g L}^{-1}$ , Pb 1.8 $\mu\text{g L}^{-1}$ , As 7 $\mu\text{g L}^{-1}$ ; Acidified: pH 5.6; H 14 mg CaCO <sub>3</sub> L <sup>-1</sup> ; Zn 14.4 $\mu\text{g L}^{-1}$ , Cu 2.4 $\mu\text{g L}^{-1}$ , Cd 0.1 $\mu\text{g L}^{-1}$ , Pb 1.4 $\mu\text{g L}^{-1}$ , As 2.6 $\mu\text{g L}^{-1}$	M	whole-life	0.10-0.29	164,000 <sup>(a)</sup> (liver) 27,000 <sup>(a)</sup> (liver)	Lithner et al., 1995	field study

Table 3.234 continued overleaf

Table 3.234 continued The bioaccumulation factor (BAF) of Cd in freshwater: the Cd concentrations in the organisms are the product of BAF and Cd concentration in water

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Cd water $\mu\text{g L}^{-1}$	BAF ( $\text{L kg}^{-1}\text{ww}$ or $\text{L kg}^{-1}\text{dw}^2$ )	References	Remark									
Cd <sup>2+</sup> -water	<i>Perca fluviatilis</i>	River Eman water	field study; liver;	M	whole life	0.1-0.2	64,000-32,000 <sup>(a)</sup>	Olsson and Haux, 1986	field study									
Cd-water	<i>Lepomis macrochirus</i>	Palestina lake, Indiana (US); H= 275-300 mg CaCO <sub>3</sub> L <sup>-1</sup> ; shallow lake (2m); moderately contaminated and contaminated sites	field study; whole fish	M	whole life	0.9	111 <sup>a</sup>	Murphy et al., 1978	field study									
	17					182 <sup>a</sup>												
	0.9					144 <sup>a</sup>												
	17					470 <sup>a</sup>												
	0.9					167 <sup>a</sup>												
	17					82 <sup>a</sup>												
	0.9					135 <sup>a</sup>												
	17					64 <sup>a</sup>												
	0.9					89 <sup>a</sup>												
	17					33 <sup>a</sup>												
Cd-water	<i>Lepomis macrochirus</i>	Skinface pond (South Carolina, US); pH 4.6, 6 mg O <sub>2</sub> L <sup>-1</sup> ; uncontaminated	field study, whole fish	M	499 (after stocking)	0.17	240 <sup>a</sup>	Wiener and Giesy, 1979	field study									
	Cd-water									<i>Cyprinus carpio</i> <i>Barbus plebejus</i>	Sakarya river basin (Turkey); pH ~7; EC 350-850 $\mu\text{S/cm}$	field study, whole fish, 4 sampling occasions	M	whole life	0.06-0.6	340-2,300 <sup>a</sup>	Barlas, 1999	field study
															0.06-0.6	280-2,500 <sup>a</sup>		

Table 3.235 Secondary poisoning of Cd in freshwater

Test substance	Organism	Medium	Test conditions	Nominal/measured	Duration (d)	Food mg kg <sup>-1</sup> ww	EC <sub>50</sub> g/kg <sub>ww</sub>	References
CdCl <sub>2</sub>	<i>Gammarus pulex</i>	Dechlorinated tap water	Semi-static; T 15°C, constant aeration; fed <i>Phytium</i> mycelium	M	4 21	150-170 <sup>(a)</sup>	150-170 (50) 150-170 (100)	Duddridge and Wainwright, 1980

### 3.2.7.3 The terrestrial compartment

#### 3.2.7.3.1 Bioconcentration and bioaccumulation factors in soil

Bioconcentration of Cd in the terrestrial compartment is defined as the net result of the Cd uptake, distribution and elimination in an organism due to exposure to Cd in soil only.

Results of cadmium bioaccumulation studies in soil are presented in **Table 3.237** and a summary of the bioaccumulation factors is given in **Table 3.236**. All BAF values were calculated from the soil:biota concentration ratios. Most organisms are earthworms and the Cd levels are expressed on dry or wet weight basis. All the data on earthworms are obtained from specimens with guts voided prior to analysis.

Table 3.236 The bioaccumulation factors (BAF's) of soil dwelling organisms

	Min	Max	Median	5 <sup>th</sup> percentile	n
Earthworms- wet weight basis ( $\text{kg}_{\text{dw}}/\text{kg}_{\text{ww}}$ )	4	32	15	5	11
Earthworms- dry weight basis ( $\text{kg}_{\text{dw}}/\text{kg}_{\text{dw}}$ )	1.6	151	15	5	85
Arthropoda - dry weight basis ( $\text{kg}_{\text{dw}}/\text{kg}_{\text{dw}}$ )	0.05	18.8	1.4	0.30	45

Cadmium is concentrated from the soil into earthworms organisms (BAF values all higher than 1). Most important factors affecting the bioaccumulation of Cd by earthworms are the Cd concentration of the soil, soil type, pH, soil organic matter and CEC.

The influence of the Cd content of the soil on the bioaccumulation of Cd is illustrated in most of the studies. Cadmium concentrations in earthworms increase with increasing Cd levels in a non-proportional way (i.e. Wright and Stringer, 1980; Ma, 1982). As a result, the BAF decreases with increasing soil Cd (see **Figure 3.24**). Wright and Stringer (1980) compared Cd content in earthworms and soil from pastures near a large Pb and Zn smelting plant and a control area 9-km away. Cadmium concentrations in the earthworms were several times the value in the soil. For all species, the Cd BAF values however were significantly lower at the contaminated site than at the control site. The soil Cd concentration in the contaminated site was 7-9 folds higher than in the control site. Spurgeon and Hopkin (1996) calculated the BAF of Cd for different earthworm species at 22 locations around a primary smelting plant. For all worm species, body burdens increased with increasing soil Cd levels. No evidence was found for species specific accumulation. The BAF values ranged from 2.59 to 115  $\text{kg}_{\text{dw}}/\text{kg}_{\text{dw}}$ . There was an inverse relationship between the BAF's for earthworms and the concentration of Cd in soils. In addition, soil pH and OM were found to affect the BAF of Cd for earthworms. Beyer et al. (1982) examined Cd in earthworms (*Lumbricidae*) from agricultural sites amended with sewage sludge and from experimental control plots. Earthworms from sludge amended sites contained 12 times more Cd than worms from the control sites. The BAF values were lower in contaminated soil than in the control soils. Liming the soil slightly decreased the Cd body burden of the earthworms and high Zn concentrations in soil substantially reduced Cd in earthworms. Morgan and Morgan (1988) examined Cd content in worms in 12 heavily polluted soils of non-ferrous metaliferous mines. A significant correlation was found between the Cd in earthworm and total Cd content of the soils. Gish and Christensen (1973) measured Cd content of topsoil and earthworms near 2 highways (Maryland). Cd contents in both soil and worms decreased with

increasing distance from the roadways. Andersen (1979) studied Cd uptake by *Allolobophora spp.* and *Lumbricus terrestris* in soil receiving sewage sludge. The sludge application reduced the Cd content in the worms whereas soil Cd concentrations were more than doubled by the sludge application.

The influence of soil type, pH, CEC and the organic matter content of the soil was studied by Ma (1982). The body burden of Cd in earthworms was higher in sandy soils ( $21\text{--}35\text{ mg kg}^{-1}_{\text{dw}}$ ) than in loamy soils ( $12.2\text{--}32\text{ mg kg}^{-1}_{\text{dw}}$ ), although the soil concentration of Cd was higher in the latter. The BAF increased with decreasing the pH, CEC and soil organic matter content. The soil pH was the most important soil factor for the BAF.

Hunter et al. (1987a) performed a field study in the vicinity of a major copper refinery housing copper/cadmium alloying plant. Invertebrates from contaminated and semi-contaminated (1 km from the plant) grasslands all showed significant elevation of total body Cd concentrations relative to the control site. Detritivorous soil macrofauna showed accumulation of Cd (10-20 times) with respect to concentrations in refinery site organic surface soil and plant litter. Herbivorous invertebrates showed body:diet concentration factors of 3-5 times. Biotransfer of Cd to carnivorous invertebrates reveals marked differences in Cd accumulation by predatory beetles and spiders. Seasonal changes in the abundance, species composition and age structure of invertebrate populations caused marked variation in Cd contamination levels throughout the year.

Figure 3.24 The bioaccumulation factors (BAF  $\text{kg kg}^{-1}$ ) of earthworms as a function of the Cd concentration in soil ( $\text{mg kg}^{-1}$ )

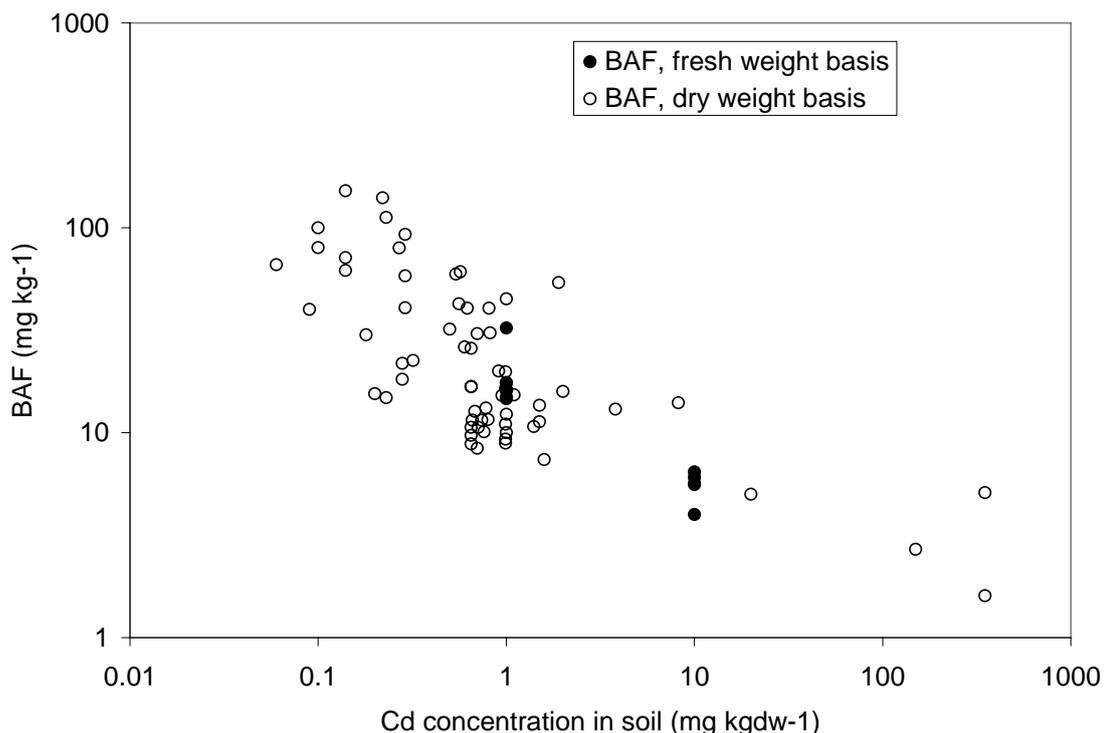


Table 3.237 Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration

Test substance	Organism	Medium	Test conditions	Equilibration period (d)	Duration (d)	Soil mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>dw</sub> <sup>soil</sup> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(a)</sup> )	References	Remark
Cd-soil	<i>Lumbricus terrestris</i>	control soil of orchard (Long Ashton); pH 6.5; average biomass 113.7 g/m <sup>2</sup> ; Cd 1 µg/g <sub>dw</sub> ; Pb 92 µg/g <sub>dw</sub> ; Zn 89 µg/g <sub>dw</sub>  Polluted soil of pasture (Sevenside); pH 6.8; average biomass 85.8 g/m <sup>2</sup> ; Cd 10 µg/g <sub>dw</sub> ; Pb 147 µg/g <sub>dw</sub> ; Zn 617 µg/g <sub>dw</sub>	control soil	/	whole life	1	14.64	Wright and Stringer, 1980	field study
	<i>Allolobophora caliginosa</i>		polluted soil			10	5.58		
			control soil			1	32.45		
	<i>Allolobophora tuberculata</i>		polluted soil			10	6.43		
	<i>Allolobophora chlorotica</i>		control soil			1	17.55		
	<i>Allolobophora longa</i>		polluted soil			10	/		
	<i>Allolobophora rosea</i>		control soil			1	14.91		
			polluted soil			10	5.65		
			control soil			1	16.01		
			polluted soil			10	3.99		
			control soil			1	16.27		
			polluted soil			10	6.06		
Cd-soil	<i>Allalobophora</i> sp. + <i>Lumbricus</i> sp. + <i>Octolasion</i> sp.	soil	Bodine soil	/	whole life	0.32	22.5 <sup>a</sup>	Van Hook, 1974	field study
			Captina soil			0.2	15.5 <sup>a</sup>		
			Clairborne soil			0.28	21.8 <sup>a</sup>		
			Emory soil			0.8	11.6 <sup>a</sup>		
			Linside soil			0.28	18.2 <sup>a</sup>		
			Rarklin soil			0.23	14.8 <sup>a</sup>		
Cd-soil	<i>Lumbricus terrestris</i> + <i>Lumbricus rubellus</i> + <i>Lumbricus castaneus</i> + <i>Allolobophora caliginosa</i> + <i>Allolobophora chlorotica</i> + <i>Allolobophora rosea</i>	Polluted soil around a primary smelting place; pH 5.56-7.32; OM 15-29.9%		/	whole life	/	2.59 <sup>(a)</sup>	Spurgeon and Hopkin, 1996	field study
							6.11 <sup>(a)</sup>		
							3.81 <sup>(a)</sup>		
							6.53 <sup>(a)</sup>		
							5.99 <sup>(a)</sup>		
							4.86 <sup>(a)</sup>		
							23 <sup>(a)</sup>		
							10.2 <sup>(a)</sup>		
							11.4 <sup>(a)</sup>		
							22.8 <sup>(a)</sup>		
							64.3 <sup>(a)</sup>		
							13.2 <sup>(a)</sup>		
			19.8 <sup>(a)</sup>						
			9.26 <sup>(a)</sup>						
			32.6 <sup>(a)</sup>						
			115 <sup>(a)</sup>						

Table 3.237 continued overleaf

Table 3.237 continued Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration

Test substance	Organism	Medium	Test conditions	Equilibration period (d)	Duration (d)	Soil mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>dw</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(a)</sup> )	References	Remark
Cd-soil	<i>Lumbricadea</i> sp.	Landsdale1 loam	control; pH 5.9-6.3	/	whole life	0.06	66 <sup>(a)</sup>	Beyer et al., 1982	agricultural soil amended or not with sludge
			sludge; pH 5.5-6.2			3.8	13 <sup>(a)</sup>		
		Hagerstown silt loam	control; pH 5.4-6.4; CEC 9 meq/100g; OM 3%			0.18	30 <sup>(a)</sup>		
			sludge; pH 4.9-6; CEC 13 meq/100g; OM 4.9%			0.91/0.55	20 <sup>(a)</sup>		
		Landsdale2 loam	control; pH 4.9-6.4; CEC 8 meq/100g; OM 2.5%			0.14/0.05	62 <sup>(a)</sup>		
			Sludge; pH 4.6-6.3; CEC 8 meq/100g; OM 2.8%			1.9/1.6	54 <sup>(a)</sup>		
Readingston silt loam	control; pH 5.3-6.1; CEC 10 meq/100g; OM 2.6%	0.09/0.08	40 <sup>(a)</sup>						
	sludge; pH 5.5-6.1; CEC 11 meq/100g; OM 3.8%	8.2/5.7	14 <sup>(a)</sup>						
Cd-soil	<i>Lumbricus rubellus</i> <i>Dendrodrilus rubidus</i>	Topsoil of control soil and 12 heavily contaminated soils of non-ferrous metalliferous mines; pH 4.3-7.8; OC 1-27%; CEC 8-77 meq/100g	control	/	whole life	1	10 <sup>(a)</sup>	Morgan and Morgan, 1988	field study
			polluted			0.1-350	80 <sup>(a)</sup> - 1.6 <sup>(a)</sup>		
			control			1	45 <sup>(a)</sup>		
		polluted				0.1-350	100 <sup>(a)</sup> - 5.1 <sup>(a)</sup>		

Table 3.237 continued overleaf

Table 3.237 continued Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration

Test substance	Organism	Medium	Test conditions	Equilibration period (d)	Duration (d)	Soil mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>dw</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(a)</sup> )	References	Remark		
Cd-soil	<i>Lumbricus terrestris</i> + <i>Allolobophora chlorotica</i> + <i>Allolobophora trapezoides</i> + <i>Allolobophora turgida</i>	Topsoil along two highways (Maryland): B-W parkway; silt-clay; pH 6.97; OM 4.96-7.3 US-Highway1 ; pH 6.88-6.96; OM 4.8-6.36	B-W parkway 3 m	/	whole life	1.59	7.4 <sup>(a)</sup>	Gish and Christensen, 1973	field study		
			6.1 m	0.78		13.2 <sup>(a)</sup>					
			12.2 m	0.68		12.7 <sup>(a)</sup>					
			24.4 m	0.71		10.6 <sup>(a)</sup>					
			48.8 m	0.74		11.5 <sup>(a)</sup>					
			US-Highway1 3 m	0.95		15.2 <sup>(a)</sup>					
			6.1 m	0.66		11.5 <sup>(a)</sup>					
			12.2 m	0.76		10.1 <sup>(a)</sup>					
			24.4 m	0.65		9.7 <sup>(a)</sup>					
			48.8 m	0.7		8.4 <sup>(a)</sup>					
Cd-soil	<i>Allolobophora longa</i>	experimental plots: soil 1: K-fertilised; pH 5.9	soil 1	/	whole life	0.29	40.7 <sup>(a)</sup>	Andersen, 1979	micplots		
			soil 2	0.14		71.4 <sup>(a)</sup>					
			soil 2: NPK-fertilised (300 kg N/ha); pH 5.7	soil 3		0.65	8.8 <sup>(a)</sup>				
				soil 4		0.99	9.3 <sup>(a)</sup>				
			<i>Allolobophora caliginosa</i>	soil 3 Vejlen sewage sludge (30 T/ha containing 14.6 mg Cd/kg <sub>dw</sub> ); pH 5.8)		soil 1	0.29				
						soil 2	0.14				
						<i>Allolobophora rosea</i>	soil 3			0.65	10.6 <sup>(a)</sup>
							soil 4			0.99	11 <sup>(a)</sup>
	<i>Allolobophora chlorotica</i> <i>Lumbricus terrestris</i>	soil 4: Lundtofte sewage sludge (30 T/ha containing 34.1 mg Cd/kg <sub>dw</sub> ); pH 6	soil 1	0.29		92.8 <sup>(a)</sup>					
			soil 2	0.14		151.4 <sup>(a)</sup>					
			soil 3	0.65		16.8 <sup>(a)</sup>					
			soil 4	0.99		19.8 <sup>(a)</sup>					
			soil 3	0.65		16.8 <sup>(a)</sup>					
			soil 4	0.99		16.4 <sup>(a)</sup>					
			soil 1	0.29		58.3 <sup>(a)</sup>					
			soil 3	0.65		25.8 <sup>(a)</sup>					
soil 4	0.99	8.88 <sup>(a)</sup>									

Table 3.237 continued overleaf

Table 3.237 continued Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration

Test substance	Organism	Medium	Test conditions	Equilibration period (d)	Duration (d)	Soil mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>dw</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(b)</sup> )	References	Remark
Cd-soil	detrivorous invertebrates			/	whole life			Hunter et al., 1987a	field study
	<i>Collembola</i>		control			0.8	2.6 <sup>(a)</sup>		
			1 km site			6.9	1.7 <sup>(a)</sup>		
	<i>Isopoda</i>		refinery			15.4	3.4 <sup>(a)</sup>		
			control			0.8	18.4 <sup>(a)</sup>		
			1 km site			6.9	18.8 <sup>(a)</sup>		
	<i>Diplopoda</i>		refinery			15.4	15.0 <sup>(a)</sup>		
			control			0.8	7 <sup>(a)</sup>		
			1 km site			6.9	2.1 <sup>(a)</sup>		
	<i>Oligochaeta</i>		refinery			15.4	1.2 <sup>(a)</sup>		
			control			0.8	5.1 <sup>(a)</sup>		
			1 km site			6.9	4.9 <sup>(a)</sup>		
	<i>Diptera</i>		refinery			15.4	6.9 <sup>(a)</sup>		
			control			0.8	2.8 <sup>(a)</sup>		
			1 km site			6.9	1.0 <sup>(a)</sup>		
	herbivorous insects		refinery			15.4	1.6 <sup>(a)</sup>		
	<i>Orthoptera</i>								
			control			0.8	0.24 <sup>(a)</sup>		
	<i>Formicidae</i>		1 km site			6.9	0.046 <sup>(a)</sup>		
			refinery			15.4	0.12 <sup>(a)</sup>		
			control			0.8	1.5 <sup>(a)</sup>		
	<i>Hemiptera</i>		1 km site			6.9	0.8 <sup>(a)</sup>		
			refinery			15.4	2.4 <sup>(a)</sup>		
			control			0.8	1.0 <sup>(a)</sup>		
<i>Lepidoptera</i> (larvae)		1 km site			6.9	0.5 <sup>(a)</sup>			
		refinery			15.4	0.7 <sup>(a)</sup>			
<i>Curculionidae</i>		control			0.8	0.8 <sup>(a)</sup>			
		1 km site			6.9	1.0 <sup>(a)</sup>			
		refinery			15.4	1.4 <sup>(a)</sup>			
Carnivorous insects		control			0.8	0.8 <sup>(a)</sup>			
<i>Coleoptera</i>		1 km site			6.9	0.5 <sup>(a)</sup>			
		refinery			15.4	1.0 <sup>(a)</sup>			

Table 3.237 continued overleaf

Table 3.237 continued Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration

Test substance	Organism	Medium	Test conditions	Equilibration period (d)	Duration (d)	Soil mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>ww</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(a)</sup> )	References	Remark
	<i>Carabidae</i>		control			0.8	0.8 <sup>(a)</sup>		
			1 km site			6.9	0.7 <sup>(a)</sup>		
			refinery			15.4	0.9 <sup>(a)</sup>		
	predatory larvae		control			0.8	0.9 <sup>(a)</sup>		
			1 km site			6.9	0.8 <sup>(a)</sup>		
			refinery			15.4	1.0 <sup>(a)</sup>		
	<i>Araneida</i>		control			0.8	2.8 <sup>(a)</sup>		
	<i>Lycosidae</i>		1 km site			6.9	1.2 <sup>(a)</sup>		
			refinery			15.4	1.4 <sup>(a)</sup>		
	<i>Linyphiidae</i>		control			0.8	3.3 <sup>(a)</sup>		
			1 km site			6.9	5.0 <sup>(a)</sup>		
			refinery			15.4	6.6 <sup>(a)</sup>		
	<i>Opiliones</i>		control			0.8	3.0 <sup>(a)</sup>		
			1 km site			6.9	2.7 <sup>(a)</sup>		
			refinery			15.4	5.8 <sup>(a)</sup>		
			control			0.8	3.5 <sup>(a)</sup>		
			1 km site			6.9	3.7 <sup>(a)</sup>		
			refinery			15.4	6.0 <sup>(a)</sup>		
CdCl <sub>2</sub>	<i>Lumbricus rubellus</i>	sandy loam soil	17% clay; OM 8%; pH 7.3; CaCO <sub>3</sub> 5.5%; ; T 15°C moisture content 35-40%; food: dried alder leaves	/	84	0.5	32 <sup>(a)</sup>	Ma, 1982	Laboratory study
	<i>Allolobophora caliginosa</i>					20	5 <sup>(a)</sup>		
Cd-soil		marine clay loam;		up to 1 decade	whole life	150	2.7 <sup>(a)</sup>		Field study
			30% clay; CEC 26.3 meq/100g; OM 5.8%; pH 7.1; 0 T compost/ha			1	12.3 <sup>(a)</sup>		
			30% clay; CEC 24.5 meq/100g; OM 6.7%; pH 7; 20 T compost/ha			1.4	10.7 <sup>(a)</sup>		
						1.5	11.3 <sup>(a)</sup>		

Table 3.237 continued overleaf

Table 3.237 continued Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration

Test substance	Organism	Medium	Test conditions	Equilibration period (d)	Duration (d)	Soil mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>ww</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(a)</sup> )	References	Remark
		sandy loam;	30% clay; CEC 25.1 meq/100g; 8.4%; pH 6.9; 40 T compost/ha			0.6	26.2 <sup>(a)</sup>		
			10% clay; CEC 9.4 meq/100g; OM 2.8%; pH 6.6; 0 T compost/ha			0.7	30.4 <sup>(a)</sup>		
			10% clay; CEC 10.5 meq/100g; OM 4%; pH 7; 20 T compost/ha			1	17.5 <sup>(a)</sup>		
		riverine clay loam;	10% humus CEC 12.3 meq/100g; OM 4.9%; pH 7; 40 T compost/ha			1.1	15.3 <sup>(a)</sup>		
			40% humus; CEC 26.4 meq/100g; OM 6.9%; pH 5.3; 0 T compost/ha			1.5	13.6 <sup>(a)</sup>		
			40% humus; CEC 28.7 meq/100g; OM 9.2%; pH 5.8; 20 T compost/ha			2	15.9 <sup>(a)</sup>		
			40% humus; CEC 28.7 meq/100g; OM 9.7%; pH 5.9; 40 T compost/ha						
		peaty sand;	10% humus CEC 20.5 meq/100g; OM 12.4%; pH 4.7; 0 T compost/ha			0.23	112.2 <sup>(a)</sup>		
			10% humus CEC 19.2 meq/100g; OM 11.2%; pH 5.2; 20 T compost/ha			0.57	60.9 <sup>(a)</sup>		
			10% humus CEC 18.3 meq/100g; OM 13.6%; pH 5.8; 40 T compost/ha						
			7% humus CEC 13.5 meq/100g; OM 6.4%; pH 5.4; 0 T compost/ha			0.81	40.5 <sup>(a)</sup>		
		sandy podzolized soil;	7% humus CEC 12.7 meq/100g; OM 7.4%; pH 5.4; 20 T compost/ha			0.27	79.6 <sup>(a)</sup>		
			7% humus CEC 23.2			0.56	42.6 <sup>(a)</sup>		
						0.82	30.7 <sup>(a)</sup>		

Table 3.237 continued overleaf

Table 3.237 continued Bioaccumulation factors in soil. The Cd concentrations in the biota are the product of BAF and soil Cd concentration

Test substance	Organism	Medium	Test conditions	Equilibration period (d)	Duration (d)	Soil mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>ww</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(b)</sup> )	References	Remark
		plaggen soil;	meq/100g; OM 8.1%; pH 5.7; 40 T compost/ha			0.22	140 <sup>(a)</sup>		
			3% humus CEC 5.3 meq/100g; OM 2.8%; pH 4.8; 0 T compost/ha			0.54	59.4 <sup>(a)</sup>		
			3% humus CEC 6.1 meq/100g; OM 3.7%; pH 5.5; 20 T compost/ha			0.62	40.5 <sup>(a)</sup>		
			3% humus CEC 7.1 meq/100g; OM 4.3%; pH 6; 40 T compost/ha						

### 3.2.7.3.2 Secondary poisoning within the lower terrestrial foodchain

Russell et al. (1981) studied Cd toxicity to *Helix aspersa* by feeding with Cd-enriched food during 30 days. The Cd concentration in tissue increased with increasing Cd content of the food. Reproduction was unaffected by the Cd in food up to  $10 \text{ mg kg}^{-1}_{\text{dw}}$  (concentration in food). Reproduction was significantly reduced at  $25 \text{ mg kg}^{-1}_{\text{dw}}$ .

A case study on Cd bioaccumulation in the lower food chain was made for the plant (wheat)-insect (aphids)-predator (lacewings) pathway (Merrington et al., 2001). A low Cd soil was fertilised with high Cd P-fertiliser and Cd concentrations, resulting in higher Cd in soil and in wheat shoots. Aphids feeding on the wheat plants of the fertilised soil had 3 times higher Cd concentrations than those feeding on the control plants. However, lacewings showed no significant accumulation of Cd and no differences in larval performance were recorded. This illustrates that this pathway does not lead to Cd bioaccumulation.

No  $\text{PNEC}_{\text{oral}}$  will be derived for lower terrestrial organisms due to lack of sufficient data and because secondary poisoning is assessed for organisms of a higher trophic level (mammals and birds).

Table 3.238 Secondary poisoning within the lower terrestrial foodchain

Test substance	Organism	Medium	Test conditions	Endpoint	Nominal/measured	Duration (d)	NOEC mg kg <sup>-1</sup> <sub>dw</sub>	LOEC mg kg <sup>-1</sup> <sub>dw</sub>	EC <sub>25/50</sub> mg kg <sup>-1</sup> <sub>dw</sub>	References
CdCl <sub>2</sub>	<i>Helix aspersa</i>	moist quartz sand covered by a piece of woven glass towel; food: ground Purina Lab-Chow supplemented with CaCO <sub>3</sub>		shell growth reproduction	N	30	25 10	100 (20) 25 (28)	300 (95) 50 (69)	Russell et al., 1981

### 3.2.7.4 The sediment compartment

#### 3.2.7.4.1 Bioaccumulation in sediment

Most of the BAF's of benthic organism are lower than 1 (either fresh weight based or dry weight based, **Table 3.239**). The BAF's are smaller for vertebrates than for invertebrates. The BAF's of benthic organisms are generally smaller than BAF's for soil-invertebrate transfer (see **Figure 3.24**). Data on marine organisms indicate larger BAF values than given here (details not shown). However, BAF values of marine organisms are not used in this risk assessment.

Table 3.239 The BAF values of some benthic organisms

	Min	Max	Median
invertebrates, wet weight (kg <sub>dw</sub> /kg <sub>ww</sub> )	0.38	0.44	0.43
invertebrates, dry weight (kg <sub>dw</sub> /kg <sub>dw</sub> )	0.01	1.15	0.28
vertebrates, wet weight (kg <sub>dw</sub> /kg <sub>ww</sub> )	0.006	0.18	0.07

The body burden Cd generally increases with increasing Cd concentration in the sediment but levels off at higher Cd contents of the sediment (Francis et al., 1984). Low BAF values can therefore be found at high Cd concentrations in the sediment. The Cd concentrations in the oligochaete *Lumbricus variegatus* were similar in field contaminated sediments, containing about 5 µg Cd g<sup>-1</sup><sub>dw</sub>, and in sediments spiked up to 750 µg Cd g<sup>-1</sup><sub>dw</sub> (Ankley et al., 1994; Peterson et al., 1996). The BAF values therefore differ by more than one order of magnitude between both systems. These observations were made for two different sediments (one from a pond, the other from a river) and differences in metal immobilisation between the sediments may explain different Cd availability in the sediments.

The influence of contact time in the sediment on the BAF was illustrated by data of Francis et al. (1984). Cd accumulation and toxicity in fish (largemouth bass) and amphibian (leopard frog) was measured in embryo-larval stages. Largemouth bass accumulated, at all sediment concentrations, significantly more Cd than leopard frog. The differences in BAF's between the species were attributed to differences in contact time of the organisms with the sediment. Bass eggs and larvae have direct contact with sediment throughout the exposure period whereas goldfish and leopard frog dwell in the water column above the sediment.

The BAF's collected in this review are based on a maximal exposure time of 50 days and may underestimate longer-term BAF values.

Van Hattum et al. (1993) studied the influence of temperature and pH on the uptake of Cd in *Asellus aquaticus*. No significant pH effects on Cd uptake were observed. Increasing temperature from 5-20°C, however, significantly increased Cd uptake about fourfold.

Table 3.240 Bioaccumulation of Cd in benthic organisms

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Equilibration period (d)	Duration (d)	Sediment mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>ww</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(a)</sup> )	References
Cd-sediment	<i>Lumbricus variegatus</i>	contaminated sediment from lower Fox river (Wisconsin)	40-60g <sub>dw</sub> sediment + Lake Superior water; T 22°C; semi-static; Cu 64-90 mg kg <sup>-1</sup> <sub>dw</sub> ; Zn 208-347 mg kg <sup>-1</sup> <sub>dw</sub> ; Pb 102-150 mg kg <sup>-1</sup> <sub>dw</sub> ; Cr 71-118 mg kg <sup>-1</sup> <sub>dw</sub> ; no food addition	M-total	1	30	5.2	0.38	Ankley et al., 1994
							4.1	0.44	
							5.8	0.43	
CdCl <sub>2</sub>	<i>Lumbricus variegatus</i>	Cd spiked natural sediment of small mesotrophic pond(Minnesota); 0.74 µmol/g <sub>dw</sub> SEM and 4.6 µmol S/g <sub>dw</sub>	org. density 10000 org/m <sup>2</sup> SEM/AVS = 0.4 SEM/AVS = 0.8 org. density 25000 org/m <sup>2</sup> SEM/AVS = 0.4 SEM/AVS = 0.8	M-total	11	14	450	0.02 <sup>a</sup>	Peterson et al., 1996
							754	0.03 <sup>a</sup>	
							382	0.01 <sup>a</sup>	
							714	0.01 <sup>a</sup>	
Cd-sediment	<i>Asellus aquaticus</i>	natural sediment from the polluted lake Ketelmeer and the uncontaminated lake Oostvaardersplassen (Nijprooch) + mixture of tap and deionized water; 100 g <sub>ww</sub> sediment + 400 ml water	semi-static; lake Ketelmeer: 2% OC; 1% clay, 13% silt; Pb 48 mg kg <sup>-1</sup> <sub>dw</sub> ; Cu 27 mg kg <sup>-1</sup> <sub>dw</sub> ; Zn 319 mg kg <sup>-1</sup> <sub>dw</sub> ; Fe 5100 mg kg <sup>-1</sup> <sub>dw</sub> ; T 5°C  T 10°C T 20°C pH 5 (T 20°C) pH 8 ( T 20°C) lake Oostvaarders plassen: 5% OC; 8% clay, 70% silt; Pb 84 mg kg <sup>-1</sup> <sub>dw</sub> ; Cu 25 mg kg <sup>-1</sup> <sub>dw</sub> ; Zn 221 mg kg <sup>-1</sup> <sub>dw</sub> ; Fe 16400 mg kg <sup>-1</sup> <sub>dw</sub> ;  T 5°C T 10°C T 20°C	M-total	7	50			Van Hattum et al., 1993
								0.28 <sup>a</sup>	
								1.02 <sup>a</sup>	
								1.15 <sup>a</sup>	
								1.1 <sup>a</sup>	
								1 <sup>a</sup>	
								0.25 <sup>a</sup>	
								0.5 <sup>a</sup>	
	0.5 <sup>a</sup>								

Table 3.240 continued overleaf

Table 3.240 continued Bioaccumulation of Cd in benthic organisms.

Test substance	Organism	Medium	Test conditions	Nominal/ Measured	Equilibration period (d)	Duration (d)	Sediment mg kg <sup>-1</sup> <sub>dw</sub>	BAF (kg <sub>dw</sub> /kg <sub>ww</sub> or kg <sub>dw</sub> /kg <sub>dw</sub> <sup>(a)</sup> )	References
CdCl <sub>2</sub>	<i>Rana pipiens</i>	natural stream sediment; 250 g <sub>dw</sub> sediment (pH 7.9-8.4) or distilled deionized water (control) +350 ml reconstituted water	DO 6.6-8.1 mg L <sup>-1</sup> , T 22.1-22.5 °C, pH 7.9-8.4; sed: OM 2.3%, Cd <sub>T</sub> 1.02 mg kg <sup>-1</sup> , Zn <sub>T</sub> 108.2 mg kg <sup>-1</sup> , Hg <sub>T</sub> 0.052 mg kg <sup>-1</sup> , Fe <sub>T</sub> 5.52%; 5.52% sand, 35.4% silt, 12% clay	M	0.42	7	1	0.08	Francis et al., 1984
							10	0.034	
							100	0.0031	
	1000						0.013		
	<i>Micropterus salmoides</i>						1	0.18	
							10	0.072	
							100	0.15	
1000		0.006							

dw Dry weight basis;

ww Wet weight basis;

a) Dry weight basis;

SEM Simultaneously extractable metals. This is the sum of the metals cadmium, lead, nickel, zinc and copper in the sediment simultaneously extracted with the AVS and is expressed in µmol/g<sub>dw</sub>.; equilibration period: time of equilibration after spiking the pristine sediments or time of stabilisation after mixing the contaminated sediment and water, prior to exposure'.

### 3.2.7.5 Toxicity to mammalian and avian organisms

#### 3.2.7.5.1 Derivation of the PNEC<sub>oral</sub>

The TGD suggested method for risk assessment of secondary poisoning is based on modelling critical pathways such as the soil-worm-bird or water-fish-bird food chains (Romijn et al., 1994). The PNEC<sub>oral</sub> for mammals and birds is derived from feeding studies with Cd salt spiked diets. Nine feeding studies have been selected here (see **Table 3.242**). This compilation is based on sub-chronic and chronic studies and has excluded acute studies, mixed metal feeding studies and experiments where Cd was injected in the test animals. Four studies were selected with birds and 5 studies with mammals.

The PNEC<sub>oral</sub> can be calculated from the lowest NOEC using an assessment factor. The assessment factors for the feeding test are based on the TGD (TGD, 1996, p.350) and are 10 for the 90 day feeding test with mallard ducks (reproduction as endpoint) and 10 for the chronic study with monkey. The PNEC<sub>oral</sub> could also be calculated using statistical extrapolation. The underlying assumption is a log-logistic distribution of species sensitivity to dietary Cd (see **Table 3.241**). This approach has been used in the risk assessment of secondary poisoning of Spurgeon and Hopkin (1996) and Smit et al. (2000). No species mean NOEC's are calculated from the 2 studies with either rats and mallard ducks. The 2 studies on rats were performed with very different exposure time and the studies with mallard ducks have different endpoints. Averaging per species *increases* the HC<sub>5</sub> (50 and 95% confidence) of the mammal and bird data (not shown).

Table 3.241 Calculation of PNEC<sub>oral</sub> (mg kg<sup>-1</sup> food) using the assessment factor method (AFM) or the statistical extrapolation method (SEM; Aldenberg and Slob, 1993)

	AFM	SEM	
	NOEC/AF	HC <sub>5</sub> at 50% (and 95%) confidence	significance*
	mg kg <sup>-1</sup> food		
Mammals (n=5)	0.30	1.9 (0.14)	***
Birds (n=4)	0.16	0.75 (0.007)	***
Combined (n=9)	0.16	1.6 (0.35)	***

\* Goodness of fit;

\*\*\* Is significant at 1% level of significance.

- The assessment factor method invariably leads to the lowest PNEC<sub>oral</sub>. There is currently no guideline in the TGD to use the statistical extrapolation method to derive a PNEC<sub>oral</sub> and it is proposed to use the AF method as a first approach to assess secondary poisoning.

The suggested PNEC<sub>oral</sub> is therefore calculated as the lowest NOEC in the database and using and AF of 10, yielding

$$\text{PNEC}_{\text{oral}} = 0.16 \text{ mg kg}^{-1} \text{ fresh weight}$$

and is expressed as the fresh weight based Cd concentration in the food of the predator. Note that this PNEC is situated at the lowest NOEC of this database and which is the NOEC of the feedings studies with mallard ducks discussed above.

**Table 3.242** Mammalian and avian toxicity data from laboratory feeding studies. Concentrations are expressed per unit fresh weight of the food. Bold and underlined NOEC data are used to estimate the HC<sub>5</sub>

Test substance	Organism	Medium	Duration (d)	Endpoint	NOEC (mg Cd/kg)	Cat*	LOEC (mg Cd /kg) (%effect)	References
<b>Mammals</b>								
CdCl <sub>2</sub>	2.5 y old rhesus monkey <i>Macaca mulatta</i>	pelleted food	3,280 (9 y)	growth	<u>3</u>	1	10 (~25)	Masaoka et al., 1994
CdCl <sub>2</sub>	8 wk old Yorkshire barrows (pig) <i>Sus scrofa domestica</i>	diet: mixture of yellow corn, soybean meal, meat and bone meal, dehydrated alfalfa meal, trace minerals and vitamins	42	growth	<u>50</u>	1	150 (60)	Cousins et al., 1973
CdCl <sub>2</sub>	4 m old lamb <i>Ovis amon aries</i>	diet: mixture of primary corn, cotton seed hulls and soybean oil meal	191	growth	<u>15</u>	1	30 (20)	Doyle et al., 1974
CdCl <sub>2</sub>	rat <i>Rattus norvegicus</i>	basal animal diet: Altromin-R, powdered	728 (2y)	grth	<u>10</u>	1	50	Löser, 1980
CdCl <sub>2</sub>	5 wk old rat <i>Rattus norvegicus</i>	basal diet: wheat flour, casein, lard, minerals and vitamins	56	growth	<u>15</u>	2	30 (8)	Groten et al., 1991
<b>Birds</b>								
CdCl <sub>2</sub>	first-year adult mallard duck <i>Anas platyrhynchos</i>	commercial duck breeder mash coated with Cd dissolved in propylene glycol	90	spermatogenesis	<u>1.6</u>	1	15.2	White et al., 1978
CdCl <sub>2</sub>	1 d old mallard duckling <i>Anas platyrhynchos</i>	food	84	kidney lesion haemoglobin concentrations	<u>10</u> 10	1	20 20	Cain et al., 1983
CdSO <sub>4</sub>	6 m old White Leghorn laying hen <i>Gallus domesticus</i>	purified soybean-glucose diet	28	egg production	<u>12</u>	1	48 (39)	Leach et al., 1978
CdCl <sub>2</sub>	Japanese quail (after hatching) <i>Coturnix c. japonica</i>	purified basal diet (35% soybean protein)	42	growth	<u>38</u>	2	75(15)	Richardson et al., 1974

\* NOEC classification (see Section 3.2.1.2).

The risk of secondary poisoning of fish eating birds by Cd is predicted to be smaller than the direct effects of Cd in the aquatic environment (see Section 3.3). This is readily demonstrated using BCF's of fish in **Table 3.232**. Cadmium concentrations in whole fish at the proposed  $PNEC_{\text{water}} = 0.19 \mu\text{g Cd/l}$  (see Section 3.2.2.7) is predicted to range between 0.0001 and 0.12 mg Cd/kg fresh weight using the whole range of BCF's (0.5-623 l/kg fresh weight, **Table 3.232** and **Table 3.233**). These Cd concentrations are below the  $PNEC_{\text{oral}}$  for birds or birds and mammals. This assessment is made for freshwater systems and not for marine environments. Nephrotoxic lesions ascribed to Cd have been found in sea birds from areas that are relatively uncontaminated and where natural Cd may be the source (Nicholson et al., 1983; IPCS, 1992b). We propose that our assessment should not be used for the marine environment where the bioaccumulation of Cd differs from that in freshwater dominated systems.

The risk of secondary poisoning in the soil-worm-bird/mammal is predicted to be far more critical than the risk of soil Cd affecting plants, invertebrates or micro-organisms. This is readily demonstrated using the BAF's of Cd in earthworms (see **Table 3.236**). Cadmium concentrations in earthworms at the proposed  $PNEC_{\text{soil}} = 2.3 \text{ mg Cd/kg}$  (see Section 3.2.3.7) is predicted to range between 9.2 and 74 mg Cd/kg fresh weight using the whole range of BCF's (4-32 kg/kg fresh weight, see **Table 3.236**). All these concentrations are above the  $PNEC_{\text{oral}}$  of birds, mammals or birds and mammals and even overlap the LOEC range of the feeding studies.

The model for secondary poisoning of mammals and birds in the soil-worm-birds/mammals may, however, be questioned in case of Cd: concentrations of Cd in earthworms sampled in uncontaminated areas typically range between 1-10 mg Cd/kg fresh weight (see **Table 3.237**) and are generally higher than the  $PNEC_{\text{oral}}$  proposed here. It is either possible that soil Cd at background is indeed at risk for carnivorous mammals and birds or it is possible that the model that compares earthworm Cd with dietary Cd in feeding studies is overprotective. Beyer (2000) concluded on this approach that 'assessors have been overly cautious in evaluating toxicity of Cd'. Spurgeon and Hopkin (1996) used this model for risk assessment of secondary poisoning by Cd in the vicinity of a smelter and concluded that 'it is unlikely to describe risk to predators correctly'. Spurgeon and Hopkin (1996) have argued that the model is overly protective because of

- (I) the problems of quantifying the BAF: a mean BAF would overestimate earthworm concentrations at more contaminated sites because the BAF decreases with soil Cd (see, for example, **Figure 3.24**).
- (II) higher availability of Cd in metal salt spiked meals in the laboratory tests than Cd in worms
- (III) use of unrepresentative species for the predators

Other authors suggest that the model is not sufficiently protective and that additional safety factors should be used to account for differences in metabolic rate between laboratory and field animals, differences in caloric content between the laboratory diets and field prey, differences in food assimilation efficiency, differences in bioavailability of the toxic compound etc. (see Smit et al., 2000 for references).

One of the key assumptions in the model is that equal food Cd concentration leads to equal effects in laboratory animals and field animals. None of the laboratory tests reviewed here have fed earthworms to the animals as the principal source of Cd. Earthworms from even uncontaminated areas have Cd concentrations close to effect concentrations in Cd salt spiked laboratory meals. The assumption of equal effects at equal total Cd intake can be tested

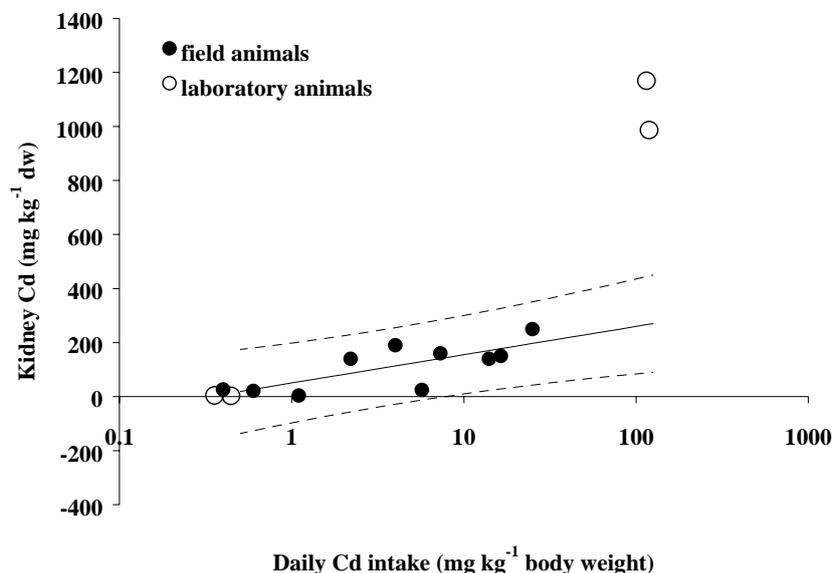
indirectly by comparing internal Cd dose (body burden) between laboratory and field animals at equal Cd intake. This comparison will be made here.

Cadmium intake by wildlife is probably most documented in shrews (*Sorex araneus*) because this mammal usually has a high Cd body burden (Hunter et al., 1989). Shrews have a high dietary Cd intake rate and feed on invertebrates active at the ground surface supplemented with soil dwelling macrofauna (Hunter et al., 1987b). Earthworms can be the major source of dietary Cd in shrews (Ma et al., 1991). Kidney Cd concentrations up to 550 mg kg<sup>-1</sup> dry weight have been observed in shrew (Hunter et al., 1989), i.e. close to critical concentration (see next section). Data on cadmium intake rates and body burden Cd have been compiled by Shore and Douben (1994) from 4 different studies. Kidney Cd concentrations increase with increasing Cd intake rate. This increase is linear at low intake rate but levels off at higher intake. Shore and Douben (1994) combined the data from four different studies and found a significant linear relation between the log Cd intake rate and the kidney Cd (see **Figure 3.25**, P<0.015). A laboratory feeding trial has been performed with shrew fed a CdCl<sub>2</sub> spiked diet (Dodds-Smith et al., 1992a&b). The body burden Cd (kidney Cd) after only 11 weeks exposure at the high Cd diets is significantly above that predicted by the log-linear regression line on field animals (see **Figure 3.25**). A drawback in this analysis is the extrapolation from the regression line since Cd intake rate in the laboratory trials is about fourfold higher than the highest Cd intake rate recorded in field shrew. Taken together, this analysis suggests that Cd is more available in laboratory spiked meals than in the diet of field animals.

A recent feeding study compared Cd availability to cattle from hay grown on a smelter affected substrate with hay spiked with Cd salts (spiking at corresponding concentrations). The kidney Cd of cattle fed hay grown on the smelter affected substrate was 3-fold above that of control animals whereas it was increased 12 fold in the Cd spiked hay treatment (Stuzynski et al., 2000). Clearly, Cd availability is higher in Cd salt spiked meals than in dietary Cd.

These arguments suggest that risk of secondary poisoning by Cd may be overestimated when based on Cd salt feeding studies. Therefore, an alternative approach will be used based on renal thresholds. The TGD allows that field data are used in this type of risk assessment provided that interpretation is made with caution (TGD 1996, p. 346). This effects assessment will only be made for mammals for which dose-response curves can be established. The assessment for terrestrial birds will be discussed in the risk characterisation because there no paired data of soil Cd /kidney Cd for birds were found.

Figure 3.25 Cd intake and kidney Cd in free living common shrew (*S. araneus*) and in laboratory cultivated shrew (control and Cd salt spiked diet). The log-linear regression and 95% prediction interval is made on field animal data (compilation of Shore and Douben, 1994). Data of laboratory animals is derived from Dodds-Smith et al. (1992 a&b)



### 3.2.7.5.2 An alternative approach for wildlife in the terrestrial environment based on renal thresholds

The alternative strategy to estimate the risks of secondary poisoning by Cd using renal threshold was formulated by Spurgeon and Hopkin, 1996. This strategy was not elaborated in that paper but this method was already adopted in pathway calculations of the US-EPA 503 sludge regulations (Chaney and Ryan, 1991).

The alternative method uses kidney Cd concentrations of wildlife as an indicator of Cd exposure and risk. The kidney is regarded as the critical organ in *chronic* Cd toxicity. With continued exposure, there is a continual increase in Cd concentration in the renal cortex until a critical value is reached and histopathological changes and renal dysfunction is found (proximal tubular cell necrosis, proteinuria and glycosuria; Scheuhammer, 1987 and references therein). This critical value should be regarded as a sublethal endpoint. The risk of secondary poisoning will be assessed by calculating the exposure at which this critical value is not exceeded for wildlife.

The proposed approach overcomes the uncertainties in the traditional approach which uses foodchain modelling (i.e. soil-worm-mammal modelling) because the proposed approach does *not* require assumptions about the diet (e.g. 100% earthworms) and about Cd bioavailability during transfer soil-food-wildlife (i.e. the BAF value and assumption of equal exposure at equal diet Cd between spiked meals and environmental Cd).

The *ecological relevance* of kidney damage as the critical endpoint in this assessment deviates from traditional endpoints such as growth or reproduction which have obvious ecological relevance. Indeed, the relationship between ecological fitness and kidney damage is unknown and which is the major difficulty in understanding effects of Cd in wildlife (Cooke and Johnson, 1996). The kidney has spare functional capacity and proteinuria or calciuria might be tolerated without progression to renal failure (Cooke and Johnson, 1996). Seabirds showing signs of nephrotoxicity were 'outwardly healthy' (Nicholson et al., 1983). A beaver population from the

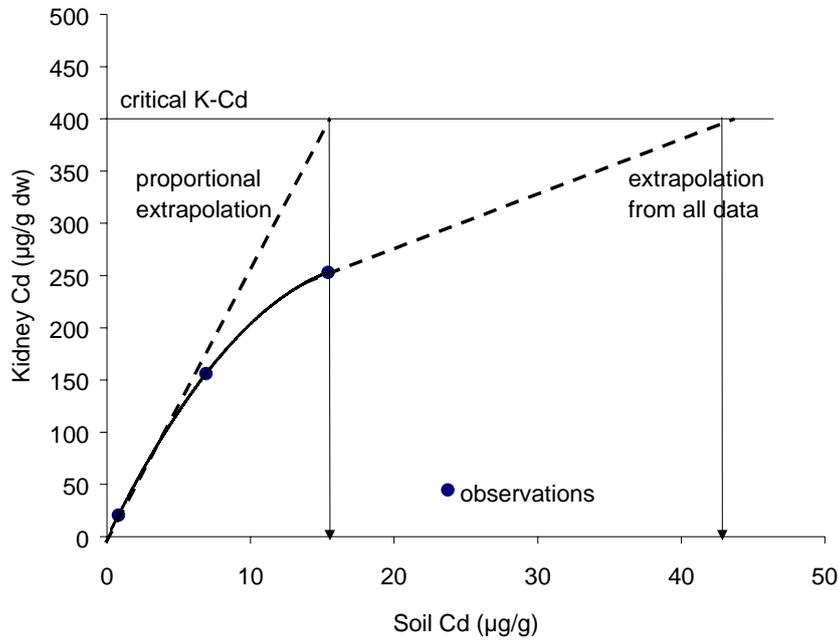
Mulde (a tributary of the Elbe in Germany) had average kidney Cd concentrations of 467  $\mu\text{g/g dw}$  (above the threshold proposed below). The fertility of this population was higher than 3 other population that had lower kidney Cd concentrations (Nolet et al., 1994). The authors conclude that the habitat quality seemed to determine the fertility and that Cd did not seem to interfere with fertility. Kidney damage in shrews (*S. araneus*) caught in a polluted smelter site was identified by electron microscopy although urine analyses showed no evidence for clinical renal dysfunction and animals were 'in good condition' (data of Hunter, 1984, quoted in Cooke and Johnson, 1996).

Dietary deficiencies can exacerbate Cd toxicity and one example was found where effects in wildlife due to Cd was related to kidney damage (as judged from exceedance of critical kidney Cd concentrations) and which was related to Ca deficiency (see bottom of this section: field validation). Therefore, we propose to use renal dysfunction as an endpoint with ecological relevance, realising that this endpoint leads to a more conservative approach than traditional endpoints in most conditions.

Kidney Cd of wildlife such as shrews, moles and badgers is markedly increased at sites with elevated Cd (Ma, 1987; Ma and Broekhuizen, 1989; Ma et al., 1991; Hendriks et al., 1995). Some of the wildlife field data do allow to estimate a dose (soil Cd) response (kidney Cd) slope. The critical soil Cd that is needed to reach the critical kidney Cd can be calculated with this slope. This critical soil Cd ( $\text{Cd}_{\text{soil,crit}}$ ) could then be considered as an acceptable concentration in soil assessed for secondary poisoning. This approach would only yield assessments based on animals for which kidney Cd data are available at different Cd exposure. Alternatively, critical soil Cd concentrations could also be derived based on a proportional extrapolation from any paired set of soil/kidney Cd concentration data, allowing to include more species in the assessment. **Figure 3.26** illustrates this approach. The proportional extrapolation method contains a safety factor since kidney Cd only increases proportionally with the dose at low concentrations. The less than proportional increase of kidney Cd with soil Cd is observed in most studies and may be explained by e.g. avoidance or metal interactions for Cd absorption (most gradient studies are derived from sites with mixed metal pollution).

Kidney-Cd concentrations of wildlife are compiled in **Table 3.243**. The data are mean or median Cd concentrations for 9 different mammal species (no data found for birds). Paired sets of soil Cd/kidney-Cd were found for 8 mammal species. Most of these studies have measured Cd concentrations at 2 or more locations differing in metal exposure (smelters).

**Figure 3.26** Two methods to estimate the critical Cd in soil (arrows) that would lead to critical Cd concentrations in the kidney of mammals: proportional extrapolation based on one data point (here: at lowest soil Cd) or extrapolation from a regression line fitted to all data. Data from Cd in common shrew (*S. araneus*) in a transect study (Hunter et al., 1989)



**Table 3.243** Kidney Cd concentrations in mammals and predicted critical soil Cd concentrations at which renal threshold (K-Cd) may be exceeded. Predictions are based on proportional extrapolation (Figure 3.26). Bold and underlined data are used for risk assessment

Species		Site	Soil pH	Soil Cd µg/g	Kidney Cd µg/g dw	Predicted critical soil Cd (µg/g)		Reference:	Remark
						Critical K-Cd 200 µg/g dw	Critical K-Cd 400 µg/g dw		
badger	<i>Meles meles</i>	NL			9-213 49-405			Ma and Broekhuizen, 1989	n=15: 4-5 y old animals, habitat not close to floodplains of Meuse n=9: 4-5 y old animals, habitat close to floodplains of Meuse
beaver	<i>Castor fiber</i>	NL		24	55(113 in adults)	42.5	<u>85 (adults based)</u>	Nolet et al., 1994	soil:0-5 cm: Biesbosch estuary: young animals-modelling predicts K-Cd = 113 mg kg <sup>-1</sup> dw in adults
		DE			467	-	-		Elbe region: Mulde (adults)
		DE		-	50	-	-		Elbe region: Elbe (adults)
		DE		-	30	-	-		Elbe region: Elbe (adults)
		DE		-	20	-	-		Elbe region: Elbe (adults)
				-		-	-		Elbe region: Heide (adults)
common shrew	<i>Sorex araneus</i>	UK	5.2	0.6	10.9	11.0	22.0	Read and Martin, 1993	soil: litter layer: K-Cd in mature animals
			5.4	1	37	5.4	10.8		
			4.4	2	9.3	43.0	86.0		
			5.05	1.7	41.3	8.2	16.5		
			4.9	3.3	154	4.3	<u>8.6</u>		
			4.85	19.9	142	28	56.1		
common shrew	<i>Sorex araneus</i>	UK		0.8	20.5	7.8	<u>15.6</u>	Hunter et al., 1989	soil: 0-5 cm
				6.9	156	8.8	17.7		
				15.4	253	12.2	24.3		

Table 3.243 continued overleaf

**Table 3.243 continued** Kidney Cd concentrations in mammals and predicted critical soil Cd concentrations at which renal threshold (K-Cd) may be exceeded. Predictions are based on proportional extrapolation (Figure 3.26). Bold and underlined data are used for risk assessment

Species		Site	Soil pH	Soil Cd µg/g	Kidney Cd µg/g dw	Predicted critical soil Cd (µg/g)		Reference:	Remark
						Critical K-Cd 200 µg/g dw	Critical K-Cd 400 µg/g dw		
common shrew	<i>Sorex araneus</i>	UK		0.75	25.7	5.8	11.7	Hunter and Johnson, 1982	soil: 0-5 cm
				3.1	139	4.5	<u>8.9</u>		
				8.5	193	8.8	17.6		
common shrew	<i>S. araneus</i>	NL	6.1	2.9	126-200	2.9	<u>5.8</u>	Ma et al., 1991	soil: 0-10 cm, A <sub>0</sub> horizon Cd is 5.5 µg/g; range of means in season
			3.5	0.3	14-51	1.2	<u>2.4</u>		soil: 0-10 cm, A <sub>0</sub> horizon Cd is 1.2 µg/g; range of means in season
common shrew	<i>Sorex araneus</i>	NL		1.8	11	32.7	<u>65.5</u>	Hendriks et al., 1995	soil: 0-20 cm; Rhine floodplains
				6.4	21	61.0	121.9		
cottontail rabbit	<i>Sylvilagus floridanus</i>	U.S.		-6	166	7.2	14.5	Storm et al., 1994	Palmerston-site: soil: A1 horizon
				-60	380	31.6	63.2		
				-10	284	7.0	<u>14.1</u>		
cottontail rabbit	<i>Sylvilagus floridanus</i>	U.S.		0.1	5.3	3.8	<u>7.5</u>	Dressler et al., 1986	soil: 0-15 cm
				0.4	12.3	6.5	13.0		soil: 0-15 cm; soil received sludge
field vole	<i>Microtus agrestis</i>	UK		0.8	1.7	94.1	188.2	Hunter et al., 1989	soil: 0-5 cm
				6.9	23.9	57.7	115.5		
				15.4	88.8	34.7	<u>69.4</u>		
field vole	<i>Microtus agrestis</i>	UK		0.75	1.3	115.4	230.8	Hunter and Johnson, 1982	soil: 0-5 cm
				3.1	4.06	152.7	305.4		
				8.5	23.3	73.0	<u>145.9</u>		

Table 3.243 continued overleaf

**Table 3.243 continued** Kidney Cd concentrations in mammals and predicted critical soil Cd concentrations at which renal threshold (K-Cd) may be exceeded. Predictions are based on proportional extrapolation (Figure 3.26). Bold and underlined data are used for risk assessment

Species		Site	Soil pH	Soil Cd µg/g	Kidney Cd µg/g dw	Predicted critical soil Cd (µg/g)		Reference:	Remark
						Critical K-Cd 200 µg/g dw	Critical K-Cd 400 µg/g dw		
field vole	<i>Microtus agrestis</i>	NL	6.1	2.9	1-3	193.3	<u>386.7</u>	Ma et al., 1991	soil: 0-10 cm, A <sub>0</sub> horizon Cd is 5.5 µg/g; range of means in season
			3.5	0.3	0.1-0.3	200.0	<u>400.0</u>		soil: 0-10 cm, A <sub>0</sub> horizon Cd is 1.2 µg/g; range of means in season
mole	<i>Talpa europea</i>	NL	5.2	1.7	112	3.0	<u>6.1</u>	Ma, 1987	soil: 0-10 cm; Budel pasture
			6	6	224	5.4	10.7		
			6.5	9.2	221	8.3	16.7		
			4.1	0.3	186	0.3	<u>0.6</u>		soil: 0-10 cm; Budel heath site
mole	<i>Talpa europea</i>	FI			186			Pankakoski et al., 1993	Helsinki metropolitan area, adult animals only
					82				rural area, adult anim pproacy
pygmy shrew	<i>Sorex minutus</i>	UK	5.2	0.6	7.9	15.2	<u>30.4</u>	Read and Martin, 1993	soil: litter layer; K-Cd in mature animals
			5.4	1	5.9	33.9	67.8		
			4.4	2	7.9	50.6	101.3		
			5.05	1.7	12.1	28.1	56.2		
			4.9	3.3	18.7	35.3	70.6		
			4.85	19.9	49.9	79.8	159.5		
white-tailed deer	<i>Odocoileus virginianus</i>	U.S.		6-100	70	17.1	<u>34.3</u>	Storm et al., 1994	Palmerston-site: soil A1 horizon
woud mouse	<i>Apodemus sylvaticus</i>	UK		0.8	2	80.0	160.0	Hunter et al., 1989	soil: 0-5 cm
				6.9	8.5	162.4	324.7		
				15.4	41.7	73.9	<u>147.7</u>		

Table 3.243 continued overleaf

**Table 3.243 continued** Kidney Cd concentrations in mammals and predicted critical soil Cd concentrations at which renal threshold (K-Cd) may be exceeded. Predictions are based on proportional extrapolation (Figure 3.26). Bold and underlined data are used for risk assessment

Species		Site	Soil pH	Soil Cd µg/g	Kidney Cd µg/g dw	Predicted critical soil Cd (µg/g)		Reference:	Remark
						Critical K-Cd 200 µg/g dw	Critical K-Cd 400 µg/g dw		
woud mouse	<i>Apodemus sylvaticus</i>	UK		0.75	1.46	102.7	<u>205.5</u>	Hunter and Johnson, 1982	soil: 0-5 cm
				3.1	5.5	112.7	225.5		
				8.5	7.4	229.7	459.5		

### Critical concentration of Cd in kidney

There are several reviews of the critical kidney Cd concentrations in laboratory animals (IPCS, 1992a), small mammals (Cooke and Johnson, 1996) and birds (Furness, 1996). The individual studies will not be discussed here but attention will be given to the conflicting evidence that has suggested lower limits.

The WHO has reviewed several studies on test animals (mouse, rat, rabbit, pig, horse, monkey and bird; IPCS, 1992a). Histological tubular lesions are usually observed at 200-300 µg Cd/g wet weight. In some studies on rats, monkeys, horses and birds certain effects were seen at lower levels. The WHO concludes that 'if one wishes to establish a range of values for the critical concentration in individuals at which a small but significant part of the exposed population will show effects, animal studies indicate that a renal cortex level of about 100-200 µg/g wet weight is likely to coincide with such a range' (IPCS, 1992a). This range corresponds with whole kidney, dry weight based values of 400-800 µg/g dw (wet weight concentrations are about 0.2 time dry weight concentrations and whole kidney concentrations are about 0.8 times kidney cortex values).

There are reports of kidney damage in wildlife at concentrations below the range suggested by WHO. Nicholson et al. (1983) identified nephrotoxicity in seabirds at whole kidney concentrations of 100-200 µg/g dw, about fourfold lower than the WHO criterion. Kidneys, however, also contained Hg (5-15 µg/g dw). Starlings were injected CdCl<sub>2</sub> and showed similar kidney lesions compared to the seabirds at comparable tissue Cd concentrations. However, the Cd dosed animals may not be representative for the seabirds because of the acute exposure of the test animals. Chmielnicka et al. (1989) suggested that the WHO criterion should be revised after identifying nephrotoxicity in Cd dosed rats at kidney Cd concentrations of 30 µg/g wet weight (about 120 µg/g dw). However, this study was also based on an acute dose (injections during 8 weeks and histopathological effects in the liver after only 2 weeks), suggesting that it may not be relevant for a realistic chronic exposure (Beyer, 2000). Leffler and Nyholm (1996) reported nephrotoxicity in bank voles (*Clethrionomus glareolus*) collected close to the smelter in Rönnskärsverken (Sweden) and in a control site. The voles from the contaminated area had increased proteinuria and increased kidney Cd concentrations. The proteinuria was identified at only 4 µg/g wet weight (whole kidney, about 20 µg/g dw). A comment on that paper was written by Elinder (1997) about the very low value at which nephrotoxicity was found. Elinder concluded that this study was confounded, basically because the voles urinated more in the contaminated site. The authors have responded to this comment that other factors (other metals, biotope characteristics) may also have been involved in the proteinuria (Nyholm and Leffler, 1997).

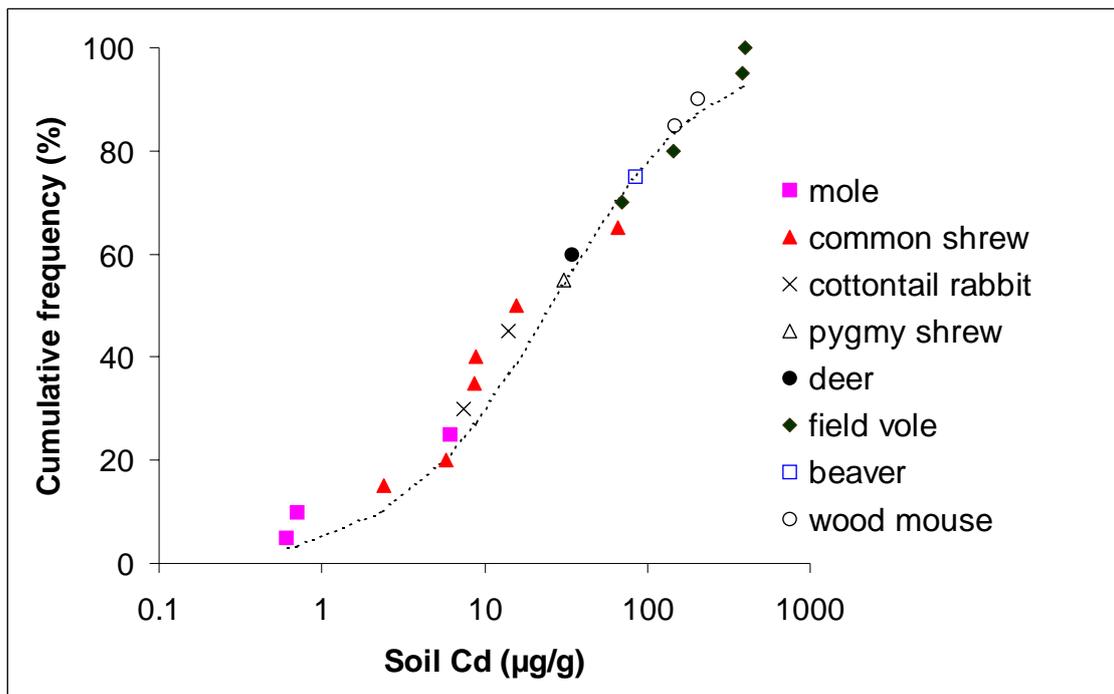
We propose to use the lower limit of the WHO suggested critical range of Cd concentration for our assessment, i.e. 100 µg Cd/g wet weight in the renal cortex or 400 µg Cd/g dw. The WHO suggested range is based on the largest review of animal data and Cooke and Johnson (1996) similarly suggested 100 µg Cd/g wet weight as a critical concentration. This RAR repeats the WHO conclusions that mean renal cortex Cd should reach 200 µg/g wet weight to observe tubular proteinuria (see Section 4 of this report in a separate document). There is indeed conflicting evidence suggesting lower limits (Nicholson et al., 1983, Chmielnicka et al., 1989 and Leffler and Nyholm, 1996) but there are arguments that these studies may be less relevant for chronic exposure to Cd-only contamination in wildlife (see above).

### Critical soil Cd concentrations for wildlife

The critical soil Cd concentration is defined as that concentration at which a critical kidney Cd concentration of 400  $\mu\text{g/g dw}$  (whole kidney) is predicted using a proportional extrapolation from each paired soil/kidney Cd concentration set (see **Figure 3.26**). The lowest critical soil Cd concentration was selected from each transect study or when only a range in soil or kidney Cd concentrations was available (see **Table 3.243**). Different values were derived from the studies of Ma because the soil properties were markedly different between sites, clearly leading to different Cd exposure (see **Table 3.243**). Twenty (20) values of critical Cd concentrations were derived from 8 different mammal species. The frequency distribution of the 20 values illustrates that moles and shrews typically have high kidney Cd concentrations which is related to the high Cd intake rate (see **Figure 3.27**).

This compilation of field data will be used to derive a critical soil Cd concentration for terrestrial mammals ( $\text{Cd}_{\text{soil, crit}}$ ). We propose to derive this value with statistical extrapolation. The distribution of values (see **Figure 3.27**) reflects site specific species sensitivity if it is assumed that there are no differences in renal threshold between species. In this regard, this distribution is conceptually equal to a distribution of Cd thresholds from toxicity tests in soil.

**Figure 3.27** Cumulative frequency of the critical soil Cd concentration at which the critical kidney Cd concentration (400  $\mu\text{g/g dw}$ ) may be exceeded in the average population of different species. The line is the log-logistic curve fitted on all individual data



**Table 3.244** Prediction of critical soil Cd for terrestrial mammals based on values at which the critical kidney Cd concentration (400 µg/g dw) may be exceeded in the average population of different species. The critical soil concentrations is either the lowest value in the database or the HC<sub>5</sub> predicted by statistical extrapolation (Aldenberg and Slob, 1993)

	Lowest value	Statistical extrapolation (log-logistic model)	
		HC <sub>5</sub> at 50% (and 95% confidence interval)	significance <sup>*</sup>
Critical soil Cd (µg/g)			
all data selected in Table 3.243 (n=20)	0.6	0.9 (0.2-2.3)	***
Excluding data from soils with pH < 4.2 (n=16)	5.8	3.3 (1.0-7.1)	***
Geometric means of species (n=8)	1.4	1.5 (0.1-5.7)	***

<sup>\*</sup> Goodness of fit;

\*\*\* Is significant at 1% level of significance.

The statistical extrapolation method (log-logistic distribution) predicts that the HC<sub>5</sub> for protecting mammals is 0.9 µg/g. The HC<sub>5</sub> is higher when based on species mean values. Averaging data is not defensible: the data of Ma (1987, moles) and Ma et al. (1991, shrews) have shown that soil acidity leads to higher Cd concentration in the prey (earthworms) and higher body burden in the predator. Averaging data leads to a loss of information and species may not be protected in these soils. If the data from soils with reported pH < 4.2 are excluded (i.e. 4 values excluded), the HC<sub>5</sub> increases from 0.9 to 3.3 µg Cd/g. Ma and van der Voet (1993) successfully predicted the Cd exposure to shrew for different values of soil pH and % organic matter. This model is useful to derive soil criteria that vary with soil properties. The model has not been incorporated in our assessment because it was validated with only 1 predator species and because soil properties are unknown for most other data. However, this generic HC<sub>5</sub> overestimates the risk associated to wildlife in pH neutral soils as indicated by the monitoring data of moles from Ma, 1987: while kidney Cd is already at 200 µg/g dw in acid soils near soil background values (0.3 µg/g), these kidney Cd concentrations are only found in pH neutral soils at soil Cd concentrations > 6 µg/g and which is well above the HC<sub>5</sub> of 0.9 µg/g.

The HC<sub>5</sub> for protecting mammals is about twofold *below* the PNEC<sub>soil</sub> derived for protecting plants, soil fauna and microflora. Effectively this assessment suggests that biotransfer of Cd from soil to higher trophic levels is the most critical pathway for Cd. This HC<sub>5</sub> value is mainly driven by the data on moles by Ma (1987) and, to a lesser extent, by data on shrews (Ma et al., 1991) and are valid for acid soils (soil pH < 4.1, see **Table 3.243**). These soils are relatively uncontaminated, i.e. the predicted critical soil Cd concentrations derived from these data contain a safety factor due to the proportional extrapolation. No data were found on moles or shrews in soils that are acid and that contain high Cd concentrations.

Assessment of secondary poisoning is obviously very complex. There is currently only little field evidence that attributes pathological injury to Cd (Beyer, 2000). This assessment here reveals that Cd may have a potential risk to mammals at only moderate soil Cd concentrations. Before reaching conclusions, this assessment should be evaluated. The assessment may underestimate risk for mammals because:

- the value of the renal threshold (400 µg/g dw) that may be too high according to some studies (see previous section for a discussion).

- the assumption that the renal threshold is the same for all species. There is, however, currently no evidence suggesting that this is the case (Beyer, 2000).
- average kidney Cd data of populations were used, and not upper percentiles. Effectively, the assessment would protect the average population of a species and not individuals. Some source documents have reported individual data. The number of individuals with kidney Cd concentrations above 400 µg/g dw is small and we have not found such values reported below the soil HC<sub>5</sub> = 0.9 µg/g (details not shown).

On the other hand, this assessment has used margins of safety because:

- critical soil Cd concentrations are predicted by the proportional extrapolation (see **Figure 3.26**) and the lowest value was chosen from each study. The critical kidney Cd is never reached at or beyond the predicted ‘critical soil Cd concentrations’ in each transect. As an example, the critical soil Cd for the common shrew predicted from the transect study of Hunter et al. (1989) is 15.6 µg Cd/g (see **Table 3.243**). The observed kidney Cd at the largest soil Cd (15.4 µg Cd/g) is 253 µg/g, i.e. only 60% of the critical kidney Cd. A proportional extrapolation from the data at the highest Cd concentration predicts that soil Cd should reach 24.3 µg Cd/g before the critical kidney Cd is reached. This means that the most conservative critical soil Cd estimate (15.6 µg/g) has a margin of safety of 1.6 (=24.3/15.6) or higher (**Figure 3.26** suggests a factor of about 3). The HC<sub>5</sub> is driven by data where the kidney Cd was still below the renal threshold. In addition, there is only 1 documented population with a mean/median kidney Cd concentrations above the renal threshold (the beaver population in the contaminated Elbe region, no soil Cd concentration known).
- the renal dysfunction is a sublethal endpoint and field data suggest that its relationship with ecological fitness still has to be demonstrated (Cooke and Johnson, 1996). One study was found for birds where ecological effects can be related to renal dysfunction at kidney Cd concentrations above the proposed kidney threshold (see below: field validation).
- the HC<sub>5</sub> is driven by indicator organisms that are, probably, more documented than non-indicator organisms.
- the HC<sub>5</sub> is driven by the mole and shrew thresholds applicable to acid sandy soil (pH 4.2) and which represent a reasonable worst case scenario. The HC<sub>5</sub> excluding these soils is > 3 fold above the ‘generic’ HC<sub>5</sub>.

### *Field validation*

Cadmium toxicity (ecological effects) towards wildlife in the field was recently reported for the white-tailed ptarmigan *Lagopus leucurus* (bird) in a Cd contaminated area of the Colorado Rocky Mountains (Larison et al., 2000). Evidence for ecological effects related to Cd are: increased mortality in the contaminated area for the adult female birds compared to that in an uncontaminated area, higher mortality for metal-contaminated ptarmigans and a distinctly lower female:male ratio in the adult population in the contaminated area. Ptarmigans are herbivorous and commonly eat willow buds and recently grown shoots of willow, both food items that are elevated in Cd but low in calcium. The low calcium diet exacerbates Cd poisoning as shown for humans (Chapter 4). Elevated kidney Cd (> 400 µg/g dw, i.e. above the threshold chosen here) was found in adult birds in the contaminated area and which was associated with 8-10% lower bone calcium (and more fragile bones) compared to values in individuals with kidney Cd < 400 µg/g dw. The calcium metabolic disorders may be related to renal tubular damage. The larger effects on adult females than on males is explained by the foraging habitat of females that dwell longer in the Cd contaminated area than males and by their larger calcium demand for egg-laying females. Soil Cd concentrations are not directly reported in that study. The area is known

as the Colorado ore-belt and well over a thousand mines, mostly abandoned, are situated there. The rocks and mineralised materials in the mining area contain, on average,  $75 \mu\text{g Cd/g}_{\text{dw}}$ . The concentrations of Cd encountered in the surface waters and sediments of that area are  $> 5 \mu\text{g L}^{-1}$  and  $15.2 \mu\text{g Cd/g}_{\text{dw}}$  (Nash et al., 2001 and Church et al., 2000). All these data show that environmental Cd concentrations are  $> 7$ -fold above corresponding EU average (see Section 3.1.3.4) suggesting that also the soil Cd is  $> 7$  fold above EU average (i.e. soil Cd  $> 2.1 \mu\text{g Cd/g}_{\text{dw}}$ ). That soil Cd value is above the generic HC<sub>5</sub> of  $0.9 \mu\text{g Cd/g}_{\text{dw}}$ .

### Conclusion

We propose a critical soil Cd concentration to protect mammals from soil borne Cd as

$$\text{Cd}_{\text{soil,crit}} = 0.9 \mu\text{g Cd/g}_{\text{dw}}$$

which is the HC<sub>5</sub> of values at which the critical kidney Cd concentration ( $400 \mu\text{g/g dw}$ ) may be exceeded in the average population of 8 different species. This value is driven by the mole and shrew thresholds derived from data valid for acid sandy soils (pH 4.2). This value is below the PNEC<sub>soil</sub> for direct effects on higher plants, soil fauna or soil microbial processes. The risk characterisation of Cd in soil should be based on protecting mammals.

### 3.3 RISK CHARACTERISATION

#### 3.3.1 Introduction

The risk characterisation is based on a comparison of the PEC with PNEC values. **Table 3.245** summarises the PNEC values that were calculated in the effects assessment (see Section 3.2).

Table 3.245 The PNEC values derived in Section 3.2

	Value	Units	Remark
PNEC <sub>water</sub>	0.19	µg Cd/L	dissolved fraction
PNEC <sub>water</sub>	$0.09 * (H/50)^{0.7409}$	µg Cd/L	for refined risk characterisation if hardness is known (see Section 3.2.2.6.4); dissolved fraction; not to be used below H=40
PNEC <sub>soil</sub>	1.15-2.3	mg Cd/kg <sub>dw</sub>	based on ecotoxicity
PNEC <sub>soil</sub>	0.9 (selected)	mg Cd/kg <sub>dw</sub>	based on secondary poisoning to mammals (local and regional)
PNEC <sub>sediment</sub>	2.3	mg kg <sup>-1</sup> <sub>dw</sub>	PNEC is not corrected for bioavailability AVS and OC based normalisation could be used for regional as well as site-specific risk characterisation
PNEC <sub>micro-organisms</sub>	20	µg Cd/L	dissolved fraction only
PNEC <sub>oral</sub>	0.16	mg Cd/kg <sub>diet fw</sub>	birds/mammals

Different effects assessments have led to different PNEC<sub>soil</sub> values for local risk estimates. The lowest PNEC for soil is based on the assessment of secondary poisoning to mammals. The risk of secondary poisoning is conventionally assessed separately from the direct toxic effect because the predators do not sample 100% of their food in the local environment. However, the PNEC<sub>soil</sub> for secondary poisoning is determined by effects on organisms with a reasonably small habitat (moles and shrews) and we propose that local soil Cd concentrations should not exceed this PNEC as well. Therefore the PNEC<sub>soil</sub> = 0.9 mg kg<sup>-1</sup> is proposed for local risk assessment.

#### 3.3.2 Risk characterisation for production and use (excluding batteries)

##### 3.3.2.1 The aquatic compartment (including sediment and STP)

The risk factors (PEC/PNEC ratio) for local water (dissolved fraction) and sediment concentrations are given in **Table 3.246**. The PNEC was not corrected for water hardness because of lack of site-specific water hardness information. No bioavailability corrections were made for Cd in sediment because of lack of useful site-specific information.

**Table 3.246** Local risk characterisation for water and sediment. The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L and the PNEC<sub>sediment</sub> is 2.3 mg Cd/kg<sub>dw</sub> (Table 3.245). The factor risk for sediments is calculated for the concentration of added Cd (C<sub>local</sub>sediment, Table 3.85) and for the added and regional Cd (total Cd, i.e. PEC<sub>local</sub>sediment, Table 3.85) without correction for bioavailability

Category	N°	PEC <sub>local</sub> <sub>water</sub> µg L <sup>-1</sup>	Factor risk water	Factor risk sediment		year
				Added	Total	
Cd-production	1	1.37	7.2	71.2	72.3	1996
	2	0.59	3.1	26.7	27.9	1996
	3*	0.15*	0.8*	1.9	3.1	1996
	4*	0.52*	2.7*	23	24.2	1996
	5	5.5	29	307	307.7	1996
	6	0.11	0.6	0.0	1.2	1996
	7 <sup>£</sup>	0.32*	1.7*	11.5	12.7	1996
	8	0.12	0.7	0.6	1.8	1996
	9*	0.13*	0.7*	0.8	2.0	1999
	10	0.11	0.6	0.0	1.2	1996
	11	0.11	0.6	0.0	1.2	1996
	13*	0.69*	3.6*	33	33.7	1996
	CdO-producers	11	0.11	0.6	0.0	1.2
12		0.11	0.6	0.0	1.2	1993
Cd-stabilisers	F	0.11	0.6	0.0	1.2	1996
	G	0.29	1.5	10.0	11.1	1996
	H	0.14	0.7	1.5	2.7	1996
	I	0.13	0.7	0.7	1.9	1996
	J	0.11	0.6	0.0	1.2	1996
	K	0.69	3.6	32.7	33.9	1996
	L	0.11	0.6	0.0	1.2	1996
	M	0.11	0.6	0.0	1.2	1996
	windows manufacturer	0.11	0.6	0.0	1.2	1996
Cd-pigments	A	0.26	1.4	8.2	9.3	1996
	B	0.11	0.6	0.0	1.2	1996
	C	0.15	0.8	2.3	3.4	1996
	D	0.14	0.8	1.7	2.8	1996
	E	0.11	0.6	0.0	1.2	1996
Cd-plating	EU	2.9	15	155.2	156.3	1996
Cd-alloys	EU	1.81	9.5	95.8	97	1996

\* Emission to the sea;

n.a. Not available;

£ Recently delivered data were not yet taken into account, this will be done during the development of the Risk Reduction Strategy.

The table predicts elevated risks for the aquatic ecosystem at 11 locations/scenarios and risk to benthic organisms at all sites/scenarios. The risk for the Cd alloy processing sites is based on a generic scenario (see Section 3.1.2.1.1).

High risks are estimated for the sediment on the basis of PEC and PNEC values without correction for bioavailability, irrespective of the use of added or total Cd concentrations ( $C_{local, sediment}$  or  $PEC_{local, sediment}$ ). Moreover, several sites in the production and processing area have a risk for benthic organisms irrespective of the regional background (see local added Cd,  $C_{local, sediment} > PNEC_{sediments}$ ).

#### *Emissions to freshwater*

There are 6 sites (covering 3 scenarios) and 2 further scenarios with risk factors above 1 based on calculated local concentrations. Measured Cd concentrations (see **Table 3.84**) in the receiving water remove some concern for two of the three sites where data are available: risk factors reduce to 5.6 (site 1), and 0.5 (site 2). The latter value, although measured, is judged less reliable than the calculated because it relates to a previous year (< 1996), is rather poorly documented and is therefore of questionable representativeness for the reference reporting year (1996). Risk at the Cd producing plant 5 is high (risk factor 29). This risk is substantiated by the measured Cd concentration ( $5 \mu\text{g L}^{-1}$ ) which corresponds very well with the calculated  $PEC_{local}$  ( $5.5 \mu\text{g L}^{-1}$ ). An unknown factor in the risk assessment is the sedimentation rate of Cd after the on-site STP. This factor is not included here and may be of importance for an improved risk characterisation. The variability of the  $PEC_{regional}$  (which is added to  $C_{local}$  to estimate the  $PEC_{local}$ ) can only add to the uncertainty of the risk for these sites where the added Cd ( $C_{local}$ , see **Table 3.5**) is below the PNEC, i.e. at 2 sites (site G and A). However, the difference between  $C_{local}$  and the PNEC is  $< 0.05 \mu\text{g L}^{-1}$ , which is a small value for a regional PEC. Therefore, the uncertainty about the  $PEC_{regional}$  is unlikely to be of importance for the risk characterisation at these sites.

#### *Emissions to the sea*

Using the PNEC freshwater risk factors are above 1 at the Cd producing plants 4, 7 and 13 that emit effluents to the sea. Measured Cd concentrations (see **Table 3.84**) at site 7 reduce the risk factor to below 1 but increase concern at site 4 and 13 (risk factor up to 16). However, this risk characterisation is only indicative as no PNEC was derived for marine species.

Based on PECs and PNEC without correction for bioavailability, the risks for benthic organisms are elevated at all sites. Risk is always predicted even if emissions are zero because the regional Cd concentration in sediment is above the  $PNEC_{sediment}$  (i.e.  $2.3 \text{ mg kg}^{-1}_{dw}$ ). The regional Cd concentration in sediment is the 90<sup>th</sup> percentile of measured data. At 15 producing and processing sites/areas there is a predicted risk irrespective of the regional background (see local added Cd,  $C_{local, sediment} > PNEC_{sediments}$ ). Measured local Cd concentrations (not available) could remove concern. Moreover, the risk characterisation could also be refined by including indicators of Cd bioavailability. This can be achieved by measuring the organic carbon normalised excess of SEM over AVS. This refinement should use a worst case approach to account for seasonal variation in AVS and it is suggested that the AVS approach should be further validated (see Section 3.2.4.3) (**conclusion (i)**). Furthermore, an uncertainty analysis regards the impact of an EU-wide variability in  $PEC_{regional}$  (as a default approach in the absence of site-specific data) on the risk characterisation at local level, is not yet included. Both aspects, bioavailability and variability impact, will be implemented in an update of the risk assessment report once the results of the **conclusion (i)** program are agreed at TC NES level (see separate document, 'RAR Stage II').

The risk for micro-organisms in sewage treatment plants is investigated for on-site as well as off-site sewage treatment plants (STP).

#### *On-site waste water treatment plants*

Information from the specific production and processing sites indicates that methods to remove cadmium from discharge to water are generally in place. However, no detailed data are available. The ratio of the effluent Cd concentration (see **Table 3.1**) to PNEC micro-organisms (see **Table 3.245**) predicts risk to the on-site STP for a number of sites in the production area (Cd metal) and in the processing areas, pigments, plating and alloys. The risk ratio ranges from 0.02 to 22 and is higher than 1 at 14 locations. There is a possibility that risk is overpredicted. Several toxicity tests (including sludge respiration test) showed that Cd affects micro-organisms of an STP at only about 1 mg Cd/L in the dissolved fraction (see Section 3.2.6). The  $PNEC_{STP}$  was calculated from the lowest NOEC using an assessment factor, yielding a  $PNEC_{micro-organisms}$  that is about 50-fold below the lowest LOEC and where sludge respiration was less than 30% affected (see Section 3.2.6). There is only 1 site (site 2 of the Cd producers) where the lowest NOEC is exceeded. Measured data may remove the concern. Wastewater treatment at the plants in the Cd metal production area are based on physical-chemical principles only (see also IPPC report on the best available techniques in the non ferrous metals industries, May 2000). Therefore, it is proposed that the conclusions related to the risk for micro-organisms in the on-site WWTP (STP) are considered as indicative only and are not taken forward to the section 5 (general conclusions).

#### *Off-site waste water treatment plants (municipal sewage treatment plants)*

For producers of Cd metal and CdO, no discharge occurs to municipal sewage system, as these sites do emit to surface/sea water or do not emit at all to the aquatic compartment<sup>52</sup>. Therefore, the risk assessment of Cd and CdO producers for off-site STP is not relevant. Risk to off-site STP is only relevant for the processors that potentially have emissions to sewer systems. Only three stabiliser production-sites have not reported flows of receiving water (see **Table 3.1**). The Cd concentration in the effluent of these sites is already lower than the  $PNEC_{micro-organisms}$  suggesting no risk. The Cd plating and alloy scenario can potentially emit to off-site STP and the predicted Cd concentrations in the effluent is 0.081 and 0.05 mg Cd/L, respectively (**Table 3.1**). Assuming no further dilution in the STP (i.e. default effluent flow of 2,000 m<sup>3</sup> day<sup>-1</sup> and default STP capacity of 2000 m<sup>3</sup> day<sup>-1</sup>) and assuming 60% removal rate in STP, there remains still a risk (risk factor 1.6 (=0.0324/0.02) and 1.0 (=0.02/0.02)<sup>53</sup>). Apart from requests via the Lead company, no attempt was made by the Rapporteur to actively retrieve detailed data directly from the concerned sector. The predicted Cd concentrations in the effluents of the Cd pigment scenarios range from 0.002 to 0.08 mg Cd/L (**Table 3.1**). Assuming no further dilution in the STP (i.e. default effluent flow of 2,000 m<sup>3</sup> day<sup>-1</sup> and default STP capacity of 2,000 m<sup>3</sup> day<sup>-1</sup>) and assuming 60% removal rate in STP, there is a risk for the Cd pigment scenario with the highest Cd concentration in the effluent (Risk factor 1.6 (=0.032/0.02): **conclusion (iii)**).

<sup>52</sup> For Cd metal producers: Industry statements, Zinc RAR; for CdO producers: no release of water effluent.

<sup>53</sup> There is no dilution of the plating effluent in the water treatment plant in this scenario. As a dilution of 2 would remove the risk, UK suggested that it would be worth trying to obtain information on possible water volumes from that use (UK EA comments, Jan. 2003).

## Regional and continental Cd concentrations

### *Calculated values*

The predicted Cd concentrations in water have been calculated for a range in K<sub>p</sub> values (see **Table 3.157**). At the average K<sub>p</sub> values, the PEC/PNEC ratio's are 0.6 (regional) and 0.3 (continental). The PEC's are larger if the K<sub>p</sub> is lower. At the lowest value of K<sub>p</sub> (17 10<sup>3</sup> L kg<sup>-1</sup>) PEC/PNEC ratio's are 1.8 (regional) or 1.7 (continental). The predicted concentrations in sediment have also been calculated for a range of K<sub>p</sub> values. At the average K<sub>p</sub> values, the PEC/PNEC ratio's are 4.4 (regional) and 1.4 (continental). The PEC's are lower if the K<sub>p</sub> is lower. At the lowest value of K<sub>p</sub> (17 10<sup>3</sup> L kg<sup>-1</sup>) PEC/PNEC ratio's are 3 (regional) or 1.3 (continental). At the largest value of K<sub>p</sub> (224 10<sup>3</sup> L kg<sup>-1</sup>) PEC/PNEC ratio's are 4.5 (regional) and 1.4 (continental).

### *Measured values*

It is proposed to refine the risk characterisation with measured data which may be more relevant given the uncertainties in emissions, their geographical distribution, the wide range in natural environments, contributions from historic pollution etc.

### *Water*

Two assessment methods and a sensitivity analysis are presented. First of all, data from an EU-wide survey have been assessed. The FOREGS Geochemical Baseline Program (FGBP) study determined a mean Cd concentration in European surface waters of 0.01 µg L<sup>-1</sup> and a 90<sup>th</sup> percentile of 0.1 µg L<sup>-1</sup>, leading to risk factors of 0.05 to 0.5.

Secondly, a compilation of recent (> 1995) data sets of EU countries has been made and data are classified in a tiered approach depending on the available background information (see **Table 3.184** and **Table 3.185**). The lowest number refers with data with highest quality, the higher number refer to data with lower quality but including those of the lowest number (i.e. a cumulative number of data). The first tier is a risk characterisation with the set of data with reliability index (RI) 1 which allow a 'bioavailability correction', i.e. a correction of the PNEC based on water hardness. However, it was only possible to make such corrections for water hardness for the dataset of Sweden with RI 1 and restricted to the data with hardness > 10 mg CaCO<sub>3</sub>/L. In that case, risk factors were calculated for each monitoring point as the ratio of PEC to the hardness corrected PNEC. The 90<sup>th</sup> percentile of these risk factors is below 1 and is represented in **Table 3.247**. The tiers 2 and 3 are the risk characterisations on data which do not allow bioavailability correction but for which the detection limit of Cd is at least 2-fold below the PNEC<sub>water</sub>. The tier 2 used data for which fractionation (dissolved or not) was known, the tier 3 also included data where information on fractionation was unknown. In that latter case, data with unknown fractionation were assumed to be identical to dissolved concentrations which are considered a conservative approach. From the table it can be seen that risk factors are all below 1 in tier 2 unless no outlier exclusion is made in the UK database, in which case risk factor > 1 due to 20 sampling sites (of the 728 sites) with large Cd that are excluded in the analysis as proposed by the rapporteur (thus excluding outliers). It is unknown what the source of Cd is in these sites. However risk factors > 1 are also found in tier 3 and tier 4 (case-by-case analysis) for the U.K and the Walloon region.

**Table 3.247** Regional risk characterisation for water in datasets varying in data quality (RI\*). The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L (Table 3.245). Risk characterisation of dataset with RI=1 included bioavailability corrections (hardness correction) and risk factor given is 90<sup>th</sup> percentile of risk factors. Datasets with RI>1 include also data of classes with lower RI index (i.e. cumulative number of data). Data refer to period 1995-2002 and details about data treatment are given in Table 3.184

RI*	Country	n	90 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	Factor risk	Supporting information: inclusion of outliers	
					90 <sup>th</sup> percentile [µg L <sup>-1</sup> ]	Factor risk
1	Sweden	5,466	0.04 <sup>§</sup>	0.54	0.04 <sup>§</sup>	0.58
2	Finland	803	0.0575	0.30	0.0575	0.30
	Germany	608	0.07	0.39	0.07	0.39
	Norway	985	0.055	0.29	0.055	0.29
	Sweden***	8,999	0.044	0.23	0.044	0.23
	The Netherlands	1825	0.07	0.38	0.12	0.63
	Greece	39	0.18	0.93	0.18	0.93
	UK (WIMS)	6,905	0.15	0.79	0.87	4.6
3	Finland	803	0.06	0.30	0.06	0.30
	Germany	608	0.07	0.39	0.07	0.39
	Greece	39	0.18	0.93	0.18	0.93
	The Netherlands	1,825	0.07	0.38 <sup>§</sup>	0.12	0.63
	Norway	985	0.06	0.29	0.06	0.29
	Sweden***	8,999	0.04	0.23	0.04	0.23
	U.K. (ECN)	10	0.31	1.6	0.31	1.6
	U.K. (WIMS)	6,905	0.15	0.79	0.87	4.6
4	Belgium; France, Italy,; Germany (datasets for the Main and Weser from the LAWA database); Portugal; Spain and The UK (COMMPS)			case-by-case (see text)		

\* RI 1: DL<0.1 µg L<sup>-1</sup>, Cd fractionation: D or ED (D: dissolved Cd; ED: estimated dissolved Cd) and water hardness known; RI 2: DL<0.1 µg L<sup>-1</sup>, Cd fractionation: D or ED; RI 3: DL< 0.1 µg L<sup>-1</sup>, Cd fractionation: D, ED or U (Unknown=assumed dissolved); RI 4: all data;

n Number of values in the dataset;

\*\* Including the dataset of Skjelkvale et al. (1999) ; no hardness data known for individual points in this dataset;

§ The Dutch rapporteur expressed concern about the P90 values>PNEC at the monitoring sites on the rivers Schelde and Maas located at the border with Belgium (risk factors 1.6 and 1.1 respectively) while the average P90 values of these rivers in The Netherlands both show risk factors <1.0 (details not shown). Preference was given by the MSR to calculate the P90 value of the entire river system rather than to a P90 value of one site on a river because the TGD states that 'The mean of the 90<sup>th</sup> percentiles of the individual sites within one region is recommended for regional PEC determination';

§ The average of P90 values of different sampling sites for the RI=1 data. The factor risk is based on the 90<sup>th</sup> percentile of individual values as the hardness changes within the sampling sites.

The risk factor for the Swedish data with  $RI=1$  is 0.54. This risk factor is obtained after correction for water hardness using the formula for water hardness correction as presented in Section 3.2.2.6.4 and using the proposed  $PNEC_{water}$  for soft waters (from  $40 \text{ mg L}^{-1}$  down to  $10 \text{ mg L}^{-1} \text{CaCO}_3$ ) of  $0.08 \text{ } \mu\text{g Cd L}^{-1}$ . Uncorrected, the risk factor would become 0.22. As the corrected risk factor is much higher than the uncorrected one, it is advisable to use values corrected for water hardness for soft waters, when available. There are no data of  $PNEC_{water}$  for the very soft waters (H below about  $10 \text{ mg CaCO}_3/\text{L}$ ) and these areas may be unprotected by the proposed  $PNEC_{water}$  for soft water ( $0.08 \text{ } \mu\text{g Cd L}^{-1}$ ). Therefore, there is a need for testing the Cd toxicity in these very soft waters (**conclusion (i)** is drawn).

The data of Sweden in RI 2 and 3 are not corrected for water hardness.

Outliers have been removed in the calculation of P90 values to exclude local point sources in the regional assessment. The effect of either including or excluding outliers only marginally affects the risk characterisation except in UK (WIMS database) where the 20 outliers (of 728 sites) have a large impact on the average P90 (note: risk factor is 0.25 for the median P90 of the entire database, including these outliers). In all data-sets, the number of outliers was always less than 10% of the entire database. It is unknown what the source of Cd is in these outliers.

Datasets assigned as RI4 are considered least reliable because, most importantly, the reporting limit is near or above the PNEC. These databases will be considered on a case-by-case basis below. In some cases (Belgium, UK and France) it is still possible to make a risk characterisation for (part) of the region:

- Belgium

The Flemish region: 94% of the data in the 2000-2002 dataset of the Flemish Environment Agency (VMM) are smaller than the DL. The dataset has reporting limits exceeding  $0.1 \text{ } \mu\text{g L}^{-1}$ . The P90-value ( $0.17 \text{ } \mu\text{g L}^{-1}$ ) is within the reporting limits and is therefore considered unreliable. The Walloon region: the reporting limit exceeds the critical value of  $0.1 \text{ } \mu\text{g L}^{-1}$  defined in this report and even exceeds the PNEC, therefore this database was not included in **Table 3.247**. However the P90 value exceeds the critical reporting limit and can be considered as a reliable value because the P90 value is calculated from the rank in the observed frequency distribution and not from the rank in a curve fitted to the frequency distribution. This means that the P90 is not affected by the exact values of data at lower percentiles. All values below the reporting limit have been set to half the reporting limit. The P90 value indicates a risk for the Walloon region (risk factor: 3.5).

- France

The datasets for France were designated RI 4 and not included in the risk characterisation. The reporting limits are unknown or exceed  $0.1 \text{ } \mu\text{g L}^{-1}$  or the dataset is not considered representative for a region. A small dataset with reliable background information was available for the river Seine. That dataset was considered too small to represent the French river dataset for the Seine has a P90 value of 0.06 and a corresponding risk factor of 0.32, i.e. no risk is predicted for the Seine River.

- Germany

The data for the Main and Weser contained sampling points for which the DL was higher or identical to  $0.1 \text{ } \mu\text{g L}^{-1}$ . However, the average P90 value for these rivers is 0.04 and  $0.09 \text{ } \mu\text{g L}^{-1}$  respectively, suggesting no risk.

- The UK

The COMMPS dataset for the UK (n=1244) was designated RI 4 as the reporting limits exceed  $0.1 \mu\text{g L}^{-1}$ . It was, therefore, not included in the **Table 3.247**. The P90 value, however, exceeds the reporting limits and can be considered reliable for reasons discussed above. This P90 values indicates a risk for the UK (risk factor: 2.26). The risk factor increases to 5.36 by including the outliers (1.5% of the entire dataset).

- Italy

The Italian dataset was considered not to be representative for the Italian region. The few values largely exceed those encountered in literature and the reporting limits exceed  $0.1 \mu\text{g L}^{-1}$ . The dataset itself is highly questionable as it indicates a 10-fold decrease of the risk factor from the year 1995 to the year 1996 (the risk factor decreases from 60 to 9.2). The dataset was designated RI 4 and not included in the risk characterisation.

- Portugal

The dataset for Portugal, although very extensive, was not included in the risk characterisation as the reporting limits exceed  $0.1 \mu\text{g L}^{-1}$ . Moreover, 84% of the data have values < DL. The P90 values of different rivers are generally situated within the reporting limits interval and are, therefore, considered unreliable. The P90 value of the River Oeste might still be useful: the P90 value is  $0.02 \mu\text{g L}^{-1}$  but this value is below the DL ( $0.03 \mu\text{g L}^{-1}$ ). Since the DL is far below the PNEC, this P90 vlaues suggests no risk in that river.

- Spain

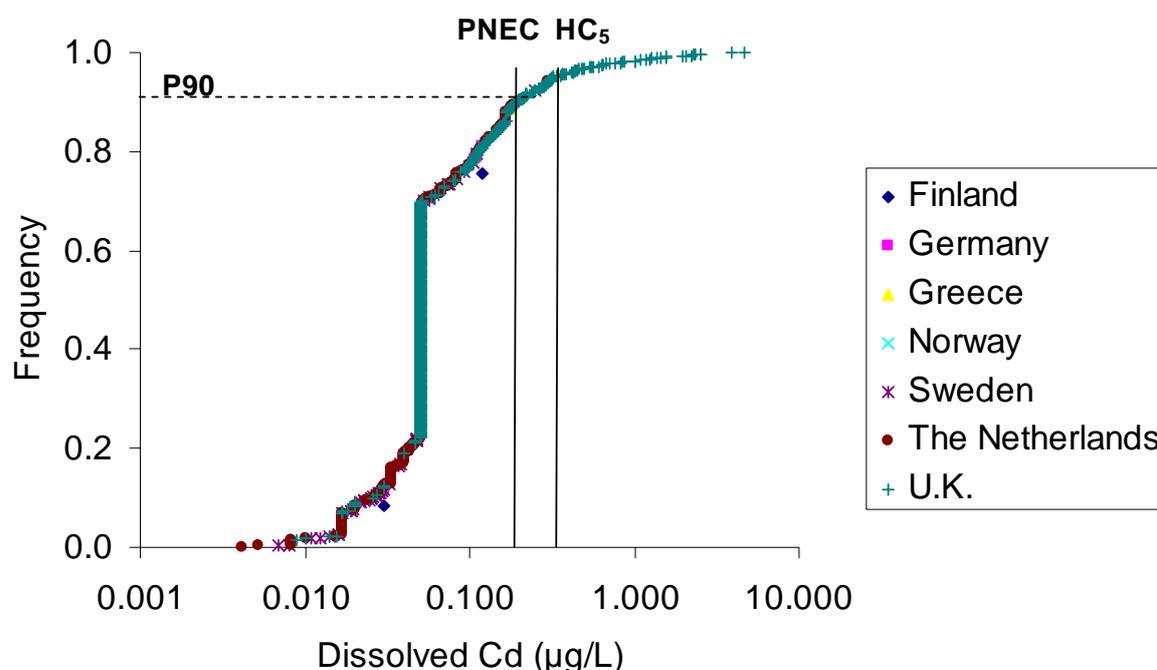
The dataset for Andalusia was not included as it obtains high values because of a historical contamination of the Guadalquivir river. The results can, therefore, not be considered to represent ambient Cd concentrations of Spanish waters. The COMMPS dataset for Spain was not included as the reporting limit, as well all the values in the dataset, equal  $0.1 \mu\text{g L}^{-1}$ . The resulting risk factor of 0.53 (=0.1/0.19), however, indicates no risk but the risk coefficient is highly uncertain.

### *Uncertainty analysis*

The frequency distribution of individual 90<sup>th</sup> percentiles is plotted relative to the PNEC derived from the HC<sub>5</sub> with an assessment factor (AF) 1 or 2. The 90<sup>th</sup> percentiles refer to data with RI 3 with outliers excluded and the values are either 90<sup>th</sup> percentiles of individual sites (Sweden, Germany, The Netherlands, UK-WIMS database) or, when no such data are available, the 90<sup>th</sup> percentiles of a dataset in which each site was only reported once (Greece, UK-ECN database, Norway, Finland). The uncertainty surrounding the PNEC is related to several aspects: statistical aspects (confidence limits on the HC<sub>5</sub> estimated from the SSD) and more general concerns such as species representativity, the inherent uncertainty about NOEC values compared to benchmark values, mixed pollution etc. (see Section 3.2). These uncertainty factors have crystallised in the AF=2 which was agreed. The majority of 90<sup>th</sup> percentiles are below the PNEC while the risk cannot be excluded for about 10% of the P90 values (note that P90 values from data with RI4 such as Walloon region are not included). The choice of the assessment factor AF (i.e. either  $0.19 \mu\text{g L}^{-1}$  by including the AF=2 as proposed or  $0.38 \mu\text{g L}^{-1}$  with AF=1) only affects the conclusion of risk for a relatively limited number of data that fall in the range  $0.19\text{-}0.38 \mu\text{g L}^{-1}$  (6% of the data used in **Figure 3.28**). In terms of regions at risk, it should be noted that the choice of the AF (1 or 2) does only affect the conclusion for the small ECN database of UK whereas for the remaining countries (including UK, using the larger WIMS database) the choice of the AF (1 or 2) does not affect the conclusion about risk, in contrast with the discussion about

the exclusion of outliers. For datasets with lower reliability (RI 4), the risk factor is  $> 1$  for UK (COMMPS dataset) and the Walloon region, and, again, this conclusion remains irrespective of the value of the AF for the PNEC.

**Figure 3.28** Cumulative frequency of P90 values of dissolved Cd concentrations in EU surface waters. Relative to the PNEC derived from the HC<sub>5</sub> with an assessment factor (AF) 1 or 2. The AF=2 is agreed to be used for the PNEC and reflects most of the uncertainties. The P90 values refer to data with RI 3 and the values are either 90<sup>th</sup> percentiles of individual sites (Sweden, Germany, The Netherlands, UK-WIMS database) or, when no such data are available, the 90<sup>th</sup> percentiles of a dataset in which each site was only reported once (Greece, UK-ECN database, Norway, Finland). n=1020 with 70% of data from UK and 25% of the data from The Netherlands



To conclude: no regional risk is predicted based on the majority of 90<sup>th</sup> percentiles of dissolved Cd values in EU with reliability index 1 to 3 (i.e. acceptable detection limit). Regional risk for the aquatic ecosystem cannot be excluded in certain regions such as UK and the Walloon<sup>54</sup> region of Belgium. For the UK, the conclusion on risk is largely based on 20 of the 728 sites where elevated Cd was found and these outliers (unknown source) drive the conclusion about risk for the UK. This shows that the risk of Cd in freshwater is borderline. A **conclusion (iii)** is proposed. The overall conclusion is based on datasets evaluation with and without exclusion of outliers. The methodology proposed by the rapporteur i.e. exclusion of outliers that are detected by a statistical approach only was not endorsed by MSs. It should be noted however, that although a large number of measured data is available, more information is needed for better characterising the risks to surface water in EU. In particular data from eastern and southern Europe are underrepresented in the entire dataset, detection limits are often too high and the fractionation is often not reported. Current actions (e.g. Water Framework Directive) are already taking such measures. Special attention should be paid to waters with low hardness (H below 10 mg CaCO<sub>3</sub> L<sup>-1</sup>).

<sup>54</sup> Industry analysed the data of 2000 showing that the P90 is largely affected by sites with historical pollution; the more recent databases revealed no risk, however this was not verified by MRS.

**Table 3.248** Regional risk characterisation for sediment. The factor risk = PEC/PNEC. The  $PNEC_{\text{sediment}}$  is 2.3 mg Cd/kg<sub>dw</sub> (Table 3.245). All values are without correction for bioavailability

	n	90 <sup>th</sup> percentile [mg Cd/kg <sub>dw</sub> ]	Factor risk	Supporting information: inclusion of outliers	
				90 <sup>th</sup> percentile [mg Cd/kg <sub>dw</sub> ]	Factor risk
Belgium (VMM)	512	1.59	0.69	1.75	0.76
France	315	2.86	1.24	3.86	1.68
France - Artois-Picardië	126	2.05	0.89	37	16.08
France- Rhône-Méditerranée	66	0.93	0.4	0.93	0.4
Spain	8	2.20	0.96	8.3	3.63
Sweden	297	2.97	1.29	2.97	1.29
The Netherlands	18	3.69	1.60	11.48	3.31
Supporting information: 90 <sup>th</sup> percentile of Cd in suspended matter		8.5	3.7		

### *Sediment*

Analysis based on PEC and PNEC values without correction for bioavailability: the limited data presented in **Table 3.248** show risk factors varying from 0.4 to 1.6. The P90 value of the concentration of Cd in suspended matter in The Netherlands exceeds that of the P90 value of sediments. This suggests that risk factors based on suspended matter, as a model for newly deposited sediments, are even larger than those for whole sediment samples. The exclusion of outliers (see Section 3.1.3.4.3) largely affects the magnitude of the risk factors. For Belgium the risk factor increases from 0.69 to 0.76 by taking into account the outliers of the VMM dataset. 6.5% of the values in the VMM dataset (including outliers) exceed the  $PNEC_{\text{sediment}}$ . Including the COMMPS dataset would render a risk factor of 3.57. For France, the risk factor for the Artois-Picardië region is 0.89 and would augment to 16.08 if the outliers were taken into account with 19.8% of the values in the dataset (including outliers) exceeding the  $PNEC_{\text{sediment}}$ . The uppermost outlier is the Deule with a risk factor of 156. The risk factor for the Rhône-Méditerranée region is 0.4 with 1.5% of the values in the dataset exceeding the  $PNEC_{\text{sed}}$ . If only the outliers of the COMMPS dataset were taken into account, the risk factor for France would augment from 1.24 to 1.68. The limited dataset from RWS for The Netherlands counts 4 values (of the 12) exceeding the  $PNEC_{\text{sediment}}$ . When including the one outlier of the COMMPS dataset for The Netherlands, the risk factor for The Netherlands would augment from 1.6 to 3.31. When including the outlier of the COMMPS dataset for Spain, the risk factor for Spain augments from 0.96 to 3.63. The Swedish risk factor is 1.29 with 19.19% of the dataset exceeding the  $PNEC_{\text{sed}}$ . The total risk factor would augment from 1.16 to 2.03 by only taking into account the COMMPS values that were discerned as outliers in the limited datasets of The Netherlands and Spain.

A large uncertainty surrounds the  $PNEC_{\text{sediment}}$  (2.3 mg Cd/kg<sub>dw</sub>) and, hence, the risk characterisation. The PNEC was calculated from one single chronic toxicity test using an AF of 50. The AVS/SEM method might further specify the  $PNEC_{\text{sediment}}$  value but this is subject of the **conclusion (i)** program on sediments.

Uncertainties surrounding the effects of Cd in sediments are related to the speciation of Cd in the sediment, e.g. the fraction of Cd present as insoluble sulphides. More information about the

relationship between Cd speciation and Cd toxicity is given in the RAR Stage II: **conclusion (i)** bioavailability in sediment (see separate document).

### 3.3.2.2 The terrestrial compartment

The ratio PEC/PNEC for local soil risk assessment is given in **Table 3.249**. The selected PNEC<sub>soil</sub> value is 0.9 mg kg<sup>-1</sup><sub>dw</sub>, which is the lowest PNEC<sub>soil</sub> value and which is based on secondary poisoning to mammals (see **Table 3.245**).

Risk is predicted at one location (site 2 of the Cd producers), the risk factors range from 0.5-1.1. This conclusion should be treated with caution. The local soil concentrations are calculated after 10 years exposure. The residence time of Cd in soil exceeds 100 years and predicted Cd concentrations after 50 years with current emissions will result in risk factors that are above 1 at the Cd producing sites 2, 3 and 5; **Conclusion (iii)**<sup>55</sup> Due to the long residence time of Cd in soil and the persistent availability (Smolders et al., 1999), such contamination should be avoided. Soil Cd is predicted to increase by more than 60% in 10 years at three sites (site 2, 3 and 5 of the Cd producers). These three sites have high emissions (> 800 kg Cd year<sup>-1</sup>) and the highest emission factors are well above those of the other producers (> 3 kg Cd tonne<sup>-1</sup>, **Table 3.2**). It is recommended that emission reduction measures should be adopted to reach emission factors that are similar to these of the other producers.

**Table 3.249** Local risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value = 0.9 mg kg<sup>-1</sup><sub>dw</sub> is equivalent to 0.79 mg kg<sup>-1</sup><sub>ww</sub> (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3.245)

Use-category	Plant N°	PEC <sub>local soil</sub> mg kg <sup>-1</sup> <sub>ww</sub>	Factor risk soil	Year
Cd-production	1	0.37	0.5	1996
	2	0.85	1.1	1996
	3	0.59	0.7	1996
	4	0.36	0.5	1996
	5	0.63	0.8	1996
	6	0.36	0.5	1996
	7	0.41	0.5	1996
	8	0.36	0.5	1996
	9	0.39	0.5	1996
	10	0.36	0.5	1996
CdO-producers	11	0.36	0.5	1996
	12	0.36	0.5	1993

Table 3.249 continued overleaf

<sup>55</sup> This conclusion was adapted in light of the "2002 Update". Section 3.3.3.4.1.

**Table 3.249 continued** Local risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value = 0.9 mg kg<sup>-1</sup><sub>dw</sub> is equivalent to 0.79 mg kg<sup>-1</sup><sub>ww</sub> (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3..245)

Use-category	Plant N°	PEC <sub>local soil</sub> mg kg <sup>-1</sup> <sub>ww</sub>	Factor risk soil	Year
Cd-stabilisers	F	0.36	0.5	1996
	G	0.36	0.5	1996
	H	0.36	0.5	1996
	I	0.36	0.5	1996
	J	0.36	0.5	1996
	K	0.36	0.5	1996
	L	0.36	0.5	1996
	M	0.36	0.5	1996
	window manufacturer	0.36	0.5	1996
	Cd-pigments	A	0.36	0.5
B		0.36	0.5	1996
C		0.36	0.5	1996
D		0.36	0.5	1996
E		0.36	0.5	1996
Cd-plating	EU	0.36	0.5	1996
Cd-alloys	EU	0.58	0.7	1996

The regional risk assessment of soils should be based on the measured soil Cd concentration (see **Table 3.190**) or using the regional PEC<sub>soil</sub> that is calculated with the detailed model 2 (for agricultural soils) or with EUSES (= model 1) for natural and industrial soils (see **Table 3.250**).

Model 2 was developed to assess the risks of Cd in agricultural soils. The predicted soil Cd concentrations after 60 years with current emissions range from 0.20 to 0.44 mg kg<sup>-1</sup><sub>dw</sub>. These concentrations are lower than the lowest PNEC<sub>soil</sub> for mammals (see **Table 3.250**).

**Table 3.250** Regional risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value is based on secondary poisoning to mammals (Table 3.245). PEC values derived from Table 3.183

Scenario	PEC <sub>soil</sub> after 60 years [mg kg <sup>-1</sup> <sub>dw</sub> ]	PNEC <sub>soil</sub>	Factor risk soil
<b>Agricultural soils</b>			
1. low input-low output (pH 6.8)	0.257	0.9	0.29
2. low input-high output (pH 5.8)	0.203	0.9	0.23
3. average input-low output	0.385	0.9	0.43
4. average input-high output	0.310	0.9	0.34
5. high input-low output	0.411	0.9	0.46

Table 3.250 continued overleaf

**Table 3.250 continued** Regional risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value is based on secondary poisoning to mammals (Table 3.245). PEC values derived from Table 3.183

Scenario	PEC <sub>soil</sub> after 60 years [mg kg <sup>-1</sup> dw]	PNEC <sub>soil</sub>	Factor risk soil
<b>Agricultural soils</b>			
6. high input-high output	0.339	0.9	0.38
7. high input-very low output (worst case Mediterranean)	0.439	0.9	0.49
8. EU average	0.318	0.9	0.35
<b>Natural and Industrial soil (PEC<sub>soil</sub>= PEC<sub>soil</sub> at steady state)</b>			
	0.322	0.9	0.35

### Measured values

Average soil Cd concentrations typically range between 0.1 and 1.6 mg kg<sup>-1</sup><sub>dw</sub>. The average (or median) Cd concentrations in natural and agricultural soils have risk factors 0.1-1.0 (mean 0.4). Corresponding factors for the 90<sup>th</sup> percentiles are 0.4-1.6 (see **Table 3.251**). Soil Cd concentrations are often affected by soil type (texture and %OM) because background Cd is related to these properties. As an example, the 90<sup>th</sup> percentiles of German sand, loss and clay soils have been averaged (see Section 3.1.3.4.2 – terrestrial compartment). The data were selected and compiled from the data set “Hintergrundwerte für anorganische und organische Stoffe in Böden” (LABO, 1998). Risk factors are 0.62 for the sandy soils, 0.74 for the loamy (loss –ok ) soils and 0.98 for the clay soils. Reported 90<sup>th</sup> percentiles of soil Cd are often, but not always, classified per soil groups. The lack of a harmonised way of reporting 90<sup>th</sup> percentiles obscures the regional EU risk characterisation.

Local concentrations are often higher than the PNEC<sub>soil</sub> values, either due to pollution or due to high background concentrations. High background concentrations (> 2 mg kg<sup>-1</sup>) in soil are often associated with low plant availability (e.g. Mench et al., 1997). There is no information on Cd toxicity to the soil ecosystem or to mammals in such soils. Soils with historic Cd contamination (smelters) have Cd concentrations that are often several folds higher than the PNEC<sub>soil</sub> for soil organisms or for mammals. The elevated Cd in smelter affected soils is generally associated with elevated Zn concentrations. The usual Zn/Cd ratio is about 100 in these soils. The PNEC<sub>soil</sub> of Zn, added above background, is only 27 mg kg<sup>-1</sup><sub>dw</sub> (RAR Zn, 2004) whereas the PNEC<sub>soil</sub> of Cd is 0.9 mg kg<sup>-1</sup><sub>dw</sub>. In a smelter affected soil containing 2.5 mg Cd/kg and 250 mg kg<sup>-1</sup> Zn (background about 50 Zn kg<sup>-1</sup>) it is likely that Zn and not Cd will be toxic to soil organisms.

### Uncertainty analysis

If 90<sup>th</sup> percentiles of soil Cd concentrations are used, risk cannot be excluded in one region (see **Table 3.251**). Reported 90<sup>th</sup> percentiles are averaged per country as a surrogate for region. No attempt was made to discriminate soil classes. The risk is predicted for the UK when using the PNEC<sub>soil</sub> of 0.9 mg Cd/kg derived from the study of secondary poisoning. This PNEC<sub>soil</sub> has a large (statistical) uncertainty and the limited data available suggest that risk for secondary poisoning is mainly pronounced in very acid soils because data from such soil types has triggered the PNEC value (see Section 3.2.3.6.3). As an illustration, the PNEC<sub>soil</sub> increases from 0.9 mg Cd/kg to 3.3 mg Cd/kg if data on acid soils (pH <4.2) are excluded in the derivation of the PNEC (see Section 3.2.3.6.3). Practically this means that the risk in UK could be excluded if the P90 values do not refer to acid soils, which is unknown. This analysis is qualitative because

there is no validated model to estimate risk to mammals taking soil pH into account (see Section 3.2.3.6.3). Moreover, even if risk to secondary poisoning can be excluded, risk to soil microbial process in UK soils cannot be excluded because it falls within the range of the proposed  $PNEC_{soil}$  based on direct toxicity to soil microbial processes (see **Table 3.245**). Taken together, regional soil Cd concentrations predict risk in one EU country for which data are available, but the uncertainty surrounding the PNEC values for soil suggests that risk is borderline. A conservative **conclusion (iii)** is proposed.

**Table 3.251** Regional risk characterisation for soil. The factor risk =  $PEC/PNEC$ . The  $PNEC_{soil}$  is 0.9 mg Cd/kg<sub>dw</sub> (Table 3.245)

Location	90 <sup>th</sup> percentile [ $\mu\text{g kg}^{-1}$ ]	Factor risk
Belgium	0.51	0.56
France	0.85	0.94
Germany	0.65	0.73
Sweden	0.39	0.43
The Netherlands	0.83	0.92
The United Kingdom	1.40	1.56

### 3.3.2.3 Secondary poisoning

Effects of soil-borne Cd on mammals has already been included in the previous section since this pathway is more critical than direct effects on higher plants, soil fauna or soil microbial processes.

The  $PEC_{oral}$  for birds is calculated as ranges with  $PEC_{soil}$  and  $PEC_{water}$  and with the range in BAF and BCF values derived from the compilations in Section 3.2.7.

The  $PEC_{oral}$  of worms is 5.4-9.1 mg kg<sup>-1</sup><sub>ww</sub> (Table 3.252) if based on a median BAF for worms and is 1.4-19 mg kg<sup>-1</sup><sub>ww</sub> if based on the entire range of BAF's for worms. The  $PNEC_{oral}$  for birds is 0.16 mg kg<sup>-1</sup> diet, i.e. the  $PEC/PNEC$  ratio varies between 9 and 121, with most ratios consistently above 1. This suggests that Cd concentration in the worms may be at risk for the birds, even at ambient soil Cd concentrations.

The  $PEC_{oral}$  of fish is <0.1-3.6 mg kg<sup>-1</sup><sub>ww</sub> if based on a median BCF for fish and is <0.01-148 mg kg<sup>-1</sup><sub>ww</sub> if based on the entire range of BCF and BAF's for fish. The  $PNEC_{oral}$  for birds is 0.16 mg kg<sup>-1</sup> diet, i.e. the  $PEC/PNEC$  ratio varies between <0.1-930 with most ratios, however, consistently below 1. This suggests that Cd concentration in the fish may be at risk for the birds in some situations. The  $PEC_{oral}$  at ambient Cd concentration in water (<0.3  $\mu\text{g Cd/L}$ ) is 0.004 mg Cd/kg<sub>ww</sub> using the median BCF for fish and is 0.19 mg kg<sup>-1</sup><sub>ww</sub> based on the highest BAF or BCF value for whole fish. The first value is well below the  $PNEC_{oral}$  for birds, the latter is 1.2 fold the  $PNEC_{oral}$  suggesting potential risk at ambient concentrations. This conclusion should be put into perspective: BAF or BCF values of whole fish are typically about 100 L/kg<sub>ww</sub> with few extremes above 500 L/kg<sub>ww</sub> and at which risk factors are above unity (see **Table 3.232** and **3.233**).

For different reasons it is felt that even the large  $PEC/PNEC$  ratio in water (local) or soil (at local and ambient concentrations) for birds may not reflect a severe risk:

- (I) Kidney or liver Cd concentrations in terrestrial birds are below concentrations that are assumed to be acceptable (Furness, 1996-see below for more details) despite that measured Cd concentrations in worms from uncontaminated areas often exceed the  $PEC_{oral}$ ;
- (II) the  $PEC_{oral}$  is based on Cd salt spiked meals thereby overestimating Cd availability to the test animals (see Section 3.2.7.5.1);
- (III) birds may not sample 50% of their food as worms in a contaminated area.

The risk of Cd to birds may be refined with field data and critical tissue concentrations. This assessment is yet not possible due to the lack of dose (soil/food Cd)-response (tissue concentration). Tissue concentrations of Cd in birds have been reviewed by Furness (1996). Kidney Cd concentrations in pelagic seabirds are several orders of magnitude higher than in terrestrial seabirds. We will not make any risk assessment here for marine birds as discussed in Section 3.2.7.4.1. Furness (1996) suggests a critical Cd concentration of  $100 \mu\text{g g}^{-1}_{ww}$  (about  $400 \mu\text{g/g}_{dw}$ ). This threshold is the same as suggested for mammals (see Section 3.2.7.5.1) Mean kidney Cd concentration in the kidney of terrestrial birds is below  $11 \mu\text{g/g}_{ww}$  and individual highest concentrations ( $70 \mu\text{g g}^{-1}_{ww}$ ) have been found in feral pigeons collected around Heathrow airport (presumably enriched with Cd from tire debris, Hutton and Goodman, 1980). A recent survey in Italy reported low kidney Cd concentration ( $< 8 \mu\text{g g}^{-1}_{dw}$ , or  $< 2 \mu\text{g g}^{-1}_{ww}$ ) in top predators little owl and common buzzard (Battaglia et al., 2005). It has been surprisingly difficult to show elevated Cd in birds inhabiting environments supposedly polluted by Cd (Furness, 1996). Kidney Cd in top predators barn owl and kestrel from the metal polluted Kempen (NL) are  $24 \pm 26 \mu\text{g g}^{-1}_{dw}$  and  $4.8 \pm 6 \mu\text{g g}^{-1}_{dw}$  respectively (Gorree et al., 1995), i.e. well below the critical value. The only exception with clearly elevated Cd exposure in a contaminated area are the white tailed ptarmigan (*Lagopus leucurus*) with kidney Cd concentrations up to about  $200 \mu\text{g g}^{-1}_{ww}$  (as observed in Colorado, U.S.A.) which is 2-fold above the toxic threshold (Larison et al., 2000). The large exposure is related to the diet (herbivorous with preference for willow) as discussed in Section 3.2.7.5.1. The corresponding concentrations in samples from a non-contaminated environment are maximally  $40 \mu\text{g g}^{-1}_{ww}$ , i.e. below the toxic threshold. The elevated Cd exposure for that species is found in an area where soil Cd is estimated to be at least  $2 \text{ mg Cd/kg}$  (see Section 3.2.7.5.1). As none of the regional or local soil Cd concentrations in this study are  $> 2 \text{ mg Cd/kg}$ , we conclude that risk of Cd for this species (rare in Europe) is unlikely at the  $PEC_{soil}$  considered.

**Table 3.252** The predicted environmental concentrations in food ( $PEC_{oral}$ ). The choice for the parameters and the risk for secondary poisoning are discussed in the text.

$$PEC_{oral} = (0.5PEC_{local} + 0.5PEC_{regional}) * BC(A)F$$

	$PEC_{local}$ min-max $\text{mg kg}^{-1}_{ww}$ (or $\mu\text{g L}^{-1}$ )	$PEC_{regional}$ $\text{mg kg}^{-1}_{dw}$ (or $\mu\text{g L}^{-1}$ )	BAF - BCF median (min-max) $\text{kg}_{dw} \text{kg}_{ww}^{-1}$ (or $\text{L kg}_{ww}^{-1}$ )	$PEC_{oral}$ $\text{mg kg}^{-1}_{ww}$
soil-worm	0.36-0.85	0.36	15 (4-32)	5.4-9.1 (median BAF) 1.4-19.4 (range of BAF)
water-fish	0.1-477	0.11	15 (0.5-623)	0.002-3.6 (median BCF) <0.001-148 (range of BCF/BAF)

### 3.3.2.4 The atmospheric compartment

A quantitative risk characterisation for exposure of organisms to airborne cadmium is not done because there are no useful data on the effects of airborne cadmium in environmental organisms and thus no PNEC air could be derived. The PECs in air are used for the risk assessment of man indirectly exposed via the environment (see Section 4 of this report in a separate document). Inorganic cadmium air emissions are primarily associated with particulates in the air. Emission to air will settle out to soil. The impact of industrial air emissions at local scale is therefore included in the conclusions on the terrestrial compartment.

### 3.3.2.5 Conclusions<sup>56</sup>

Environmental Cd concentrations that were either modelled (based on local emissions from Cd/CdO production or processing and on diffuse emissions) or measured were combined with the effects assessment that was largely based on dose ( $\text{Cd}^{2+}$  salts)-response (chronic toxicity) studies. The effects assessment was based on protecting mammals from soil borne Cd. The following is concluded:

- Modelled freshwater dissolved Cd concentrations based on-site-specific emission data (without water hardness corrections) exceed the freshwater  $\text{PNEC}_{\text{water}}$  at 11 sites where Cd is produced or processed, 3 of which have emissions into the sea. The measured Cd concentrations usually reduce concern. For one site risk is predicted if based on modelled concentrations but not if based on measured concentrations. However, the measured concentration refers to two years before the reference year and will therefore not be preferred over the modelled concentration. Risk at Cd containing alloy production-sites cannot be excluded. There is potential risk for *on-site* STP at a number of Cd producing<sup>57</sup> and processing sites (pigments, plating and alloys). Measured site-specific (toxicity) data may remove this concern
- There is potential Cd toxicity for off-site STP due to emissions from Cd plating, pigment and alloy industry.
- Modelled sediment concentrations (without bioavailability correction) result in elevated risks for benthic organisms<sup>58</sup> at all sites/scenarios. Risk is always predicted even if emissions are zero because the regional Cd concentration in sediment is above the  $\text{PNEC}_{\text{sediment}}$ . The regional Cd concentration in sediment is the 90<sup>th</sup> percentile of measured data. No risk is predicted using average or median sediment Cd concentration and if emissions are zero. On the other hand, at 15 producing and processing sites/areas i.e. 7 Cd-production-sites and 8 Cd-processing sites (i.e. stabiliser production, pigment production and the generic scenarios 'Cd plating' and 'Cd alloys'), there is predicted risk irrespective of the regional background (see local added Cd,  $\text{C}_{\text{local sediment}} > \text{PNEC}_{\text{sediments}}$ ). Measured local Cd concentrations (not available) could remove concern. A refined risk characterisation could be performed at these sites using an AVS and Organic Carbon based normalisation. To that latter perspective, a **conclusion (i)** was decided.

<sup>56</sup> These conclusions were adapted in light of the "2002 Update". Section 3.3.3.4.1

<sup>57</sup> The type of the WWTP at the plants in the production area (Cd metal) being based on physical-chemical principles only, it is proposed that the conclusions related to the risk for micro-organisms in the on-site WWTP are considered as indicative only and are not taken forward to the Section 5 (general conclusions).

<sup>58</sup> After the TMIV'02 last visit discussion on cadmium in sediment a number of MSs (UK, F, DE) and Industry commented on the sediment assessment and the current conclusions drawn in line with the outcome of that last TM (for more details, see effects assessment and risk characterisation).

- predicted regional and continental Cd concentrations in water are below the  $PNEC_{water}$  at a mean  $K_p$  value while the risk factor is 1.7 using a  $K_p$  value that is distinctly smaller than average. No regional risk is predicted based on the majority of 90<sup>th</sup> percentiles of measured data from monitoring programmes with acceptable detection limit. Regional risk for the aquatic ecosystem cannot be excluded in certain regions such as UK and the Walloon region of Belgium.
- In general, the current local standards for emissions to water mentioned in permits (maximum Cd concentration in the effluent and the volume of discharged effluent) should be reconsidered in the light of the derived  $PNEC_{water}$  in order to prevent risk to the aquatic compartment.
- Regional predicted concentrations in the sediment are typically larger than the PNEC but overestimate measured concentrations. Risks for the 90<sup>th</sup> percentiles of the various European countries ranges from 0.69 to 1.6 (datasets excluding outliers). AVS/SEM analysis could remove the concern. To the latter perspective, **conclusion (i)** is decided.
- modelled local soil Cd concentrations indicate immediate risks for mammals at one Cd metal production-site. Long term predictions (> 20 years) show that current atmospheric emissions from 3 Cd metal producing sites can increase risk at the local scale. The emission factors of these sites should be reduced to those of other Cd producing plants. Given the total lack of information related to site-specific air emission data for the Cd alloy and Cd plating industry, long term risk at the local terrestrial scale cannot be excluded for these industry areas.
- predicted regional soil Cd concentrations that include different agricultural scenarios are below the  $PNEC_{soil}$ . The average (or median) measured Cd concentrations in natural and agricultural soils have risk factors 0.1-1.0 (mean 0.4). Corresponding factors for the 90<sup>th</sup> percentiles are 0.4-1.6. Risk cannot be excluded in one region but depends on the magnitude of the assessment factor chosen in the derivation of the  $PNEC_{soil}$  (either 1 or 2, see Section 3.2.3.7). Averaging of all 90<sup>th</sup> percentiles within a region is clearly affected by the dominant soil types in each region because soil Cd concentration is affected by properties such as % clay and % organic matter.
- potential risk of Cd to terrestrial birds is predicted using soil-worm-bird or water-fish-bird modelling. Field data (body burden: kidney and liver Cd data) of terrestrial birds do not indicate Cd poisoning, even in contaminated areas and in top predators. Pelagic birds have reported kidney Cd concentrations above acceptable values but no risk characterisation of marine environments was made here.

### 3.3.3 Risk characterisation for battery related life cycle steps

#### 3.3.3.1 Overview assumptions and built-in conservatism

Within the approach used in this report to estimate the cadmium emissions associated with waste management strategies such as land-filling and incinerations different assumptions have been made that lack validation due to the limited availability of data on this subject. As general premise realistic worst case conditions were taken as input values to perform the calculations but in other cases average values were used instead of worst case estimated in order to conserve the environmental realisms of the estimates. **Table 3.253** provides an overview of the assumptions and default values taken in this report and the associated level of conservatism introduced with them.

Table 3.253 Overview of the input values used in the emission calculations of MSW landfills and MSW incinerators

Subject	Parameter	Value	Best case	Typical	Realistic worst case	Worst case	Description
General data							
<u>Information NiCd batteries</u>	Cd content portable NiCd battery	13.8%					Average: referring to actual manufacturing and production data
Section 2.2.2.2	Cd content industrial NiCd battery	8%					Average: referring to actual manufacturing and production data
Section 2.2.2.4.2.2.	Weight portable NiCd battery	38 g					Average: referring to actual manufacturing and production data
Section 2.2.2.4.4.1	Sales data portable NiCd batteries	14,000 tonnes					Upper limits used
Section 2.2.2.4.4.2	Sales data industrial NiCd batteries	3,632 tonnes					Upper limits used
Section 2.2.2.4.4.3	Future sales portable NiCd batteries	13,500 tonnes					Real consumption numbers show a decrease: 11,793 tonnes in 2000 -11,265 tonnes in 2001
Section 2.2.2.5.1.1	Recycling data portable NiCd batteries	1,446 tonnes					Lowest limits used
Section 2.2.2.5.1.2	Recycling data industrial NiCd batteries	2,667 tonnes					Lowest limits used
Section 2.2.2.5.2	Recycling %	10%					
	Recycling %	75%					
<u>NiCd manufacturing/recycling sites</u>	Cd concentration effluent						90 <sup>th</sup> percentile (in general: of the individual raw measurements)
	Effluent flow						90 <sup>th</sup> percentile
	Flow receiving water						Minimal flow rate or 1/3 average flow rate
<u>Municipal Solid Waste (MSW)</u>	Cd content	10g tonne <sup>-1</sup> s					90 <sup>th</sup> percentile
*Contribution of NiCd batteries to the cadmium content of municipal solid waste: current situation* under Section 3.1.2.2.5.	Moisture content	30%					Van der Poel (1999) and other references (see text)
	Contribution NiCd battery	10%					Typical percentages are between 10-20 %
	Contribution NiCd battery	50%					Maximum NiCd battery contribution measured was 4.3g Cd/tonnes dry wt. MSW (Germany) used on the 90 <sup>th</sup> percentile value of 10 g Cd /tonnes dry wt.
*Waste management strategies in Europe* under Section 3.1.2.2.5	MSW incinerated/landfilled current situation						Average for EU.
	MSW incinerated/landfilled 100 % incineration						Additional scenario added for the sensitivity analysis

Table 3.253 continued overleaf

Table 3.253 continued Overview of the input values used in the emission calculations of MSW landfills and MSW incinerators

Subject	Parameter	Value	Best case	Typical	Realistic worst case	Worst case	Description
MSW incineration	Volume fluegass	5,500 Nm <sup>3</sup> /tonnes					Range reported in literature 5,000-6,000
"Current emissions" under Section 3.1.2.2.5.	Cd concentration in flue gass						Most often average values were used, In some cases concentrations were P90 values
Above Table 3.27	Waste water generated	2,5 m <sup>3</sup> /tonnes					Range reported in literature 0.5-2.5 m <sup>3</sup> . For the regional PEC calculations this maximum value have been used. For the local calculations both min and max have been used.
Table 3.27	Cd concentration in waste water before treatment	0.3 mg L <sup>-1</sup>					Average of measured data used for regional calculations
	Cd concentration in waste water before treatment	0.42 mg L <sup>-1</sup>					90 <sup>th</sup> percentile of measured data used for local calculations
	Cd concentration in waste water before treatment	0.76 mg L <sup>-1</sup>					Max value used for sensitivity analysis
	Removal efficiency Cd	98.8%					Based on 104 measurements and the comparison of both average evalues of influent/effluent as maximum values
Table 3.30	Cd percentage in fly ash	87%					Average value based on different literature data
	Cd percentage in bottom ash	13%					Average value based on different literature data
MSW landfill *Overall cadmium emissions from landfilling MSW* under Section 3.1.2.2.5. Table 3.1.	Cd concentration in leachate	5 µg L <sup>-1</sup>					<p>Eggenberger and Waber (2000), Flyhammar, 1995, EREF, 1999.</p> <p>90<sup>th</sup> percentile Germany &lt; 5, 80<sup>th</sup> percentile Switzerland &lt; 3, 50<sup>th</sup> percentile Sweden = 5 and &lt; 5, 50<sup>th</sup> percentile USA/France: 2.5-7</p> <p>landfills (Germany) (Krümpelbeck, 1999, average concentrations):</p> <p>1.5 years: 11 µg L<sup>-1</sup> 21-30 years: 2.8 µg L<sup>-1</sup></p> <p>landfills (Sweden) (Flyhammar et al., 1998):</p> <p>1-2 years: 40 µg L<sup>-1</sup> 20-22 years: 6 µg L<sup>-1</sup></p>

Table 3.253 continued overleaf

Table 3.253 continued Overview of the input values used in the emission calculations of MSW landfills and MSW incinerators

Subject	Parameter	Value	Best case	Typical	Realistic worst case	Worst case	Description
	Leachate volume	2,500 m <sup>3</sup> /ha					Maximum value based on average to reasonable worst case precipitation of 800 mm/y
Table 3.44	Rainfall	800 mm/y					Rainfall representative for Mid Europe and the Scandinavian countries, reasonable worst case for South Europe
Table 3.51	Surface landfill	14,7 ha					Average value of reported landfill surface areas
<u>Sewage Treatment plant</u>	Removal efficiency Cd	60%					Average value (CBS, 2002)
Regional calculations							
<u>NiCd manufacturing/recycling sites</u>	Allocation to region						Highest emitter chosen
<u>Incineration MSW</u>	Regional air emissions						Average or 90P values have been used.
	Regional water emissions						Maximum amount of water generated, average influent concentration and typical removal percentage used for calculations
<u>Landfilling MSW</u>	Regional water emissions						Maximum leachate volume (2,500 m <sup>3</sup> /ha.y) used in combination with average Cd concentration (5 µg L <sup>-1</sup> ) and average landfill surface (14,7 ha)
Local calculations							
<u>Incineration MSW</u>	Aquatic compartment						P90 value of measured influent concentrations
Section 3.1.3.2.1 Figure 3.11 (below Table 3.93)	Dilution factor	100					Based on the 10 <sup>th</sup> percentile of calculated DF with the maximum value of waste water generated (2.5 m <sup>3</sup> /tonne)
	Dilution factor	1,000					Based on the 50 <sup>th</sup> percentile of measured data and the maximum volume of waste water generated (2.5 m <sup>3</sup> /tonne). Could in fact also be considered as a realistic worst case since 75 % of the incinerators have a DF > 1,000
	Size plant	112 ktonnes					Large plant

Table 3.253 continued overleaf

Table 3.253 continued Overview of the input values used in the emission calculations of MSW landfills and MSW incinerators

Subject	Parameter	Value	Best case	Typical	Realistic worst case	Worst case	Description
	Terrestrial and atmospheric compartment						Country specific air emissions have been used. Sometimes based on P90 values measured data, sometimes highest emission factor and sometimes measured data represented average conditions.
<u>Landfilling MSW</u>	Surface landfill	20 ha					Future landfills are expected to be large (at least 20ha), High surface equals high volume of leachate generated with average Cd leachate concentration (5µg L <sup>-1</sup> ).
Below Table 3.49	Leachate volume	100 m <sup>3</sup> /d					Based on large landfill surface area and high leachate volume (2,024 m <sup>3</sup> /ha/y) during operational phase
	Dilution factor	180					Based on the release of the leachate in a river with TGD standard flow rate of 18,000 m <sup>3</sup> /d
	Local water emission						Based on large landfill surface area, high leachate volume (2,024 m <sup>3</sup> /ha/y) during operational phase, average Cd leachate concentration (5 µg L <sup>-1</sup> )
<u>Future emissions</u>	Landfill leachate concentration	50 µg L <sup>-1</sup>					According to the performed geochemical modelling on mature waste, carbonate precipitation is likely to prevent cadmium concentrations rising above 60 to 90 µg L <sup>-1</sup> . The laboratory results indicated, however, that for the aerobic columns, cadmium concentrations generally remained below 10 µg L <sup>-1</sup> suggesting that the retention mechanism is probably not precipitation alone. The leachate concentration of 50 µg L <sup>-1</sup> can be considered as a conservative/realistic worst case leachate concentration because in this case we are assuming that aerobic precipitation is the only metal retention mechanisms
*Forecasts of future battery waste arisings* under Section 3.1.2.2.5.	Future Cd content	13.2 g tonne <sup>-1</sup>					Based on 75 % collection but already 9 g tonne <sup>-1</sup> Cd due to other sources. Also future sales figures (13,500 tonnes) kept constant while evidence of decreasing trend) The same trend is supposed in 'consumption' figures
		24 g tonne <sup>-1</sup>					Based on 10 % collection but already 9 g tonne <sup>-1</sup> Cd due to other sources, Also future sales figures (13,500 tonnes) kept constant while evidence of decreasing trend) The same trend is supposed in 'consumption' figures

### **3.3.3.2 The aquatic compartment (including sediment and STP)**

The risk factors (PEC/PNEC ratio) for **local water** and **sediment** concentrations are given in **Table 3.254** for the NiCd producers and recyclers and from **Table 3.255-Table 3.260** for incinerators and landfills. By lack of relevant data, corrections for water hardness could not be done for the risk characterisation.

#### **3.3.3.2.1 Risk characterisation NiCd producing/recycling plants**

**Table 3.254** Local risk characterisation NiCd producing/recycling plants for water, sediment and STP. The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC<sub>sediment</sub> is 2.3 mg kg<sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C<sub>local</sub><sub>sediment</sub>) and for the added and regional Cd (total Cd, i.e. PEC<sub>sediment</sub>) without correction for bioavailability. The PNEC for micro-organisms is 20 µg L<sup>-1</sup>(Table 3.245)

Use-	N°	PEC <sub>local</sub> water site specific	Factor risk water site specific	PEC <sub>local</sub> water DF=1,000	Factor risk water DF=1,000	PEC <sub>local</sub> <sub>sediment</sub> DF=1,000 or site specific	Factor risk sediment DF=1,000 or site specific Total	Factor risk sediment DF=1,000 or site specific Added	C <sub>effluent</sub>	Factor risk STP	Year
Category		µg L <sup>-1</sup>		µg L <sup>-1</sup>		mg kg <sup>-1</sup> dry wt.			(mg L <sup>-1</sup> )		
NiCd- batteries	1	0.12	0.63	N/A	N/A	3.2	1.4	0.2	0.019 <sup>a</sup>	0.95	1999
	2*	0.15	0.79	0.15	0.79	8.0	3.5	2.3	0.12	n.r.	2000
	3	0.12	0.63	0.15	0.79	8.0	3.5	2.3	0.12	n.r.	2000
	4	0.18	0.94	N/A	N/A	10.5	4.6	3.4	0.13	n.r.	2000
	5	0.11	0.58	0.114	0.58	2.7	1.2	0	0.00007 <sup>a</sup>	0.005	2000
	6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	n.r.	1999
	7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	n.r.	1999
Cd recyclers	1 <sup>b</sup>	0.19	1.0	0.27	1.4	22.6	9.8	8.6	0.45	n.r.	2000
	1 <sup>c</sup>	0.13	0.68	0.17	0.89	19.8	8.6	7.5	0.17	n.r.	2000
	2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1999

N/A Not applicable – Factory 6 & 7 have no emissions to water – See Table 3.5;

a) Influent concentration STP = effluent concentration plant\*DF STP);

b) Based on P90 of daily measurements;

c) Based on average effluent concentration and average effluent flow rate;

n.r. Not relevant;

\* Emission to the sea.

## Aquatic compartment

### *Freshwater and marine*

For the NiCd batteries producing plants emitting in fresh water ecosystems there are no sites with a risk factor larger than one. Plant 4 has a risk factor of 0.94. Although the P90 of concentrations in the effluent is calculated on monthly average values (and not on daily measurements) the risk factor of 0.94, calculated on the basis of several 'parameter' worst case assumptions, is judged as being 'without concern' for aquatic organisms. For the NiCd recycling sites there is one site with an elevated risk, plant 1. If the risk characterisation is performed with the average flow rate and average cadmium concentration a risk factor of 0.89 is obtained (scenario 1b). This indicates that at plant 1, although operating fully in line with the current legislation and local permit, risk to aquatic organisms can potentially occur at specific spatial-temporal conditions.

NiCd producing plant 2 emits effluents to the marine environment. The risk factor is below 1 at that site (based on the PNEC freshwater). However, the risk characterisation is indicative only, as no PNEC was derived for marine species.

### *Uncertainty analysis*

It should be noted that an assessment factor of 2 has been included in the PNEC water derivation due to remaining uncertainty.

The uncertainty surrounding the PNEC is related to several aspects:

- Statistical aspects: for cadmium an effect database of 168 reliable tests on single species is available which contains 3 reliable LOEC's below the derived HC<sub>5</sub> (0.38 µg L<sup>-1</sup>) whereas the 9 multi species studies identified 1 LOEC below this hardness corrected HC<sub>5</sub>. This suggests that NOEC and LOEC distributions overlap in the lower concentration range and that an additional assessment factor may be necessary.
- The inherent uncertainty about NOEC values compared to the benchmark values
- Species representativity
- Mixed pollution (etc. see Section 3.2)

These factors have crystallised in the AF=2 which was agreed.

The uncertainty around the PNEC water influences the risk conclusion for the NiCd recycling plant. If no assessment factor is applied the site would not have a local risk anymore (RCR = 0.5-0.7) for the water compartment.

### *Using measured regional values*

Aforementioned exposure estimations and risk assessment are based on calculated PEC<sub>regional</sub> (i.e. 0.11 µg L<sup>-1</sup>). Preference should, however, be given to measured values when available. However in the absence of reliable and representative regional measured data in the vicinity of the individual sites the RCR values have also been calculated (results not shown) using the average of the measured P90 values for different countries (i.e. 0.12 µg L<sup>-1</sup>) and also using the median of the measured P90 values (i.e. 0.07 µg L<sup>-1</sup>),

The use of the average measured regional PEC concentration ( $0.12 \mu\text{g L}^{-1}$ ) does not change the risk conclusions for the NiCd producing sites. Only in the case of recycler 1 the observed risk ratio of 1 for a site specific dilution changes into a no risk scenario ( $\text{RCR} = 0.79$ ) when the median measured regional concentration is used as regional background.

#### Sediments (assessment without bioavailability correction)

Based on PECs and PNEC not corrected for bioavailability, the risks for benthic organisms are elevated at sites 1 to 5 for the NiCd producing plants and recycler 1. Risk factors based on ‘total’ (i.e. locally added and regional background contribution) vary between 1.2 and 9.8.

It should be noted that a risk is always predicted even if emissions are zero because the regional Cd concentration in sediment is above the  $\text{PNEC}_{\text{sediment}}$ . The regional Cd concentration in sediment is the 90<sup>th</sup> percentile of measured data. ( $2.66 \text{ mg kg}^{-1}_{\text{dry wt.}}$ ) No risk is predicted when the EU average or median sediment Cd concentration is used as regional Cd concentration. Based only on local emissions (i.e. without the background contribution), no risk is predicted at some sites if local background is low as suggested by risk factors based on locally added Cd only (e.g. plant 1). At several producing and processing sites (plant 2, 3 and 4), however, there is predicted risk irrespective of the regional background (see local added Cd,  $\text{C}_{\text{local}_{\text{sediment}}} > \text{PNEC}_{\text{sediments}}$ ). Measured local Cd concentrations (not available) could remove the concern.

Moreover, the risk characterisation could also be refined by including indicators of Cd bioavailability. This can be achieved by measuring the organic carbon normalised excess SEM Cd over AVS. This refinement should use a worst case approach to account for seasonal variation in AVS and it is suggested that the AVS approach should be further validated (see Section 3.2.4.3). To that end a **conclusion (i)** was decided by the Technical Meeting. Furthermore, an uncertainty analysis regards the impact of an EU-wide variability in  $\text{PEC}_{\text{regional}}$  (as a default approach in the absence of site-specific data) on the risk characterisation at local level, is not yet included. Both aspects, bioavailability and variability impact, will be implemented in an update of the risk assessment report once the results of the **conclusion (i)** program are agreed at TC NES level (see separate document, ‘RAR Stage II’).

#### STP (off-site)

In this study, the risk for micro-organisms in sewage treatment plants is investigated for off-site sewage treatment plants (STP) only<sup>59</sup>.

Only two plants discharge in a STP system. The ratio of effluent concentration to the  $\text{PNEC}_{\text{micro-organisms}}$  ( $20 \mu\text{g L}^{-1}$ ) is suggested as the indicator of risk for a STP (TGD, 1996). This ratio is lower than 1 for both plants. However, for the reference year 1999, the risk factor calculated for NiCd producing plant 1 is close to 1 ( $0.95$ )<sup>60</sup>. There is a possibility that the risk is over predicted. Several toxicity tests (including sludge respiration test) showed that Cd affects micro-organisms of an STP at only about 1 mg Cd/L in the dissolved fraction. The  $\text{PNEC}_{\text{STP}}$  was calculated from the lowest NOEC using an assessment factor, yielding a  $\text{PNEC}_{\text{micro-organisms}}$  that is about 50-fold below the lowest LOEC and where sludge respiration was less than 30% affected

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<sup>59</sup> Remark: the type of the on-site STP (WWTP) at the battery production-sites is essentially based on physical-chemical principles only (see information in Table 3.7).

<sup>60</sup> For the year 2000, due to the implementation of a new wastewater treatment plant and the changing in the production process and cleaning method, a significant reduction in total emission towards the municipal STP is reported (see Section 3.1.2.2.1) and based on measured data (concentration of Cd in effluent and the effluent flow) a lower PEC local and risk factor can be calculated.

(section 3.2.6). There is no site where effluent concentrations exceed about 1 mg Cd/L or the lowest NOEC ( $200 \mu\text{g L}^{-1}$ ).

For the other sites the STP risk factor is irrelevant because for these sites the industrial effluents are rejected to surface water after physico-chemical treatment on-site.

### 3.3.3.2.2 Risk characterisation MSW incinerators

Since cadmium emissions from incinerators reflect always all cadmium sources a comparative risk assessment has been made. First, the risk associated with the total cadmium emissions is given. This analysis is followed by the calculation of the risks associated with the total cadmium without NiCd batteries.

#### Freshwater

**Table 3.255** Local risk characterisation incinerators for water and STP (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The  $\text{PNEC}_{\text{water}}$  is  $0.19 \mu\text{g Cd/L}$ . The  $\text{PNEC}_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt}$ . The PNEC for micro-organisms is  $20 \mu\text{g L}^{-1}$  (Table 3.245). Total cadmium concentrations. (Dilution Scenario 1 = DF 100 and Dilution Scenario 2 = DF 1000)

	PEC local water DF = 100	Factor risk water DF = 100	PEC local water DF = 1,000	Factor risk water DF = 1,000	Ceffluent	Factor risk STP
	$\mu\text{g L}^{-1}$	-	$\text{mg L}^{-1}$	-	$\text{mg L}^{-1}$	
<u>Dilution Scenario 1 &amp; 2</u>	0.13	0.68	0.12	0.63	0.005	0.25

No risks are expected for aquatic organisms when the current estimated emission from a hypothetical local incineration plant is considered (for both dilution factor 100 and 1,000). If the effluent of a incinerator plant is released after an on-site WWTP with high Cd removal efficiency (98.8%) in a STP no toxicity to the off-site STP micro-organisms is predicted. Removing all NiCd batteries from the MSW stream has a negligible influence on the obtained risk ratios (see **Table 3.256**).

**Table 3.256** Local risk characterisation incinerators for water (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The  $\text{PNEC}_{\text{water}}$  is  $0.19 \mu\text{g Cd/L}$ . The  $\text{PNEC}_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt}$ . The PNEC for micro-organisms is  $20 \mu\text{g L}^{-1}$  (Table 3.245). Total cadmium without NiCd contribution. (Dilution Scenario 1 = DF 100 and Dilution Scenario 2 = DF 1000)

	PEC local water DF = 100	Factor risk water DF = 100	PEC local water DF = 1,000	Factor risk water DF = 1,000
	$\mu\text{g L}^{-1}$	-	$\mu\text{g L}^{-1}$	-
	Assumption NiCd batteries contributed 10 % to the overall Cd load			
<u>Dilution Scenario 1 &amp; 2</u>	0.13	0.68	0.11	0.58
	Assumption NiCd batteries contributed 50 % to the overall Cd load			
<u>Dilution Scenario 1 &amp; 2</u>	0.12	0.63	0.11	0.58

## Uncertainty analysis

### PNEC

It should be noted that an assessment factor of 2 has been included in the PNEC derivation due to remaining uncertainty. The inclusion or exclusion of this assessment factor does not influence the risk conclusions for the MSW incinerator scenarios.

### Using measured regional values

Aforementioned exposure estimations and risk assessment are based on calculated  $PEC_{\text{regional}}$  (i.e.  $0.11 \mu\text{g L}^{-1}$ ). Preference should, however, be given to measured values when available. However in the absence of reliable and representative regional measured data in the vicinity of the individual sites the RCR values have also been calculated (results not shown) using the average of the measured P90 values for different countries (i.e.  $0.12 \mu\text{g L L}^{-1}$ ) and also using the median of the measured P90 values (i.e.  $0.07 \mu\text{g L L}^{-1}$ ). The use of the average measured regional PEC concentration ( $0.12 \mu\text{g L L}^{-1}$ ) or the median regional PEC concentration ( $0.07 \mu\text{g L}^{-1}$ ) does not change the risk conclusions.

### Dilution factors

The risk conclusions are based on a realistic worst case dilution factor of 100 and a typical value of 1,000. In case the dilution factor would be below 25 at an effluent concentration of  $0.0056 \text{ mg L}^{-1} \text{ L}^{-1}$  or more, a risk would be predicted.

### Cadmium removal efficiencies

The risk conclusions are based on the use of an on-site WWTP with a removal efficiency of 98.8% and an influent concentration of  $0.47 \text{ mg L}^{-1} \text{ L}^{-1}$ . In case the removal efficiency is lower than 95.1% while the influent concentration is  $0.47 \text{ mg L}^{-1}$  or more, a risk would be predicted.

### 3.3.3.2.3 Sediments (assessment without bioavailability correction)

**Table 3.257** Local risk characterisation incinerators for sediments (at dilution factor 100 and 1,000). The factor risk =  $PEC/PNEC$ . The  $PNEC_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt.}$  The factor risk is calculated for the concentration of added Cd ( $C_{\text{local sediment}}$ ) and for the added and regional Cd (total Cd, i.e.  $PEC_{\text{sediment}}$ ) without correction for bioavailability. Total cadmium concentrations. (Dilution Scenario 1 = DF 100 and Dilution Scenario 2 = DF 1000)

	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total	Factor risk sediment DF = 100 Added	PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total	Factor risk sediment DF = 1,000 Added
	$\text{mg kg}^{-1} \text{ dry wt.}$	-	-	$\text{mg kg}^{-1} \text{ dry wt.}$	-	
<u>Dilution Scenario 1 &amp; 2</u>	5.19	2.3	1.1	2.91	1.3	0.09

For all hypothetical local incineration scenarios a risk for sediment organisms is predicted. It should be noted that risk is always predicted even if local emissions are zero because the regional Cd concentration (90<sup>th</sup> percentile of measured data i.e.  $2.66 \text{ mg kg}^{-1} \text{ dry wt.}$ ) is already above the PNEC sediment. The risk factor based on total vary is 2.1 for the realistic worst case

situation when a DF of 100 can be applied and is 1.1 for a DF of 1,000. Based only on local emissions (i.e. without the background contribution), no risk is predicted for the scenario with the dilution factor of 1,000.

**Table 3.258** Local risk characterisation incinerators for sediments (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC<sub>sediment</sub> is 2.3 mg kg<sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C<sub>local</sub><sub>sediment</sub>) and for the added and regional Cd (total Cd, i.e. PEC<sub>sediment</sub>) without correction for bioavailability. Total cadmium without NiCd contribution

	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total	Factor risk sediment DF = 100 Added	PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total	Factor risk sediment DF = 1,000 Added
	mg kg <sup>-1</sup> dry wt.	-	-	mg kg <sup>-1</sup> dry wt.	-	
Assumption NiCd batteries contributed 10 % to the overall Cd load						
<u>Dilution Scenario 1 &amp; 2</u>	4.87	2.1	0.96	2.69	1.2	0.01
Assumption NiCd batteries contributed 50 % to the overall Cd load						
<u>Dilution Scenario 1 &amp; 2</u>	3.93	1.7	0.48	2.79	1.2	0,01

Removing all NiCd batteries from the MSW stream has only a minor impact on the risk conclusions.

These results are based, however, on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A **conclusion (i)** program is ongoing. Furthermore, an uncertainty analysis regards the impact of an EU-wide variability in PEC reg (as a default approach in the absence of site-specific data) on the risk characterisation at local level, is not yet included. Both aspects, bioavailability and variability impact, will be implemented in an update of the risk assessment report once the results of the **conclusion (i)** program are agreed at TC NES level (see separate document).

### 3.3.3.2.4 Future scenarios and sensitivity analysis MSW incinerators

#### Future scenario

**Table 3.259** Local risk characterisation incinerator for water and STP (at dilution factor 100 and 1,000). Future scenarios: collection rate: 10 and 75%. The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC for micro-organisms is 20 µg L<sup>-1</sup>(Table 3.245). Total cadmium concentrations

Scenario	PEC local water DF = 100	Factor risk water DF = 100	PEC local water DF = 1,000	Factor risk water DF = 1,000	Ceffluent	Factor risk STP
	µg L <sup>-1</sup>	-	µg L <sup>-1</sup>	-	mg L <sup>-1</sup>	
MSW Incineration plant (10%; total cadmium)	0.16	0.84	0.12	0.63	0.0135	0.68
MSW Incineration plant (75%; total cadmium)	0.14	0.74	0.12	0.63	0.007	0.35

**Table 3.259** indicates no risks for the future hypothetical incineration plant (both scenarios) for aquatic organisms if a dilution factor of 1,000 is applicable. Performing the exercise for the different collection scenarios (10 and 75%) with a dilution factor of only 100 indicates also no risk for the aquatic compartment for both the 10% and 75% recycling scenario. No toxicity to off-site STP micro-organisms from the MSW local incineration plant is predicted for the future scenarios.

Removing all NiCd batteries resembles the current scenario as presented in **Table 3.256** (i.e. assumption at start that 10% of the Cd load is due to NiCd batteries).

### Uncertainty analysis

#### *PNEC*

It should be noted that an assessment factor of 2 has been included in the PNEC derivation due to remaining uncertainty.

The inclusion or exclusion of the assessment factor of 2 does not influence the conclusions.

#### *Using measured regional values:*

Aforementioned exposure estimations and risk assessment are based on calculated PEC reg (i.e.  $0.11 \mu\text{g L}^{-1}$ ). Preference should, however, be given to measured values when available. However in the absence of reliable and representative regional measured data in the vicinity of the individual sites the RCR values have also been calculated (results not shown) using the average of the measured P90 values for different countries (i.e.  $0.12 \mu\text{g L}^{-1}$ ) and also using the median of the measured P90 values (i.e.  $0.07 \mu\text{g L}^{-1}$ ). The use of the measured regional PEC does not influence the conclusion of the risk characterisation.

### **3.3.3.2.5 Sediment (assessment without bioavailability correction)**

For all future scenarios a risk is predicted for sediment organisms. Based only on local emissions (i.e. without the regional background contribution), no risk is predicted for the scenario with 10-75% collection when a DF of 1,000 is applicable. A potential risk is still apparent for the 10-75% collection when a DF of 100 is applied.

**Table 3.260** Local risk characterisation incinerators for sediments for a generic MSW incineration plant in the EU. Future scenarios: collection rate: 10 and 75% (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The  $\text{PNEC}_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt.}$  The factor risk is calculated for the concentration of added Cd ( $\text{C}_{\text{local sediment}}$ ) and for the added and regional Cd (total Cd, i.e.  $\text{PEC}_{\text{sediment}}$ ) without correction for bioavailability. Total cadmium concentrations

Scenario	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total	Factor risk sediment DF = 100 Added	PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total	Factor risk sediment DF = 1,000 Added
	$\text{mg kg}^{-1} \text{ dry wt.}$	-	-	$\text{mg kg}^{-1} \text{ dry wt.}$	-	
MSW Incineration plant (10% collection; total cadmium)	8.6	3.7	2.3	3.3	1.4	0.26
MSW Incineration plant (75% collection; total cadmium)	6.8	2.95	1.8	3.0	1.3	0.13

These results are based, however, on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A **conclusion (i)** program is ongoing (see separate document).

Removing all NiCd batteries resembles the current scenario as presented in **Table 3.258** (i.e. assumption at start that 10% of the Cd load is due to NiCd batteries).

### 3.3.3.2.6 Sensitivity analysis

**Table 3.261** Local risk characterisation incinerator for water and STP (at dilution factor 100 and 1,000). Sensitivity analysis: effluent = 0.009 mg L<sup>-1</sup>. The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC for micro-organisms is 20 µg L<sup>-1</sup>(Table 3.245). Total cadmium concentrations

Scenario	PEC local water DF = 100	Factor risk water DF = 100	PEC local water DF = 1,000	Factor risk water DF = 1,000	Ceffluent	Factor risk STP
	µg L <sup>-1</sup>	-	µg L <sup>-1</sup>	-	mg L <sup>-1</sup>	
MSW Incineration plant (10%; total cadmium)	0.14	0.68	0.13	0.68	0.009	0.45

**Table 3.261** indicates no risks (both scenarios) for the aquatic compartment for a maximal measured effluent concentration of 0.009 mg L<sup>-1</sup>

**Table 3.262** Local risk characterisation incinerators for sediments for a generic MSW incineration plant in the EU. Sensitivity analysis: effluent = 0.009 mg L<sup>-1</sup>(at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC<sub>sediment</sub> is 2.3 mg kg<sup>-1</sup> dry wt. The factor risk is calculated for the concentration of added Cd (C<sub>local</sub><sub>sediment</sub>) and for the added and regional Cd (total Cd, i.e. PEC<sub>sediment</sub>) without correction for bioavailability. Total cadmium concentrations

Scenario	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total	Factor risk sediment DF = 100 Added	PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total	Factor risk sediment DF = 1,000 Added
	mg kg <sup>-1</sup> dry wt.	-	-	mg kg <sup>-1</sup> dry wt.	-	
MSW Incineration plant (10%; total cadmium)	6.6	2.86	1.71	3.05	1.7	0.56

For all scenarios a risk is predicted for sediment organisms. Based only on local emissions (i.e. without the regional background contribution), no risk is predicted when a dilution factor of 1,000 is applicable. These results are based, however, on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A **conclusion (i)** program is ongoing (see separate document).

### 3.3.3.2.7 Risk characterisation for MSW landfills

Since cadmium emissions from landfills reflect always all cadmium sources a comparative risk assessment has been made. First the risk associated with the total cadmium emissions is given. This analysis is followed by the calculation of the risks associated with the total cadmium without NiCd batteries.

**Table 3.263** Local risk characterisation landfills (leachate concentration  $5 \mu\text{g L}^{-1}$ ) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The  $\text{PNEC}_{\text{water}}$  is  $0.19 \mu\text{g Cd/L}$ . The  $\text{PNEC}_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt.}$ . The factor risk is calculated for the concentration of added Cd ( $\text{C}_{\text{local sediment}}$ ) and for the added and regional Cd (total Cd, i.e.  $\text{PEC}_{\text{sediment}}$ ) without correction for bioavailability. The PNEC for micro-organisms is  $20 \mu\text{g L}^{-1}$  (Table 3.245). Total cadmium concentrations

Use-category	N°	PEC <sub>local water</sub>	Factor risk water	PEC <sub>local sediment</sub>	Factor risk sediment Total	Factor risk sediment Added	C <sub>effluent</sub>	Factor risk STP
		$\mu\text{g/L}$		$\text{mg kg}^{-1} \text{ dry wt.}$			$\text{mg L}^{-1}$	
MSW landfill (total cadmium)	1	0.12	0.63	3.8	1.6	0.5	0.005	n.r.
MSW landfill (total cadmium)	2	0.12	0.63	3.1	1.3	0.2	0.00024 <sup>a</sup>	0.012

n.r. Not relevant

a)  $5 \mu\text{g L}^{-1}/21$  (21 being the dilution factor in STP see Table 3.95)

No risks to the aquatic environment are observed for landfills emitting a leachate with total cadmium content of  $5 \mu\text{g L}^{-1}$ .

A risk is observed for all scenarios for the sediment compartment. However, based only on local emissions (i.e. without the background contribution) no risk is predicted at landfills with a leachate concentration of  $5 \mu\text{g L}^{-1}$ .

In **Table 3.264** the RCR values for the scenario where all NiCd batteries would be removed from the MSW stream is given. The influence on the RCR values is negligible.

**Table 3.264** Local risk characterisation landfills (leachate concentration  $5 \mu\text{g L}^{-1}$ ) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The  $\text{PNEC}_{\text{water}}$  is  $0.19 \mu\text{g Cd/L}$ . The  $\text{PNEC}_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt.}$ . The factor risk is calculated for the concentration of added Cd ( $\text{C}_{\text{local sediment}}$ ) and for the added and regional Cd (total Cd, i.e.  $\text{PEC}_{\text{sediment}}$ ) without correction for bioavailability. The PNEC for micro-organisms is  $20 \mu\text{g L}^{-1}$  (Table 3.245). All cadmium without NiCd batteries

Use-category	N°	PEC <sub>local water</sub>	Factor risk water	PEC <sub>local sediment</sub>	Factor risk sediment Total	Factor risk sediment Added
		$\mu\text{g/L}$		$\text{mg kg}^{-1} \text{ dry wt.}$		
MSW Landfill (NiCd batteries contributed for 10%)	1	0.12	0.63	3.7	1.6	0.4
MSW Landfill (NiCd batteries contributed for 50%)		0.12	0.63	3.3	1.4	0.6
MSW Landfill (NiCd batteries contributed for 10%)	2	0.12	0.63	3.1	1.3	0.3
MSW Landfill (NiCd batteries contributed for 50%)		0.12	0.63	2.9	1.3	0.3

n.r. Not relevant;

a)  $5 \mu\text{g L}^{-1}/21$  (21 being the dilution factor in STP see Table 3.95).

## Sensitivity analysis

**Table 3.265** Local risk characterisation landfills (leachate concentration  $50 \mu\text{g L}^{-1}$ ) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The  $\text{PNEC}_{\text{water}}$  is  $0.19 \mu\text{g Cd/L}$ . The  $\text{PNEC}_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt}$ . The factor risk is calculated for the concentration of added Cd ( $\text{C}_{\text{local sediment}}$ ) and for the added and regional Cd (total Cd, i.e.  $\text{PEC}_{\text{sediment}}$ ) without correction for bioavailability. The PNEC for micro-organisms is  $20 \mu\text{g L}^{-1}$  (Table 3.245). Total cadmium concentrations

Use-category	N°	PEC <sub>local water</sub>	Factor risk water	PEC <sub>local sediment</sub>	Factor risk sediment Total	Factor risk sediment Added	C <sub>effluent</sub>	Factor risk STP
		$\mu\text{g L}^{-1}$		$\text{mg kg}^{-1} \text{ dry wt}$			$\text{mg L}^{-1}$	
MSW landfill (total cadmium)	1	0.21	1.1	14.9	6.5	5.3	0.050	n.r.
MSW landfill (total cadmium)	2	0.15	0.79	6.8	3	1.8	0.0024 <sup>a</sup>	0.12

n.r. Not relevant;

a)  $50 \mu\text{g L}^{-1} / 21$  (21 being the dilution factor in STP see Table 3.95).

No risks to the aquatic environment are observed for landfills emitting a leachate with a total cadmium content of  $50 \mu\text{g L}^{-1}$  to a STP. If this leachate concentration is discharged immediately to the surface water a risk is predicted for the scenario ‘all cadmium in MSW’. Based on PEC and PNEC values not corrected for bioavailability, a risk is observed for all scenarios for the sediment compartment. These results are based, however, on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A **conclusion (i)** program is ongoing. Furthermore, an uncertainty analysis regards the impact of an EU-wide variability in PEC reg (as a default approach in the absence of site-specific data) on the risk characterisation at local level, is not yet included. Both aspects, bioavailability and variability impact, will be implemented in an update of the risk assessment report once the results of the **conclusion (i)** program are agreed at TC NES level (see separate document).

No risks are expected for the off-site STP.

### Uncertainty analysis

It should be noted that an assessment factor of 2 has been included in the PNEC derivation due to remaining uncertainty.

The uncertainty surrounding the PNEC water influences the risk conclusion for the landfill discharging a landfill leachate with a cadmium concentration of  $50 \mu\text{g L}^{-1}$  directly in a river. If no assessment factor is applied this scenario would not have a local risk anymore ( $\text{RCR} = 0.55$ ) for the water compartment.

### Using measured regional values

Aforementioned exposure estimations and risk assessment are based on calculated PEC reg (i.e.  $0.11 \mu\text{g L}^{-1}$ ). Preference should, however, be given to measured values when available. However in the absence of reliable and representative regional measured data in the vicinity of the individual sites the RCR values have also been calculated (results not shown) using the average of the measured P90 values for different countries (i.e.  $0.12 \mu\text{g L}^{-1}$ ) and also using the median of the measured P90 values (i.e.  $0.07 \mu\text{g L}^{-1}$ ).

The use of the average measured regional PEC concentration ( $0.12 \mu\text{g L}^{-1}$ ) or the median regional PEC concentration ( $0.07 \mu\text{g L}^{-1}$ ) does not change the risk conclusions.

In **Table 3.266** the RCR values for the scenario where all NiCd batteries would be removed from the MSW stream is given. The influence on the RCR values is negligible at the exception of the case where NiCd batteries for their Cd content contribute to 50% of the MSW and the landfill leachate is directly discharged to surface water. In the latter case, a reduction of the factor risk water of 23.6% is obtained, resulting in a ‘no risk’ situation.

**Table 3.266** Local risk characterisation landfills (leachate concentration  $50 \mu\text{g L}^{-1}$ ) for water and sediment. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The  $\text{PNEC}_{\text{water}}$  is  $0.19 \mu\text{g Cd/L}$ . The  $\text{PNEC}_{\text{sediment}}$  is  $2.3 \text{ mg kg}^{-1} \text{ dry wt.}$ . The factor risk is calculated for the concentration of added Cd ( $\text{C}_{\text{local sediment}}$ ) and for the added and regional Cd (total Cd, i.e.  $\text{PEC}_{\text{sediment}}$ ) without correction for bioavailability. The PNEC for micro-organisms is  $20 \mu\text{g L}^{-1}$  (Table 3.245). Total cadmium without NiCd batteries

Use-category	N°	PEC <sub>local</sub> Water	Factor risk water	PEC <sub>local</sub> sediment	Factor risk sediment Total	Factor risk sediment Added
		$\mu\text{g /L}$		$\text{mg kg}^{-1} \text{ dry wt.}$		
MSW Landfill (NiCd batteries contributed for 10%)	1	0.20	1.1	13.7	6.0	4.8
MSW Landfill (NiCd batteries contributed for 50%)		0.16	0.84	8.8	3.8	2.7
MSW Landfill (NiCd batteries contributed for 10%)	2	0.14	0.7	6.3	2.7	1.6
MSW Landfill (NiCd batteries contributed for 50%)		0.13	0.68	4.7	2.0	0.9

n.r. Not relevant;

a)  $50 \mu\text{g L}^{-1} / 21$  (21 being the dilution factor in STP see Table 3.95).

### 3.3.3.3 The atmospheric compartment

No risk characterisation can be made since no data were found on Cd toxicity for organisms in the atmospheric compartment<sup>61</sup>.

Calculated local PEC values range from  $0.561$  to  $22.6 \text{ ng/m}^3$  for NiCd batteries producers and from  $0.561$  to  $1.91 \text{ ng/m}^3$  for Cd recycling plants.

The PEC<sub>local</sub> in air at a distance of 100 m from a generic MSW incineration plant is  $7.5 \text{ ng/m}^3$  (average EU situation). Taking into account the contribution from batteries to the MSW (10%-50%), PEC local in air varies between  $1.3$  and  $4.1 \text{ ng/m}^3$ .

In the worst case situation (France) a PEC<sub>local</sub> in air of  $28.5 \text{ ng/m}^3$  can be calculated (all MSW). Taking into account the contribution from batteries to the MSW (10%-50%), PEC local in air varies between  $3.4$  and  $14.5 \text{ ng/m}^3$ .

<sup>61</sup> For health risk evaluation reference is made to the ‘global’ RAR on Cd/CdO (see Section 4 of this report in separate document as well as to Section 2.3 (legislative) control measures).

### 3.3.3.4 The terrestrial compartment

#### 3.3.3.4.1 NiCd producing/recycling plants

The ratio PEC/PNEC for local soil risk assessment is given in **Table 3.267**. The PNEC<sub>soil</sub> value is 0.9 mg kg<sup>-1</sup> dry wt and is the lowest for local risk assessment

No risk is predicted at all sites. The risk factors for soil are 0.5. This conclusion should be treated with caution. The local soil concentrations are calculated after 10 years exposure. In Section 3.1.3.1.3 it is mentioned that for Cd producing sites having high emissions to air (> 800 kg Cd/year) risk factors are above 1 when Cd concentrations are predicted in soil after 50 years aerial deposition. Since neither NiCd batteries producers nor Cd recyclers emit these high Cd quantities to air, the 50 years exposure calculation does not seem relevant in the context of this report.

#### 3.3.3.4.2 MSW incinerators

No risk to soil organisms (or higher food chain via secondary poisoning) is predicted at the hypothetical EU incineration plants.

**Table 3.267** Local risk characterisation for soil. The factor risk = PEC/PNEC. The PNEC value = 0.9 mg kg<sup>dry wt.</sup> is equivalent to 0.79 mg kg<sup>wet wt.</sup> (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3.245)

Use-category	Plant N°	PEC <sub>local soil</sub> mg kg <sup>wet wt.</sup>	Factor risk soil	Year
NiCd-batteries	1	0.36	0.5	1999
	2	0.36	0.5	1999
	3	0.36	0.5	2000
	4	0.37	0.5	2000
	5	0.37	0.5	2000
	6	0.36	0.5	1999
	7	0.37	0.5	1999
Cd recyclers	1	0.36	0.5	2000
	2	0.36	0.5	1999
MSW incineration (all scenarios and total cadmium)		0.36-0.3737	0.5	

No future scenarios were developed for this compartment.

### 3.3.4 Risk characterisation for all scenarios: update data (year 2002)

In the following subsections risk characterisation is performed for those companies/sectors that submitted new exposure data (reference year 2002). This means that the current update

assessment overwrites the RCR values and conclusions derived for corresponding companies/sectors reported in the previous stand-alone documents (global RAR, TRAR).

For the use scenarios ‘alloys’ and ‘plating’ no update exposure data were provided. Therefore the values and conclusions as previously reported remain valid.

#### **3.3.4.1 The aquatic compartment (including sediment)**

The risk factors (PEC/PNEC ratio) for WWTP/STP, local water (dissolved fraction) and sediment concentrations for the freshwater environment are given in **Table 3.268**. The PNEC was not corrected for water hardness because of lack of site-specific water hardness information.

**Table 3.268** Local risk characterisation of Cd/CdO production/processing sites for WWTP/STP, water and sediment (modelled data). The factor risk = PEC/PNEC. The PNEC<sub>micro-organisms</sub> is 20 µg L<sup>-1</sup>, The PNEC<sub>water</sub> is 0.19 µg Cd/L and the PNEC<sub>sediment</sub> is 2.3 mg Cd/kg<sub>dw</sub>. (Table 3.245). The factor risk for sediments is calculated for the concentration of added Cd (C<sub>local</sub><sub>sediment</sub>, Table 3.137) and for the added+regional Cd (total Cd, i.e. PEC<sub>local</sub><sub>sediment</sub>, Table 3.137). The results for the sediment compartment are based on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A conclusion (i) program is ongoing

Plant N°	PEC <sub>WWTP/STP</sub> (dissolved fraction)	Factor risk WWTP/STP	PEC <sub>local</sub> <sub>water</sub> (dissolved Cd)	Factor risk water	PEC <sub>local</sub> <sub>sediment</sub>	Factor risk sediment (added)	Factor risk sediment (total)	Year
	µg L <sup>-1</sup>		µg L <sup>-1</sup>		mg kg <sup>-1</sup> <sub>dw</sub>			
<b>Cd metal production</b>								
1	3.6 <sup>(d)</sup>	n.r.	0.64	3.36	71.5	29.9	31.1	2002
6	0.7	n.r.	0.11	0.58	2.7	0.01	1.2	2002
7*	50*	n.r.*	0.28*	1.46 [1.25]*	24.5*	9.5*	10.7*	2002
7*	30*	n.r.	0.21*	1.13 [0.92]*	16.2*	5.9*	7.1*	2004
<b>Cd oxide production</b>								
12 <sup>(a)</sup>	n.a.	n.a.	0.11	0.58	2.7	0	1.2	2002
<b>NiCd battery production</b>								
2*	107	n.r.	0.15	0.77	7.4	2.0	3.2	2002
3	63	n.r.	0.13	0.69	5.5	1.2	2.4	2002
4	103	n.r.	0.14	0.76	7.2	2.0	3.1	2002
6	No update data							
7	No update data							
<b>NiCd battery recycling</b>								
1	370	n.r.	0.24	1.24	19.0	7.1	8.2	2002
1 <sup>(e)</sup>	240	n.r.	0.19	1.01	13.2	4.6	5.8	2004
2 <sup>(b)</sup>	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2002

Table 3.268 continued overleaf

**Table 3.268 continued** Local risk characterisation of Cd/CdO production/processing sites for WWTP/STP, water and sediment (modelled data). The factor risk = PEC/PNEC. The PNEC<sub>micro-organisms</sub> is 20 µg L<sup>-1</sup>, The PNEC<sub>water</sub> is 0.19 µg Cd/L and the PNEC<sub>sediment</sub> is 2.3 mg Cd/kg<sub>dw</sub>. (Table 3.245). The factor risk for sediments is calculated for the concentration of added Cd (C<sub>local</sub><sub>sediment</sub>, Table 3.137) and for the added+regional Cd (total Cd, i.e. PEC<sub>local</sub><sub>sediment</sub>, Table 3.137). The results for the sediment compartment are based on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A conclusion (i) program is ongoing

Plant N°	PEC <sub>WWTP/STP</sub> (dissolved fraction)	Factor risk WWTP/STP	PEC <sub>local</sub> <sub>water</sub> (dissolved Cd)	Factor risk water	PEC <sub>local</sub> <sub>sediment</sub>	Factor risk sediment (added)	Factor risk sediment (total)	Year
	µg L <sup>-1</sup>		µg L <sup>-1</sup>		mg kg <sup>-1</sup> <sub>dw</sub>			
<b>Cd pigments production</b>								
A	19	n.r.	0.38	1.98	37.4	15.1	16.2	2003
B	19	n.r.	0.12	0.61	3.5	0.4	1.5	2003
C	121	n.r.	0.25	1.32	21.0	8.0	9.1	2003
C(90P)	80	n.r.	0.25	1.34	21.3	8.1	9.3	2004
<b>Cd stabiliser production</b>								
X WWTP	5	0.25						
X STP <sup>©</sup>	0.4	0.02	0.11	0.58	2.7	0.02	1.2	2002
Y	<5 <sup>(f)</sup>	n.r.	0.12	0.62	3.6	0.4	1.5	2002
Y	<1 <sup>(g)</sup>	n.r.	0.11	0.59	2.8	0.1	1.2	2002

\* Emission to the sea: risk characterisation is only indicative and based on PNEC freshwater and PEC<sub>reg</sub> water for freshwater. For water, Industry (Cd metal producer site 7) proposes to use 0.07 µg L<sup>-1</sup> as local (regional?) background concentration as done by NIVA (NIVA report 4606-2002) resulting in a lower RCR value of 1.25 (2002) and 0.92 (2004) respectively. However, MSR could not validate this latter value. No formal conclusions are drawn for sites emitting to the marine environment;

n.a. Not applicable;

n.r. Not relevant for the on-site WWTP (only physc-chem based);

a) No emission to water; thermal/dry process;

b) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant;

c) Cd concentration in effluent from municipal STP; calculated from Cd concentration in effluent from on-site WWTP; taking into account removal at STP: 60%; extra dilution: 2,000 m<sup>3</sup>/day/370 m<sup>3</sup>/day = 5.4;

d) The biological based wastewater purification system contains fully adapted, specialised and dedicated micro-organisms. These bacteria are not at all representative for 'standard' micro-organisms communities used in municipal STPs;

e) Emissions from the site are further reduced in 2003/2004 due to efforts to conform to ISO 14000, for which the site has been certified in February 2005;

f) Effluent analysis performed by internal laboratory (two times a month) method MIP-P-PRO-101 rev 2 year 2003;

g) Effluent analysis performed by certified external laboratory (two times a year), method EPA 200.8 (1994).

From **Table 3.268** it can be concluded that risks for freshwater aquatic organisms occur at 1 Cd metal production-sites (site 1), 1 NiCd battery recycling site (site 1) and 2 Cd-pigments producing sites (site A, C). It is to be noted that Cd metal producing plant 7 and NiCd production-site 2 emit effluents to the marine environment. No risk assessment to the marine environment is done in this report. No formal conclusions are drawn for these sites. The PECs presented in **Table 3.268** are ‘calculated’ local concentrations.

Measured Cd concentrations in surface water – presented in **Table 3.138** - are available for Cd metal production-site 1 and 7 and NiCd battery recycling site 1 and Cd stabiliser site Y.

In conclusion:

- Locally measured data near the Cd producer site 1 (i.e. 1 µg dissolved Cd/L; downstream from the site; including background and possible other sources) point there is predicted risk (risk factor: 5.3).
- For recycling site 1, risk is predicted as well by the locally measured data (i.e. 19.8 µg dissolved Cd/L, downstream from the discharge point; risk factor: 104) that however include the background and possibly other sources (historical contamination due to infiltration and run-off from old metallurgical slag heaps).
- Measurements at Cd stabiliser site Y are based on not sufficiently sensitive analytical method (detection limit too high) to make a judgment about the background and added concentrations in the receiving river.

Monitoring data are not available for any CdO producing or Cd metal/CdO processing company.

Marine environment:

- The risk characterisation for the marine environment (Cd metal producer site 7 and NiCd battery producer site 2) is based on  $PNEC_{\text{freshwater}}$  and  $PEC_{\text{reg water}}$  for freshwater. Therefore the risk characterisation for this site is only indicative. No risk assessment to the marine environment is done in this report. Industry’s representative for the Cd metal producer site 7 proposes to use  $0.07 \mu\text{g L}^{-1}\text{L}^{-1}$  as local (regional?) background concentration as done by NIVA (NIVA report 4606-2002) resulting in a lower RCR value of 1.25 (2002) and 0.92 (2004) respectively. However, MSR could not validate this latter value.

### Uncertainty analysis

The uncertainty surrounding the PNEC water is related to several aspects: statistical aspects (confidence limits on the HC5 estimated from the SSD) and more general concerns such as species representativity, the inherent uncertainty about NOEC values compared to the benchmark values, mixed pollution etc. These factors have crystallised in the AF=2 which was agreed. The uncertainty around the PNEC water influences the risk conclusion for Cd recycling plant 1 and Cd pigment plants A and C. If no assessment factor is applied the sites would not have a local risk anymore (RCR = 0.6-0.99) for the water compartment.

### Using measured regional values

Aforementioned exposure estimations and risk assessment are based on calculated PEC reg (i.e.  $0.11 \mu\text{g L}^{-1}$ ). Preference should, however, be given to measured values when available. However in the absence of reliable and representative regional measured data in the vicinity of the individual sites the RCR values have also been calculated (results not shown) using the average

of the measured P90 values for different countries (i.e.  $0.12 \mu\text{g L}^{-1}$ ) and also using the median of the measured P90 values (i.e.  $0.07 \mu\text{g L}^{-1}$ ).

The use of the average measured regional concentration ( $0.12 \mu\text{g L}^{-1}$ ) or the median of the measured P90 values ( $0.07 \mu\text{g L}^{-1}$ ) does not change the risk conclusions (based on 2002 exposure data) for the Cd metal/CdO producing or processing sites.

On the basis of PEC and PNEC values not corrected for bioavailability, risk for benthic organisms is predicted at all sites ( $\text{PEC}_{\text{local sediment}}$ ). Most sites involved in Cd production and processing have a risk for benthic organisms irrespective of the regional background ( $\text{C}_{\text{local sediment}} > \text{PNEC}_{\text{sediment}}$ ) (Cd metal production-site 1 (risk factor: 29.9); NiCd battery production-site 2, 3, 4 (risk factor: 1.2-2.0); NiCd battery recycling site 1 (risk factor: 4.6-7.1) and Cd pigments production-site A, C (risk factor: 8.0-15.1)

Measured Cd concentrations in sediments (without correction for bioavailability) – presented in **Table 3.139** - are available for all Cd metal producing sites, NiCd battery manufacturing site 4 and Cd recycling site 1.

- For Cd metal production-site 1, the measured Cd concentration in sediment sampled upstream and downstream near the discharge point is  $5 \text{ mg kg}^{-1} \text{ dw}$  and  $1.6 \text{ mg kg}^{-1} \text{ dw}$  respectively. Although still resulting in a risk factor above 1 (for the upstream Cd concentration i.e. 2.2) it is obvious that measured Cd concentrations are situated a factor 14 - 45 below the predicted concentrations; hence the risk is reduced. This site also submitted information on AVS and organic carbon content of the sediments. Using these data, the risk characterisation could further be refined (see outcome of **conclusion (i)** program, see separate document).
- Cadmium metal production-site 6 provides recent upstream and downstream measurements in sediments of  $0.64 \text{ mg Cd/kg dw}$  and  $1.14 \text{ mg Cd/kg dw}$  respectively (year 2002). As for site 1, the measured Cd concentrations are below the calculated  $\text{PEC}_{\text{sediment}}$  (2.4-4.2 times lower). Risk factors on the basis of measured data are 0.27-0.50 respectively, hence the risk is removed.
- NiCd battery manufacturing site 4 provides recent upstream and downstream measurements in sediments of  $3.3 \text{ mg Cd/kg dw}$  (100 m upstream) and  $4.6 \text{ mg Cd/kg dw}$  (3 km downstream) respectively (year 2001). Measured Cd concentrations are situated 1.6-2.2 times below the modelled sediment concentrations. On the basis of these data, the risk is reduced; risk factors varying between 1.4 and 2 are calculated. Please note that the sampling downstream is performed at a location 3 km downstream of the plant; hence influence from other sources is likely.
- Cd recycling site 1 provides recent upstream and downstream measurements in sediments of  $55 \text{ mg kg}^{-1} \text{ dw}$  and  $133 \text{ mg kg}^{-1} \text{ dw}$  respectively (year 2002). The measured Cd concentrations are 3-7 fold the calculated  $\text{PEC}_{\text{local sediment}}$  of  $19.0 \text{ mg kg}^{-1} \text{ dw}$ . On the basis of these data, risk is confirmed; risk factors are 24-58. Please note that the measured data are influenced by historical contamination (infiltration and run-off waters from old metallurgical slag heaps), hence data should be treated with caution.

For all these scenarios and sites, risk is also predicted based on the measured data that include background and possible other sources.

Monitoring data are not available for any CdO producing or other Cd metal/CdO processing company/sector.

These results are based, however, on no correction for the bioavailability of cadmium in sediments (SEM/AVS method). A **conclusion (i)** program is ongoing (see separate document: 'RAR Stage II').

Marine environment:

- For Cd metal production-site 7, discharging in a marine environment, Cd concentrations in sediment are reported near the discharge point for the sampling year 1996: 1.1 mg kg<sup>-1</sup> dw and in the open sea: 2.1-3.2 mg kg<sup>-1</sup> dw. The same observation is made as for the other Cd metal producing plants. Measured Cd concentrations, representative for the year 1996, are situated 7.7-22.3 times below the modelled sediment concentrations. On the basis of these 'old' data; a risk factor 'near the discharge point' of 0.48 would be calculated.

The risk characterisation for the marine environment is only indicative as no PNEC was derived for marine species and the PEC regional is calculated for freshwater. No conclusions are drawn on the sites emitting to the sea.

The risk for micro-organisms in sewage treatment plants is investigated for on-site waste water treatment plants (WWTP) as well as off-site sewage treatment plants (STP).

#### On-site waste water treatment plants

Information from the specific production and processing sites indicates that methods to remove cadmium from discharge to water are generally in place. However, in general no detailed and/or measured data are available.

Most wastewater treatment at the plants in the Cd production area is based on physical-chemical principles only (see also IPPC report on the best available techniques in the non ferrous metals industries, May 2000). Similar information was confirmed for NiCd battery producers and recyclers (see TRAR/batteries' related sections, Industry Questionnaire 2002/2003) and Cd containing pigments producers (pers. com., 2005). One Cd metal production plant reports the use of a biological based wastewater purification system that contains fully adapted, specialised and dedicated micro-organisms. It is clear that this type of industrial on-site waste water treatment plant cannot be compared with municipal STPs based on 'standard' micro-organism communities. Therefore, it is decided that for the aforementioned sectors, the derivation of the risk factor for the WWTP is not relevant (n.r.) (see **Table 3.268**).

#### Off-site waste water treatment plants (municipal sewage treatment plants)

For producers of Cd metal and CdO, no discharge occurs to municipal sewage systems, as these sites do emit to surface/sea water or do not emit at all to the aquatic compartment<sup>62</sup>. Therefore, the risk assessment of Cd and CdO producers for off-site STP is not relevant.

Risk to off-site STP is only relevant for the processors that have actual emissions to sewer systems. One stabiliser production-site (site X) reported to discharge its waste water to a municipal STP. Taking into account Cd removal and extra dilution of the WWTP effluent at the municipal STP (discharge rate STP/discharge rate WWTP=5.4) results in an STP effluent concentration of 0.4 µg L<sup>-1</sup>. Consequently a risk factor of 0.02 is calculated, resulting in a no risk situation for this site.

<sup>62</sup> For Cd metal producers: Industry statements, Zinc RAR; for CdO producers: no release of water effluent.

NiCd battery recycling site 2 reports that waste waters are collected and treated off-site in an external waste water treatment plant (year 2002 data: total volume of waste water: 100 m<sup>3</sup>/year; no further data are available) (year 1996 data: 35 tonnes fluid waste per year; Cd content: 20 ppm (total Cd); effluent concentration of off-site STP: 0.2 mg L<sup>-1</sup>). Although the site does not directly discharge any waste water to the receiving environment, the effluent concentration of the off-site STP is taken forward in the risk characterisation. Since the PEC<sub>STP</sub> of 200 µg Cd/L exceeds the PNEC<sub>micro-organisms</sub> of 20 µg L<sup>-1</sup>L<sup>-1</sup>, a risk occurs at the off-site sewage treatment plant (risk factor = 10).

#### Conclusions to the risk assessment for the aquatic compartment:

##### **Conclusion (iii)**

This conclusion applies to the assessment of:

- the local surface water (freshwater) at 1 Cd metal production-site (site 1), 1 NiCd battery recycling site (site 1) and two Cd pigments producing sites (A, C). Local concentrations are based on modeling. Monitoring data are available for the Cd metal production-site 1 and the NiCd recycling site 1: these data indicate risk at background level but do not allow a judgment regarding potential additional risk caused by the site's operations.
- a risk is predicted for the micro-organisms of the STP for NiCd battery recycling plant 2 discharging its effluent to an off-site STP.

##### **Conclusion (i)**

This conclusion applies to the

- For the aquatic compartment, there is a need for better information regarding the toxic effects of cadmium to aquatic organisms under low water hardness conditions. In particular, information is required on: Cd toxicity testing in very soft waters (H below about 10 mg CaCO<sub>3</sub>/L). There are no data for the very soft waters and these areas may be unprotected by the proposed PNEC<sub>water</sub> for soft water (0.08 µg Cd/L).
- For sediment<sup>63</sup>, there is a need for further information regarding the bioavailability of cadmium in order to possibly refine the assessment at regional and local level. In particular: the AVS and organic carbon normalisation should be further validated (see outcome of **conclusion (i)** study program, see separate document, 'RAR Stage II').

##### **Conclusion (ii)**

This conclusion applies to:

- the local surface water compartment for the CdO production-site and Cd recycling plant 2 because there are no emissions to water at these sites.
- the local surface water compartment for Cd metal production-site 6, the NiCd battery producing plants (2, 3, 4), Cd pigments producing site B and all Cd stabiliser production-sites (X, Y) emitting to the aquatic compartment.

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<sup>63</sup> After the TMIV'02 last visit discussion on cadmium in sediment a number of MSs (UK, F, DE) and Industry commented on the sediment assessment and the current conclusions drawn in line with the outcome of that last TM (for more details, see effects assessment and risk characterisation).

- no risk is predicted for the local sediment compartment for the CdO production-site and NiCd recycling plant 2 because there are no emissions to water and no additional risk arises from their operations.
- no risk is predicted for the micro-organisms of the STP for Cd stabiliser production-site X discharging its effluent to a municipal STP.

### 3.3.4.2 The terrestrial compartment

The ratio PEC/PNEC for local soil risk assessment is given in **Table 3.269**. The selected PNEC<sub>soil</sub> value is 0.9 mg kg<sup>-1</sup><sub>dw</sub>, which is the lowest PNEC<sub>soil</sub> value and which is based on secondary poisoning to mammals (see **Table 3.245**).

**Table 3.269** Local risk characterisation for soil (modelled data). The factor risk = PEC/PNEC. The PNEC value = 0.9 mg kg<sup>-1</sup><sub>dw</sub> is equivalent to 0.79 mg kg<sup>-1</sup><sub>ww</sub> (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3.245)

Plant N°	PECl <sub>ocal soil</sub>	Factor risk soil	Year
	mg kg <sub>ww</sub> <sup>-1</sup>		
<b>Cd metal production</b>			
1	0.37	0.47	2002
6	0.36	0.46	2002
7	0.38 – 0.45 <sup>(d)</sup>	0.48 – 0.57	2002
<b>Cd oxide production</b>			
12	0.36	0.46	2005
12	0.36	0.46	2004
<b>NiCd battery production</b>			
2 <sup>(a)</sup>	0.36	0.46	2002
3 <sup>(b)</sup>	n.d.	n.d.	n.d.
4	0.36	0.46	2002
6	No update data		
7	No update data		
<b>NiCd battery recycling</b>			
1	0.36	0.46	2002
1	0.36	0.46	2004
2	0.36	0.46	2002
2bis <sup>(c)</sup>	0.36	0.46	2002

Table 3.269 continued overleaf

**Table 3.269 continued** Local risk characterisation for soil (modelled data). The factor risk = PEC/PNEC. The PNEC value =  $0.9 \text{ mg kg}^{-1}_{\text{dw}}$  is equivalent to  $0.79 \text{ mg kg}^{-1}_{\text{ww}}$  (standard environmental characteristics, TGD) and is the lowest for local risk assessment based on toxicity mammals through secondary poisoning (Table 3.245)

Plant N°	PEC <sub>local soil</sub>	Factor risk soil	Year
	$\text{mg kg}_{\text{ww}}^{-1}$		
<b>Cd pigments production</b>			
A	0.36	0.46	2003
B	0.36	0.46	2003
C	0.36	0.46	2003
<b>Cd stabiliser production</b>			
X		00.46	2002
Y	0.36	0.46	2002

- Emission from battery manufacturing only; air emissions are broken down between two plants; battery manufacturing and Cd recycling;
  - Air emissions are not monitored. No requirement in the permit since the plant runs a wet process, therefore most emissions are releases in the water;
  - Emissions from Cd recycling unit on the site of battery manufacturing plant 4;
  - PEC<sub>local soil</sub> derived on the basis of measured aerial deposition rates;
- n.d. No data available.

Calculated PEC<sub>local soil</sub> values for all Cd/CdO production and processing sites are situated between  $0.36 \text{ mg kg}^{-1}_{\text{ww}}$  and  $0.45 \text{ mg kg}^{-1}_{\text{ww}}$ . Since the modelled PEC<sub>soil</sub> are situated below the PNEC<sub>soil</sub> - based on toxicity for mammals through secondary poisoning- none of the sites are predicted to be at risk (risk ratio: 0.6).

Comparing the modelled PEC<sub>soil</sub> for the local sites with the PNEC<sub>soil</sub> of  $1.15\text{-}2.3 \text{ mg kg}^{-1}_{\text{dw}}$  - based on ecotoxicity for soil organisms - results in the same conclusions i.e. no local risks are predicted (risk ratio: 0.2-0.4).

### Conclusion (ii)

This conclusion applies to the assessment of:

- modelled local soil Cd concentrations for Cd metal/CdO production and processing plants (10 years aerial deposition) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.

#### 3.3.4.3 The atmospheric compartment

No risk characterisation can be made since no data were found on Cd toxicity in the atmospheric compartment.

For Cd metal producers, calculated local PEC values range from  $8.2$  to  $41.8 \text{ ng/m}^3$ .

For the CdO production plant the local PEC value is varying from  $5.6 \text{ ng/m}^3$  (year 2005) to  $9.4 \text{ ng/m}^3$ .

At the Cd/CdO processing plants the PEC<sub>local</sub> in air (at a distance of 100 m) are in the following range:

- Production of NiCd batteries<sup>64</sup>: 3.2 ng/m<sup>3</sup> and 4.4 ng/m<sup>3</sup>
- Recycling of NiCd batteries: 0.6 ng/m<sup>3</sup> and 3.6 ng/m<sup>3</sup>
- Production of Cd containing pigments: 2.5 and 4.8 ng/m<sup>3</sup>
- Production of Cd containing stabilisers: 0.6 and 1.0 ng/m<sup>3</sup>

Measurements for the Cd metal producers indicate that annual average Cd concentration– in air at a distance of 300 m-450 m from the site vary between 1.8 and 8.5 ng/m<sup>3</sup>.

For NiCd battery production-site 4 an annual average Cd concentration of 0.3 ng/m<sup>3</sup> (50 m from the site) is reported.

For NiCd recycling site 1, the measured data lay in the range of 37 to 126 ng/m<sup>3</sup> (year 2002) and from 15 to 21 ng/m<sup>3</sup> (year 2004), a factor 20 to 35 higher than the calculated values.

However, it should be born in mind that measured data have been reported to be influenced also or very probably by other (industrial) sources. In all cases except one i.e. Cd metal production-site 7, the contribution of specific sources has not (yet) been investigated (semi)quantitatively.

#### **3.3.4.4 Secondary poisoning**

Effects of soil-borne Cd on mammals has already been included in the previous section since this pathway is more critical than direct effects on higher plants, soil fauna or soil microbial processes.

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<sup>64</sup> Not all production-sites submitted update exposure information. No data were provided by sites 6 and 7. Previous estimates remain valid.

## **4 HUMAN HEALTH**

(see separate document).

## 5

## RESULTS

### 5.1

### INTRODUCTION

Remarks on the scope, the approach and the limitations of the study are given in Section 0.1.

An overview of the batteries' disposal scenarios is depicted in **Figure 5.1**.

Additional note: the conclusions of this report which are formulated in section 3.3.2 and 3.3.3 are updated with exposure data for the reference year 2002 (Section 3.3.4).

Figure 5.1 Overview of the different regional and local scenarios for the disposal phase taken forward in this report (batteries' related sections)

Regional scenarios														
100 % incineration				24.4 % incineration-75.6 % landfill				100 % landfill						
Current		Future		Current				Current						
Total Cd content 10 g tonne <sup>-1</sup> dry wt.		10 % collection, total Cd content: 24 g tonne <sup>-1</sup> dry wt.		Total Cd content 10 g tonne <sup>-1</sup> dry wt.				Total Cd concentration in leachate concentration : 5 µg L <sup>-1</sup>						
Cd contribution from NiCd batteries: 10-50 %		wt. Cd contribution from NiCd batteries: 63 %		Cd contribution from NiCd bat.: 10-50 %				Cd contribution from NiCd bat.: 10-50 %						
		75 % collection, total Cd content: 13.2 g tonne <sup>-1</sup> dry wt.		Total Cd concentration in leachate concentration : 5 µg L <sup>-1</sup>										
		wt. Cd contribution from NiCd batteries: 32 %												
Local scenarios														
Local scenarios future emissions incinerators (equipped with an on-site WWTP)				Local scenarios current emissions incinerators (equipped with an on-site WWTP)				Local scenarios emissions landfills						
75 %		75 %		10 %		10 %		90 <sup>th</sup> P effluent concentration: 0.005 mg L <sup>-1</sup>						
5 µg L <sup>-1</sup>		5 µg L <sup>-1</sup>		50 µg L <sup>-1</sup>		50 µg L <sup>-1</sup>								
Dilution factor	100	1,000	100	1,000	Dilution factor	100	1,000	100	1,000	Treatm.	STP	No STP	STP	No STP

## 5.2 LOCAL LEVEL: CURRENT SITUATION (=UPDATED WITH 2002 DATA AND ASSESSMENT)

### 5.2.1 Conclusions on cadmium metal

Environment: aquatic ecosystem

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- there is a predicted local risk for the freshwater aquatic ecosystem at 5 Cd production (cadmium metal: 1 site) or Cd processing (pigments producing sites (A,C), plating and alloy) sites/scenarios. Both latter two are generic scenarios ('Cd plating' and 'Cd alloys'). Local concentrations are based on modelling using site-specific and/or standard default values and could possibly have been refined if substantial monitoring data would have been provided. Monitoring data are available for the Cd metal production-site 1: these data indicate risk at background level but do not allow a judgment regards potential additional risk caused by the site's operations.
- There is anticipated local risk at 1 recycling site where modelled freshwater Cd concentrations exceed the  $PNEC_{water}$ . This risk would be removed if no assessment factor (i.e. 2 and reflecting the uncertainty) is applied in deriving the PNEC. Monitoring data are available for this site: these data indicate risk at background level but do not allow a judgment regards potential additional risk caused by the site's operations.

**Conclusion (i)** There is a need for further information and/or testing

**Conclusion (i)** is reached because:

- the AVS and organic carbon based normalisation should be further validated to refine the risk characterisation to benthic organisms<sup>65</sup> (on local as well as on regional level).
- there is a need for testing the Cd toxicity in very soft waters (H below about 10 mg  $CaCO_3/L$ ). There are no data for the very soft waters and these areas may be unprotected by the proposed  $PNEC_{water}$  for soft water (0.08  $\mu g Cd/L$ ).

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- no risk is predicted for the aquatic ecosystem at the NiCd recycling site 2 because there are no emissions to water at this site.

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<sup>65</sup> After the TMIV'02 last visit discussion on cadmium in sediment a number of MSs (UK, F, DE) and Industry commented on the sediment assessment and the current conclusions drawn in line with the outcome of that last TM (for more details, see effects assessment and risk characterisation in the overall RAR on Cd/CdO).

- no risk is predicted for the aquatic ecosystem at Cd metal production-site 6, NiCd battery producing sites (2, 3, 4), Cd pigments producing site B and all (two) Cd stabiliser production-sites (X, Y) emitting to the aquatic compartment.
- No risk is anticipated for aquatic organisms at 2 of the 5 NiCd battery producing plants (Site 6 & 7) because they are not emitting to the aquatic compartment.
- No risk is anticipated for aquatic organisms at a hypothetical landfill currently releasing a leachate with  $5 \mu\text{g L}^{-1}$  of cadmium directly or indirectly in the aquatic environment.
- No risks to aquatic organisms are anticipated for current hypothetical incinerator (equipped with an on-site WWTP) total Cd emissions discharging in a river with a dilution factor of 100 to 1,000. Removal of NiCd batteries in the MSW has a negligible influence on the calculated risk ratios.
- No risk is predicted for the local sediment compartment for the CdO production site, some NiCd battery producers (Site 6 & 7) and NiCd recycling plant 2 because there are no emissions to water and no additional risk arises from their operations.
- There is no risk for micro-organisms if the hypothetical landfill site is discharging a leachate with a cadmium concentration of  $5 \mu\text{g L}^{-1}$  to a STP.
- There is no risk for micro-organisms if the hypothetical incinerator plant (equipped with an on-site WWTP) is discharging to a STP.

#### Environment: terrestrial ecosystem

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- there is a need for limiting the potential risks of cadmium plating and alloy production-sites.

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- modelled local soil Cd concentrations for Cd metal production and processing plants (10 years aerial deposition) indicate no risk.
- modelled local soil Cd concentrations for NiCd batteries producing and Cd recycling plants (10 years aerial deposition) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.
- modelled local soil Cd concentrations for the hypothetical MSW incineration plant (equipped with an on-site WWTP) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.

#### Environment: assessment of secondary poisoning

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- modelled local soil Cd concentrations for Cd metal production and processing plants (10 years aerial deposition) indicate no risk.
- modelled local soil Cd concentrations for NiCd batteries producing and Cd recycling plants (10 years aerial deposition) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.
- modelled local soil Cd concentrations for the hypothetical MSW incineration plant (equipped with an on-site WWTP) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.

#### Environment: atmosphere

No conclusion is reached because:

No risk characterisation was done for the atmosphere.

#### Sewage treatment plant

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- risk to on-site and off-site STP cannot be excluded for plating and alloy industry.
- risk is predicted for the micro-organisms of the STP for the NiCd battery recycling plant (site 2) discharging its effluent to an off-site STP

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- no risk is predicted for the micro-organisms of the STP for Cd stabiliser production-site X discharging its effluent to a municipal STP.

### 5.2.2 Conclusions on cadmium oxide

#### Environment: aquatic ecosystem

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- there is a predicted local risk for the freshwater aquatic ecosystem at 5 Cd production (cadmium metal: 1 site) or Cd processing (pigments producing sites (A,C), plating and alloy) sites/scenarios. Both latter two are generic scenarios ('Cd plating' and 'Cd alloys'). Local concentrations are based on modelling using site-specific and/or standard default values and could possibly have been refined if substantial monitoring data would have been provided. Monitoring data are available for the Cd metal production-site 1: these data indicate risk at background level but do not allow a judgment regards potential additional risk caused by the site's operations.

- There is anticipated local risk at 1 recycling site where modelled freshwater Cd concentrations exceed the  $PNEC_{water}$ . This risk would be removed if no assessment factor (i.e. 2 and reflecting most of the uncertainty) is applied in deriving the PNEC. Monitoring data are available for this site: these data indicate risk at background level but do not allow a judgment regards potential additional risk caused by the site's operations.

**Conclusion (i)** There is a need for further information and/or testing

**Conclusion (i)** is reached because:

- the AVS and organic carbon based normalisation should be further validated to refine the risk characterisation to benthic organisms<sup>66</sup> (on local as well as on regional level).
- there is a need for testing the Cd toxicity in very soft waters (H below about 10 mg  $CaCO_3/L$ ). There are no data for the very soft waters and these areas may be unprotected by the proposed  $PNEC_{water}$  for soft water ( $0.08 \mu g Cd L^{-1}$ )

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- no risk is predicted for the aquatic ecosystem at the NiCd recycling site 2 because there are no emissions to water at this site.
- no risk is predicted for the aquatic ecosystem at Cd metal production-site 6, NiCd battery producing sites (2, 3, 4), Cd pigments producing site B and all (two) Cd stabiliser production-sites (X, Y) emitting to the aquatic compartment.
- No risk is anticipated for aquatic organisms at 2 of the 5 NiCd battery producing plants (Site 6 & 7) because they are not emitting to the aquatic compartment.
- No risk is anticipated for aquatic organisms at a hypothetical landfill currently releasing a leachate with  $5 \mu g L^{-1}$  of cadmium directly or indirectly in the aquatic environment
- No risks to aquatic organisms are anticipated for current hypothetical incinerator (equipped with an on-site WWTP) total Cd emissions discharging in a river with a dilution factor of 100 to 1,000. Removal of NiCd batteries in the MSW has a negligible influence on the calculated risk ratios.
- No risk is predicted for the local sediment compartment for the CdO production-site, some NiCd battery producers (Site 6 & 7) and NiCd recycling plant 2 because there are no emissions to water and no additional risk arises from their operations.
- There is no risk for micro-organisms if the hypothetical landfill site is discharging a leachate with a cadmium concentration of  $5 \mu g L^{-1}$  to a STP.
- There is no risk for micro-organisms if the hypothetical incinerator plant (equipped with an on-site WWTP) is discharging to a STP.

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<sup>66</sup> After the TMIV'02 last visit discussion on cadmium in sediment a number of MSs (UK, F, DE) and Industry commented on the sediment assessment and the current conclusions drawn in line with the outcome of that last TM (for more details, see effects assessment and risk characterisation in the overall RAR on Cd/CdO).

Environment: terrestrial ecosystem

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- there is a need for limiting the potential risks of cadmium plating and alloy production-sites.

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- modelled local soil Cd concentrations for Cd metal production and processing plants (10 years aerial deposition) indicate no risk.
- modelled local soil Cd concentrations for NiCd batteries producing and Cd recycling plants (10 years aerial deposition) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.
- modelled local soil Cd concentrations for the hypothetical MSW incineration plant (equipped with an on-site WWTP) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.

Environment: assessment of secondary poisoning

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- modelled local soil Cd concentrations for Cd metal production and processing plants (10 years aerial deposition) indicate no risk.
- modelled local soil Cd concentrations for NiCd batteries producing and Cd recycling plants (10 years aerial deposition) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.
- modelled local soil Cd concentrations for the hypothetical MSW incineration plant (equipped with an on-site WWTP) indicate no risks neither for the terrestrial ecosystem nor for mammals via secondary poisoning.

Environment: atmosphere

No conclusion is reached because:

No environmental risk characterisation was done for the atmosphere.

Sewage treatment plant

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- risk to on-site and off-site STP cannot be excluded for plating and alloy industry.

- risk is predicted for the micro-organisms of the STP for the NiCd battery recycling plant (site 2) discharging its effluent to an off-site STP

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- no risk is predicted for the micro-organisms of the STP for Cd stabiliser production-site X discharging its effluent to a municipal STP.

### 5.3 LOCAL LEVEL: DISPOSAL STEP - FUTURE SITUATION AND/OR SENSITIVITY ANALYSIS

#### 5.3.1 Conclusions on cadmium metal and cadmium oxide

Environment: aquatic ecosystem

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- There is a potential risk if a hypothetical landfill site discharges a leachate with a cadmium concentration of  $50 \mu\text{g L}^{-1}$  directly to surface water. Removal of NiCd batteries (if contributing to 50% of the Cd content in MSW) will remove the risk.

**Conclusion (i)** There is a need for further information and/or testing

**Conclusion (i)** is reached because:

- the AVS and organic carbon based normalisation should be further validated to refine the risk characterisation to benthic organisms<sup>1</sup> (on local as well as on regional level).
- there is a need for testing the Cd toxicity in very soft waters (H below about  $10 \text{ mg CaCO}_3/\text{L}$ ). There are no data for the very soft waters and these areas may be unprotected by the proposed  $\text{PNEC}_{\text{water}}$  for soft water ( $0.08 \mu\text{g Cd L}^{-1}$ ).

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- If a hypothetical landfill site discharges a leachate with a cadmium concentration of  $50 \mu\text{g L}^{-1}$  indirectly to surface water (i.e. via STP) no risk to aquatic organisms is expected.
- If only the NiCd battery contribution is taken into account there is also no risk to aquatic organisms predicted for landfills emitting directly to the surface water.

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<sup>1</sup> After the TMIV'02 last visit discussion on cadmium in sediment a number of MSs (UK, F, DE) and Industry commented on the sediment assessment and the current conclusions drawn in line with the outcome of that last TM (for more details, see effects assessment and risk characterisation in the overall RAR Cd/CdO).

- No risk is anticipated to the micro-organisms in case a hypothetical incinerator equipped with an on-site WWTP, discharges to a STP under the 75% or 10% collection scenario and landfill emitting a leachate at 50 µg Cd/L to an STP.
- No risks to aquatic organisms are anticipated for the future hypothetical incinerator, equipped with an on-site WWTP, (both scenarios: 10-75% collection) discharging in a river with a dilution factor of 100 to 1,000.
- No risks to aquatic organisms are anticipated for a hypothetical incinerator, equipped with an on-site WWTP, discharging a maximum effluent concentration of 0.007-0.0135 mg L<sup>-1</sup> in a river with a dilution factor of 100 to 1,000.

#### Environment: terrestrial ecosystem/secondary poisoning

No conclusion is reached:

There was no future situation and/or sensitivity analysis performed for the terrestrial compartment or for secondary poisoning.

#### Environment: atmosphere

No environmental risk characterisation was done for the atmosphere.

## 5.4 REGIONAL LEVEL

### 5.4.1 Conclusions on cadmium metal and cadmium oxide

#### Environment: aquatic ecosystem

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- the *modelled* regional PEC of surface water has a risk factor of 0.6 using a mean  $K_p$  value for EU while the risk factor is 1.7 using a  $K_p$  value that is distinctly smaller than average. This suggests potential regional risk. However, it is proposed to use measured values for the risk characterisation because of the uncertainties in the choice of the natural background (which is combined with the added concentration to derive the regional PEC) and in the coverage of the surface water with small  $K_p$  values. Monitoring data were collected for 13 EU countries (of the EU-16 surveyed) but limitation in data quality (detection limit, geographical coverage etc.) reduced this information to 7 countries (as proxy for regions) for which conclusions can be derived. The regional averages of the 90<sup>th</sup> percentiles of measured Cd concentrations of European rivers and lakes in these regions range from 0.0395 to 0.31 µg L<sup>-1</sup>. The majority of regional averaged 90<sup>th</sup> percentiles have a risk factor < 1 whereas these values are > 1 in the UK (based on a limited dataset of 1996) and the Walloon region of Belgium. Outliers have a large impact on the risk factors as, for example, 20 sites of the 728 investigated in the largest database of UK (data of 2003) determine risk in UK. The PNEC for water was derived with an assessment factor of 2 reflecting most of the uncertainties in the effects assessment. The conclusions about risk in the 2 regions mentioned are not affected by either in- or excluding this assessment factor. During the

development of the RRS, decision about (possible) reduction measures has to take into account the information on potential cadmium emission sources in these regions. In order to better characterise the regional risks to surface water in part of the EU which have not been covered in this assessment (i.e. eastern and southern Europe are underrepresented in the entire dataset, because detection limits are often too high and because fractionation is often not reported) it might be useful to obtain more information for these regions. It may be that the foreseen monitoring actions under for example the Water Framework Directive will provide this information in the future.

#### Environment: terrestrial ecosystem

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- the 90<sup>th</sup> percentiles of measured Cd concentrations of European soils have risk factors 0.43-1.56 (mean: 0.86; data from 6 EU countries). Regional risk for the terrestrial ecosystem cannot be excluded in one region (UK). However, it should be noted that the 90<sup>th</sup> percentile for the UK falls (1.4 mg Cd/kg<sub>dw</sub>) within the range of the proposed PNEC<sub>soil</sub> values based on ecotoxicity to soil microbial processes (1.15 – 3.2 mg Cd/kg<sub>dw</sub>). Hence, risk cannot be excluded but will depend on the magnitude of the assessment factor chosen (either 1 or 2, see 3.2.3.6.2) in the derivation of the PNEC<sub>soil</sub>.

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because:

- modelled regional soil Cd concentrations that include natural soil, industrial soil and 8 different agricultural scenarios are all below the PNEC<sub>soil</sub>. All these modelled values are total concentrations that are expected after 60 years (agricultural soils) or far beyond that (natural and industrial soils) with current regional emissions to soil. The starting concentrations are EU average values for the ambient concentrations. If 90<sup>th</sup> percentiles of measured concentrations would have been used in such calculations, then risk cannot be excluded.

#### Environment: assessment of secondary poisoning

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Conclusion (iii)** is reached because:

- measured soil Cd concentrations of European soils have risk factors 0.4-1.6 for poisoning to mammals (mean: 0.86; data from 6 EU countries). Regional risk for the terrestrial ecosystem cannot be excluded in one region (UK). The uncertainty surrounding the effects assessment, however, suggests that this is a borderline situation: the available information shows that literature data on Cd uptake in mammals dwelling in acid soils sensitively influences the effects assessment. If data on acid soils (pH <4.2) are excluded from the effects assessment, a larger PNEC is obtained and risk in the UK would be excluded. That conclusion would only remove concern provided that the P90 value in UK does not refer to acid soils, which is

unknown. This analysis is, moreover, qualitative because there is no validated model to estimate risk to mammals along the entire range of soil pH.

**Conclusion (ii)** There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

**Conclusion (ii)** is reached because

- field data (body burden: kidney and liver Cd data) of birds (excluding pelagic birds) do not indicate Cd poisoning, even in top predators. No risk to mammals is predicted from modelled regional soil Cd concentrations.

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## ABBREVIATIONS

,	Comma is used to indicate thousands
.	Point is used to indicate decimals
AC	Active Carbon
AF	assessment factor
<i>Ann.</i>	Annex
Ann.	annual
Avg.	average
AVS	Acid Volatile Sulphides
BCF	bioconcentration factor
BDS	Biological DeSulfurisation
BOD <sub>5</sub>	Biological oxygen demand (to complete....)
bw	body weight / <i>Bw, b.w.</i>
°C	degrees Celsius (centigrade)
C <sub>50</sub>	median immobilisation concentration or median inhibitory concentration 1 / <i>explained by a footnote if necessary</i>
CAS	Chemical Abstract System
Cd	Cadmium (metal)
CdO	cadmium oxide
CEC	Commission of the European Communities
CEN	European Committee for Normalisation
CEPE	European Council of the Paint, Printing Ink and Artists' Colours Industry
COD	Chemical oxygen demand
CPT	Cordless power tools
d	day(s)
dl	Detection limit
DF	Dilution factor
DG	Directorate General
DRY	Dry flue air cleaning technique
DT <sub>50</sub>	period required for 50 percent dissipation (define method of estimation)
DT <sub>50lab</sub>	period required for 50 percent dissipation under laboratory conditions (define method of estimation)
DT <sub>90</sub>	period required for 90 percent dissipation (define method of estimation)
DT <sub>90field</sub>	period required for 90 percent dissipation under field conditions

	(define method of estimation)
dry wt.	dry weight / $d_w$ / DW / d.wt
EC	European Communities
EC	European Commission
EC <sub>50</sub>	median effective concentration
EEC	European Economic Community
EEE	Electrical and Electronic Equipment
EEIG	Abbreviation for former ‘Industry’s Interest Group’ working on NiCd batteries
EINECS	European Inventory of Existing Commercial Chemical Substances
ELU	Emergency Lighting Units
EPA	Environmental Protection Agency
EU	European Union
EU-16	Member states of the EU AND Norway
EUSES	European Union System for the Evaluation of Substances
ESP	Electrostatic precipitator (air cleaning technique)
FF	Fabric Filter (air cleanign technique)
FGCS	Flue Gas Cleaning System
F <sub>ww</sub>	Release factor to wastewater
f <sub>oc</sub>	Fraction of organic carbon
g	gram(s)
Global RAR	EU RAR on cadmium metal and cadmium oxide / overall RAR on Cd/CdO
GLP	Good Laboratory Practice
h	hour(s)
ha	Hectares / <i>h</i>
HDPE	
HELP	Hydrologic Evaluation of Landfill Production (US-EPA model see Schroeder)
HPLC	High Pressure Liquid Chromatography
IARC	International Agency for Research on Cancer
ICP	Inductively Coupled Plasma
IC <sub>50</sub>	median immobilisation concentration or median inhibitory concentration 1 / <i>explained by a footnote if necessary</i>
ICdA	International Cadmium Association
IND	Industry
IPPC	Integrated Pollution Prevention and Control
ISO	International Standards Organisation
IUPAC	International Union for Pure Applied Chemistry
IUTA	Institut für Energie- und Umwelttechnik

IZA	International Zinc Association
J	Joule
kg	kilogram(s)
kPa	kilo Pascals
K <sub>oc</sub>	organic carbon adsorption coefficient
K <sub>ow</sub>	octanol-water partition coefficient
K <sub>p</sub>	Solids water partition coefficient
kt	Kilotonnes / ktonnes
L	litre(s) / l
log	logarithm to the basis 10
L(E)C <sub>50</sub>	Lethal Concentration, Median
LEV	Local Exhaust Ventilation
m	Meter
µg	microgram(s)
mg	milligram(s)
MAC	Maximum Acceptable Concentration
Model I (soil)	Standard EUSES model calculation
Model II (soil)	The alternative model to calculate regional and continental concentrations in agricultural soil is based on the Cd mass balance in the plough layer (cfr section 3.1.2.4.2 of the 'global' RAR on Cd/CdO)
MOS	Margins of Safety
MS	Member States
MSR	Member State Rapporteur / RMS
MSW	Municipal Solid Waste
N/A	Not applicable / n.a.
n.d.	No data available
ng	Nanograms (to complete with conversion factor to grams)
Ni	Nickel
NiCd	Nickel-cadmium batteries / NiCd
NIVA	Norwegian Institute for Water Research
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
oc	Organic carbon
OECD	Organisation for Economic Co-operation and Development
OEL	Occupational Exposure Limit
OEM	Original Equipment Manufacturer
OJ	Official Journal

OPS model	Operational Priority Substances model
Pa	Pascal unit(s)
P90	90-percentile of a dataset (result of statistical analysis: 90% of the values in the dataset are situated below the P90)
PBE	Plastic Bonded Electrode
PEC	Predicted Environmental Concentration
pH	potential hydrogen <i>-logarithm</i> (to the base 10) of the hydrogen ion concentration {H <sup>+</sup> }
pKa	<i>-logarithm</i> (to the base 10) of the acid dissociation constant
pKb	<i>-logarithm</i> (to the base 10) of the base dissociation constant
PM10	Fine particulate matter (<10 µm)
PNEC(s)	Predicted No Effect Concentration(s)
PNEC <sub>water</sub>	Predicted No Effect Concentration in Water
(Q)SAR	Quantitative Structure Activity Relationship
Questionnaire	To collect the needed information different types of questionnaires were used dependent on the aim and the target group: Industry questionnaire: for the collection of site-specific exposure data of batteries' producers and recyclers. The initial questionnaire was sent out by Industry in 1998, updates by the rapporteur in 2000 and 2001. The Questionnaire on Batteries : was designed by the rapporteur to obtain information related to the amounts of batteries (i.e. NiCds) put on the market, collection, recycling etc on a country basis. Three subtypes were made depending on the responder: a) Member state (competent authority for the implementation of the Battery Directive); b) Collection organisation (per country) and c) EPBA. This questionnaire was sent out in 2000.
RAR	Risk assessment report
RCR	Risk Characterisation Ratio
SCTEE	Scientific Committee on Toxicity, Ecotoxicity and the Environment / CSTEE
SEM	Simultaneously extracted metal
SRB	Sulphate Reducing Bacteria
STP	Sewage Treatment Plant
St. dev.	Standard deviation
t	Metric tonnes / tonnes / T
TGD	Technical Guidance Document <sup>67</sup>
Revised TGD	Technical Guidance Document <sup>68</sup>

<sup>67</sup> Commission of the European Communities, 1996. Technical Guidance Documents in Support of the Commission Directive 93/67/EEC on risk assessment for new substances and the Commission Regulation (EC) No 1488/94 on risk assessment for existing substances. Commission of the European Communities, Brussels, Belgium. ISBN 92-827-801[1234]

<sup>68</sup> Commission of the European Communities, 2003. Technical Guidance Document on risk assessment in Support of the Commission Directive 93/67/EEC on risk assessment for new notified substances, Commission Regulation (EC) No 1488/94 on risk assessment for existing substances and Directive 98/8/EC of the European Parliament and the Council concerning the placing of biocidal products on the market. Office for Official Publications of the European Communities, Luxembourg.

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TMT	Trimercaptotriazine (floculans used in wastewater purification)
TOC	Total organic carbon
TRAR	Targeted Risk Assessment Report (this report)
UASB	Upflow Anaerobic Sludge Blanket
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products or Biological material
v/v	volume per volume ratio
VDI	Verein Deutscher Ingenieure
w/w	weight per weight ratio
w	gram weight
WET	Wet scrubbing (air cleaning technique)
WWTP	Wastewater Treatment Plant
wet wt.	Wet weight / WW / <sub>ww</sub>
y	Year

## Annex A The Nordberg-Kjellström kinetic model

The Nordberg-Kjellström model (Kjellström and Nordberg, 1978; Kjellström and Nordberg, 1985) is a linear eight-compartment kinetic model of cadmium metabolism which has the advantage of being able to calculate not only accumulation in the kidney, but in other tissues as well. It is the most detailed and commonly used model for cadmium risk assessment and is discussed in the ATSDR (1999).

The model is based on a number of approximate assumptions, but it appears to be able to calculate the long term accumulation of tissue levels under a number of different exposure situations with reasonable accuracy.

The coefficients C1 - C19 determine the transfer between compartments. In most cases, the daily transfer is assumed to be a fixed proportion of the accumulated amount in the compartment.

It describes the disposition of cadmium via the oral and inhalation routes of exposure. Dermal exposure and skin absorption were assumed to be negligible.

### Description of the model by Nordberg and Kjellström (1985):

#### *Absorption and uptake*

For inhalation exposure, the model takes into account the different deposition patterns for different size particles in nasopharyngeal, tracheobronchial, and alveolar regions of the respiratory tract. Cadmium compounds are inhaled as particulate matter, either as fumes with very small particle size or as dust. The general principles for deposition and absorption of particulate matter described by the Task Group on Lung Dynamics \* and by the Task group on Metal Accumulation \*\* were taken to be valid for cadmium and were used in this model. Particles with MMAD (mass median aerodynamic diameter) of 5 µm were assumed to distribute mainly to the nasopharyngeal region (75%) with lesser amounts depositing in the alveolar (20%) and tracheobronchial (5%) regions. Particles of 0.05 µm MMAD (i.e., cigarette smoke) were assumed to deposit 55% in the alveolar compartment, 10% in the tracheobronchial compartment and none in the nasopharyngeal compartment. The remaining amounts are exhaled. The respiratory Cd intake (A) can be diverted to the gastro-intestinal tract ( $C \cdot A$ ) due to the clearance of Cd deposited on the mucosa of nasopharynx, trachea, or bronchi. It can also be deposited in the alveoli ( $C2 \cdot A$ ) and from there be absorbed into the blood ( $C3 \cdot E1$ ). The remainder of the respiratory intake is exhaled. Some of the Cd in the alveoli is transported via alveolar clearance back to the bronchi ( $C4 \cdot E1$ ) and eventually to the gastro-intestinal tract after swallowing. Based on data given by the Task Group on Lung Dynamics, C1 was estimated at 0.1 to 0.2 for Cd fumes and at 0.4 to 0.9 for Cd dust. Calculations with different values were carried out and a best fit between calculated and empirical values was found for  $C1 = 0.1$  (fume) and 0.7 (dust). In accordance with the difference in the distribution of small (fume) and large (dust) particles, C2 was estimated to be 0.4 to .06 for fume and 0.1 to 0.3 for dust. The best fit values for all coefficients are listed in **Table A1**. The alveolar clearance is likely to be small in comparison with the rest of the lung clearance and C4 was assumed to be  $0.1 \cdot C3$ .

Cadmium intake via the gastro-intestinal tract consists of food cadmium (G) and Cd cleared from alveoli ( $C4 \cdot E1$ ) and respiratory tract ( $C1 \cdot A$ ). Most of Cd in the intestinal lumen will pass unabsorbed and the retention C5 was assumed to be in the range 0.03 to 0.1. The Cd retained in the intestinal wall will accumulate to a certain extent before being absorbed into blood. C6 was assumed to be 0.05/day, but available data are insufficient to estimate this coefficient with

accuracy. The total amount of Cd absorbed into blood each day ( $C3 \cdot E1 + C6 \cdot E2$ ) is called daily uptake ( $I \mu\text{g/day}$ ).

### *Transport and distribution*

The blood was divided into three compartments: the albumin-bound Cd (B1), the cell-bound Cd (B2), and the metallothionein-bound Cd (B3). The turn-over of Cd in B1 and B3 is very rapid and all Cd input into these compartments is assumed to have continued to other compartments within less than a day. Thus the contribution of B1 and B3 to whole blood Cd concentration is less than the calculated amounts in these compartments. This fraction (C20) was assumed to be in range 0.05 to 0.5. The part of Cd uptake ( $C7 \cdot I$ ) which is bound to metallothionein (B3) will continue mainly to kidney and urine. As about a third of the body burden after long-term exposure is in the kidneys, C7 was assumed to be 0.2 to 0.4. The B3 compartment has a limited number of binding sites and therefore, the daily flow from I to B3 was maximised by C8 (0.5 to 5  $\mu\text{g/day}$ ).

Accumulation in B2 is determined by the turn-over rate of red blood cells. The mean life of erythrocytes is 120 days which implies a half-time of 83 days and C16 would be 0.008/day. For the modelling, it was assumed that C16 would be in the range of 0.004 to 0.015/day. From B1, Cd is transferred to red blood cells (B2), liver (L), and other tissues (T), and via intestinal wall cells to faeces (F). The proportions of B1 distributed to L and T were assumed to agree approximately with their proportion of whole body burden of Cd (16% for L, 50% for T). Thus, C12 was assumed to be 0.1 to 0.4 and C9 was set at 0.4 to 0.8. The liver is a main organ for metallothionein production and it was assumed that most of the cadmium in B3 came from the liver ( $C14 \cdot L$ ). From B2, metallothionein-bound Cd will add to the B3 compartment and the B3-Cd is cleared through the kidney glomeruli. Some Cd is reabsorbed in the proximal tubuli ( $C17 \cdot B3$ ) and adds to kidney accumulation (K) and the rest is excreted via urine (U). About 95% of the glomerular filtrate of Cd-metallothionein is reabsorbed in the renal tubuli of mice, hence C17 was assumed to be in the range 0.8 to 0.98. Tubular reabsorptive capacity decreases with age. Between 30 and 80 years, it decreased 33%. In the model a similar decrease was assumed. Cd is transported back from liver, kidney, and other tissues to the blood. This is assumed to occur mainly to the B compartment ( $C10 \cdot T$ ,  $C13 \cdot L$ , and  $C18 \cdot K$ ), but the liver also contributes to B3 ( $C14 \cdot L$ ).

### *Excretion*

Almost all Cd in the body is excreted via faeces and urine. Faecal Cd consists mainly of the non-absorbed part of ingested Cd. "True" faecal excretion originates from blood via the intestinal wall ( $C11 \cdot B1$ ) and from bile ( $C15 \cdot L$ ). The main part of biliary cadmium is correlated with the amount of cadmium in liver. C15 was assumed to be in the range 0 to 0.0001/day. With long-term low level exposure faecal and urinary excretion are about the same. Urinary excretion is mainly a function of the body burden, but a part of this excretion is directly dependent on blood Cd. This has been taken into consideration by splitting urinary excretion into two parts:  $(1-C17) \cdot B3$  coming from blood and  $C19 \cdot K$  coming from kidney. At steady state, the total daily excretion would be the same as total daily uptake. In Sweden, the average adult daily Cd intake via food is about 16  $\mu\text{g}$  and the average body burden of non-smokers is about 5 mg at 50 years. With a gastro-intestinal absorption rate of 5%, the daily uptake (0.8  $\mu\text{g}$ ) would be 0.016% of body burden.

Average adult (30-60 years) urinary excretion is approximately 0.35 µg/day. Thus, the daily excretion rate for urine would be 0.007% of body burden and, by subtraction from the estimated total excretion; the faecal excretion would be 0.009% of body burden.

### *Retention and accumulation*

The main part of body burden will be found in the liver (L), the kidneys (K) and other tissues (T) (muscles, skin, and bones). C13 was set at 0 to 0.0001/ay and C14 at 0.001 to 0.003/day which in combination with C15 gave a half-time in liver between 4 and 19 years. C19 was estimated to be in the range 0.00002 to 0.0002/day, and C18 in the range 0 to 0.0001/day. The corresponding range of kidney half-times would be 6 to 38 years. It was also assumed that C19 increases linearly after age 30 with C21 each year. Initially, C21 was set at 0 to 0.000002/day. Very little data are available regarding half-times in other tissues. It was found that age-dependent accumulation curves for Cd in muscle indicate an even longer half-time than for kidney. With long-term low level exposure about half of the body burden is in other tissues, indicating that a major accumulation occurs there as well as in liver and kidneys. C10 was assumed to be in the range 0.00004 to 0.0002/day corresponding to half-times between 9 and 47 years.

Table A.1 Assumed and modelled values of coefficients (Kjellström and Nordberg, 1985)

Coefficients	Initially assumed ranges <sup>a</sup>	Unit	Values fitting to empirical data
C1	0.1- 0.2 (cigarette smoke)		0.1
	0.4 - 0.9 (factory dust)		0.7
C2	0.4- 0.6 (cigarette smoke)		0.4
	0.1 - 0.3 (factory dust)		0.13
C3	0.01 - 1	day <sup>-1</sup>	0.05
C4	0.1 · C3 = 0.001 - 0.1	day <sup>-1</sup>	0.005
C5	0.03 - 0.1		0.048
C6	0.05	day <sup>-1</sup>	0.05
C7	0.2 - 0.4		0.25
C8	0.5 - 5	µg	1
C9	0.4 - 0.8		0.44
C10	0.00004 - 0.0002	day <sup>-1</sup>	0.00014
C11	0.05 - 0.5		0.27
C12	0.1 - 0.4		0.25
C13	0 - 0.0001	day <sup>-1</sup>	0.00003
C14	0.0001 - 0.0003	day <sup>-1</sup>	0.00016
C15	0 - 0.0001	day <sup>-1</sup>	0.00005
C16	0.004 - 0.015	day <sup>-1</sup>	0.012
C17b	0.8 - 0.989		0.95
C18	0 - 0.0001	day <sup>-1</sup>	0.00001
C19cadmium	0.00002 - 0.0002	day <sup>-1</sup>	0.00014
CXd	0.01 - 0.05		0.04

Table A.1 continued overleaf

Table A.1 continued Assumed and modelled values of coefficients (Kjellström and Nordberg, 1985)

Coefficients	Initially assumed ranges a	Unit	values fitting to empirical data
C20	0.05 - 0.5		0.1
C21	0 – 0.000002	day <sup>-1</sup>	0.0000011

a If no unit is given, this means that the coefficient is a unitless proportion

b C17 decreases from age 30 to age 80 by 33%

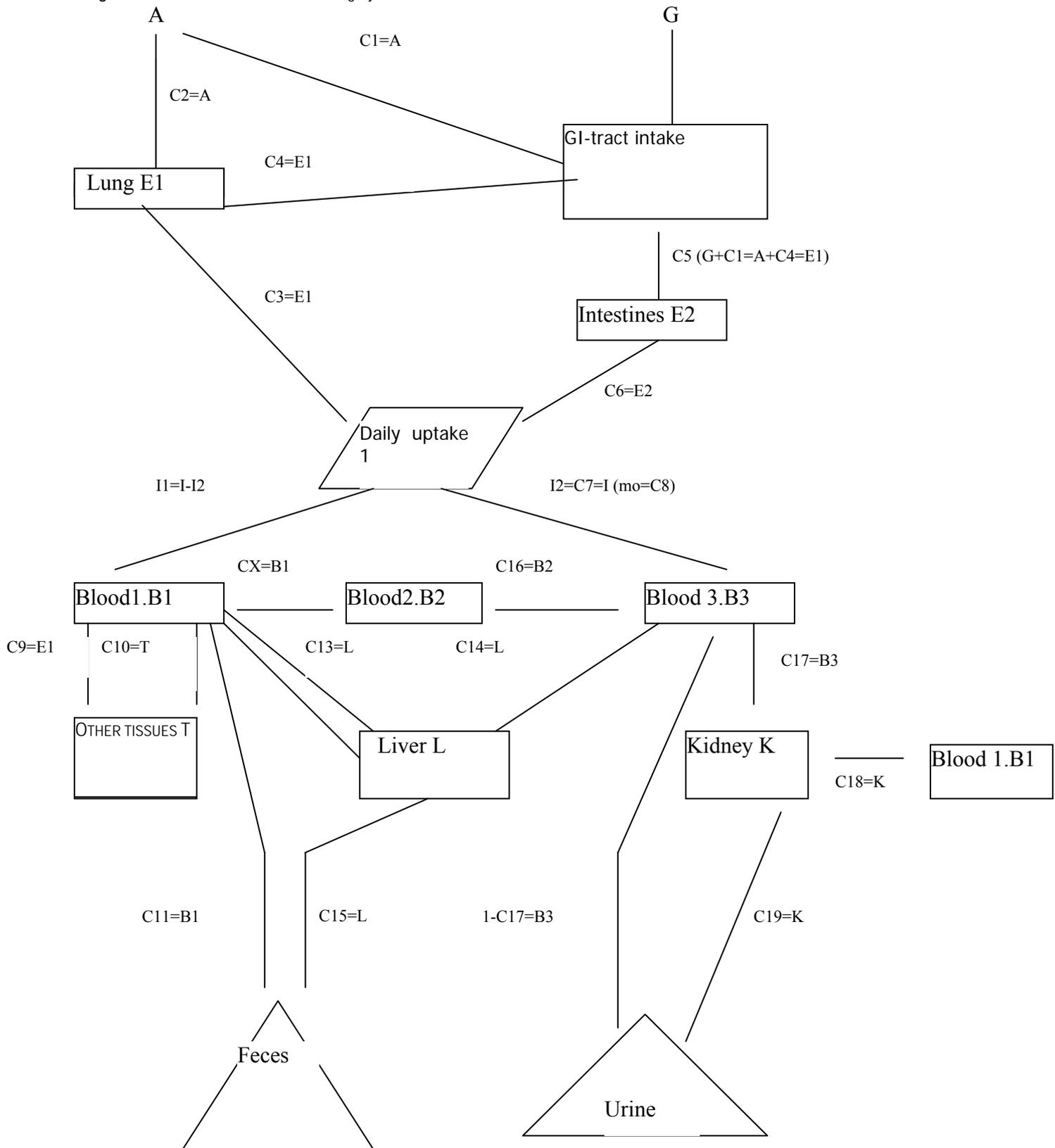
c C19 increases from age 30 with C21 each year

d  $C_x = 1 - C_9 - C_{11} - C_{12}$

\* Task Group on Lung Dynamics, Deposition and retention models for internal dosimetry of the human respiratory tract. Health Phys, 12, 173-208, 1966

\*\* Task Group on Metal Accumulation, Accumulation of toxic metals with special reference to their absorption, excretion and biological half-times. Environ Physiol Biochem, 3, 65-107, 1973

Figure A.1 Flow scheme of the Nordberg-Kjellström kinetic model of cadmium metabolism



## **Annex B Metallothionein**

### *Metallothionein*

In tissues, the majority of cadmium is bound to metallothionein, a low molecular weight protein (approximately 6,600 kDa) rich in cysteinyl thiol groups but deficient in aromatic amino acids. Metallothionein has been detected in human kidney, liver, heart, brain, testis, skin epithelial cells and in human embryonic fibroblasts from skin, muscles and lung. In animals, the protein has also been found in placenta, spleen and intestinal mucosa.

Separation techniques based on the charge properties of metallothionein, such as ion-exchange chromatography and iso-electric focusing, have shown that different forms of metallothionein often exist in the same organ. Usually two main forms of metallothionein are found: MT-I and MT-II. As a rule the total amount of metal ions bound to each metallothionein molecule is constant, but the types of metal ions might differ. Apart from having a different molar ratio of metals, the two different forms of metallothionein from the same species and tissues have also been shown to have slightly different amino acid composition (CRC, 1986). Transgenic mice deficient for MT-I and MT-II have been produced (Michalska and Choo; 1993)

Metallothionein is normally present in animal tissues in only trace amounts. Induction of its synthesis is under the control of a large group of genes and is stimulated by glucocorticoids and the essential metals Zn and Cu. Exposure to certain metals such as Cd, Hg, Zn, Ag, Cu, Mg can increase the concentration of MT in the liver and/or kidney, and possibly other tissues. It has also been observed that metallothionein can be induced by formaldehyde, carbon tetrachloride, hormones, drugs, alkylating agents, alcohol, infection, inflammation, food deprivation, irradiation (UV-X), cold, strenuous exercises. Certain metals appear to show organ specificity in regard to their ability to increase concentration of MT. For example, Hg and Zn induce the synthesis of MT in the kidney and the liver, respectively, whereas Cd induces synthesis in both the liver and the kidney (Waalkes and Goering, 1990; Kotsonis and Klaassen, 1978).

The exact physiologic functions of metallothionein are not known but it is thought to play an important role in the biological detoxification of metals, including Cd. It has been shown that following Cd exposure, Cd is predominantly associated with metallothionein and pretreatment with metals known to stimulate the synthesis of metallothionein prevents the toxicity of subsequent Cd exposure (Leber and Miya, 1976; Yoshikawa, 1973; Jin et al., 1986). A deficiency in metallothionein appears to occur in several mammalian tissues that are highly susceptible to the toxic effects of Cd. Rat, mouse, monkey testes, rat ventral prostate, hamster ovary are known to be susceptible to either the acute or/and chronic carcinogenic effects of Cd and appear to be deficient in metallothionein as assessed by biochemical analysis of Cd-binding protein (Waalkes and Goering, 1990).

The observed correlation between cellular Cd and MT is the result of the cell's responding to increased intracellular Cd levels by increasing the synthesis of MT. Experiment carried out on MT I and MT II null mice also support the conclusion that the persistence of Cd in the body is at least partially due to Cd binding to metallothionein in tissues (Liu et al., 1996). More than 60-80% of the Cd in the kidneys and liver is bound to MT. MT is, however, also found in other tissues, usually in amounts proportional to the Cd or Zn content. The biological half-time of Cd-MT appears to be in the order of days; this is considerably shorter than the biological half-life of Cd. Thus a constant synthesis of MT must take place in order to sequester the Cd ions which have been released from the degraded MT (Elinder and Nordberg, 1985, CRC).

The low molecular weight of metallothionein enables the protein to be filtered through the kidney glomerular membrane; it is subsequently reabsorbed by the proximal tubule cells where it can compete with other proteins for the reabsorption site. The Cd-metallothionein complex is degraded in lysosomes with release of Cd, which may induce metallothionein synthesis in the proximal tubule. This process continues until the capacity of the cell to synthesise metallothionein is exceeded. The renal toxicity of Cd is associated with Cd not bound to metallothionein. However, brush-border membranes of the renal tubule may be damaged by cadmium that is bound to metallothionein (Suzuki and Cherian, 1987; Cherian and Goyer, 1976).

The synthesis of MT in the kidney cells is considerably slower than in the liver cells. The tissue MT level is mainly related to the tissue deposition of the inducing metal.

In rats, the concentrations of MT and Cd in both kidney and liver increase with dose and time. However, the rates of increase of MT and Cd are not the same in the liver and the kidney. In the kidney, the ratio of Cd to MT increases with time; in the liver, however, the ratio reaches a plateau. This phenomenon may explain why in rats the liver apparently has a tolerance to Cd during prolonged exposure that is the synthesis of MT in the liver appears to keep abreast with continually increasing concentration of Cd and thus limits the concentration of the non-MT-bound-Cd. However, in the kidney the ratio continues to increase with time that may explain why renal injury is observed during prolonged Cd exposure. In other words, the amount of Cd taken up by the kidney increases at a faster rate than does the amount of MT (Elinder and Nordberg, 1985).

LD<sub>50</sub> of CdCl<sub>2</sub> by the intraperitoneal route are not different in wild type and MT-deficient animals and the distribution of Cd in tissues (24 hour post-treatment) was not different between the two strains, indicating that the basal level of MT does apparently not protect against acute Cd toxicity. Pretreatment with Zn (MT induction) protected however wildtype but not MT-deficient mice (Conrad et al., 1997). Using a similar dosing regimen (single administration of radiolabeled Cd, ip). Liu et al. (1996) confirmed that the initial distribution of Cd was not affected by the presence of MT. However, the elimination of Cd was found much faster in MT-null mice, with a 2-fold reduction of the Cd dose retained in the liver after 24 hours and later. Cd concentration in kidney continued to increase with time in control but not in MT-null mice, indicating that an important source of Cd in the kidney is the uptake of CdMT.

Alveolar macrophages were recovered by BAL from 10 healthy nonsmokers and 10 cigarette smokers to determine whether increased concentrations of Cd were present in the macrophages of cigarette smokers and whether metallothionein accumulated in response to the presence of cadmium. Cd was detected in the alveolar macrophages of all subjects, with a higher mean in cigarette smokers ( $3.4 \pm 0.5$  versus  $1.3 \pm 0.2$  ng/10<sup>6</sup> cells;  $p < 0.005$ ). There was a correlation between current smoking history (cigarettes per day) and the alveolar macrophage content of cadmium. The mean metallothionein content was similar in both groups, despite the higher Cd content in the alveolar macrophages of smokers. This could be due, according to the authors, either to the fact that Cd concentrations in cigarette smoke are insufficient to induce metallothionein synthesis or to a greater saturation of this protein (Grasseschi et al., 2003).

#### *MT and nephrotoxicity*

Results from experimental studies carried out mainly with CdCl<sub>2</sub> suggest that the Cd-metallothionein complex is a nephrotoxin when injected but when it is synthesised within the cell it may protect from cadmium toxicity temporarily.

The distribution of Cd from a nephrotoxic dose of radiolabeled Cd-MT was compared in subcellular fractions of kidney cortex of rats with pre-induced MT synthesis (by CdCl<sub>2</sub>) and of controls. In the pretreated rats, Cd in the plasma membrane and microsome fractions of renal cortex cells was mainly bound to MT and other low molecular weight proteins. In nonpretreated rats, the major part of Cd was bound to high molecular weight proteins. The animals with pre-induced MT synthesis were protected against the toxic effects of Cd-MT, whereas the control animals later developed nephrotoxic effects (Nordberg et al., 1994).

The prevalence of nephrotoxicity rather than hepatotoxicity in chronic Cd exposure may be due to several factors (WHO, 1992):

- the release of hepatic Cd-MT or its presence in the blood can result in preferential accumulation of Cd in kidneys;
- the kidney can accumulate MT mRNA in response to Cd exposure to only about half the level of the liver (Koropatnick and Cherian, 1988)

Thus the kidney may not be able to synthesise MT as efficiently as the liver in response to Cd exposure, resulting in an accumulation of non MT-Cd in the kidney but not in the liver.

Pretreatment with Cd entails increased tolerance to subsequent exposure to Cd.

Parenterally administered Cd-MT is highly nephrotoxic. The distribution of a single dose of Cd salts differs considerably from that of Cd-MT. A couple of hours after Cd salt was administered, about 50% of the dose was found in the liver and only about 10%, or less, in the kidney. However, when Cd-MT was administered, up to 90% was found in the kidneys 2 hours later (Elinder and Nordberg, 1985).

When Cd is given in the form of Cd-MT the LD<sub>50</sub> is only about one tenth of that for inorganic Cd salts. It has been suggested that the mechanism underlying this phenomenon is, probably, glomerular filtration of Cd-MT and a subsequent efficient uptake from the tubular fluid into the tubular cells by pinocytosis followed by a rapid degradation in lysosomes and release of Cd from its protein ligand in the cytoplasm. Tubular cells have a certain capacity for producing their own metallothionein which can bind Cd and thereby prevent the toxic effects of Cd ions. Following large doses of Cd-MT, the cells cannot cope with all the Cd being released and cell damage occurs. The occurrence of non MT-bound-Cd ions in the tubular cells produces the toxic effects.

The free Cd pool is sufficiently large to give rise to interact with membrane targets to block calcium transport routes, and there is deficient uptake and transport of calcium through the cell.

When injected parenterally, a high influx of Cd-MT occurring in the tubules can overload the sequestration mechanism of the de novo cellular synthesis of MT. Such acute toxicity does not occur in human exposure that takes place by oral or inhalation routes, which can only provide a limited flow of Cd-MT (Elinder and Nordberg, 1985; Vahter, 1996).

In a further experiment using a single dose of Cd intraperitoneally (25 µmole/kg as CdCl<sub>2</sub> or as Cd-MT complex), Liu et al. (1996) compared the hepatotoxic and nephrotoxic responses to CdCl<sub>2</sub> and Cd-MT, respectively. They concluded that MT plays less of a protective role in protecting against CdMT-induced nephrotoxicity than CdCl<sub>2</sub>-induced hepatotoxicity, and that Zn-induced protection against CdMT-induced nephrotoxicity does not appear to be mediated through MT.

Table B.1 Comparison of the hepatotoxic and nephrotoxic responses to CdCl<sub>2</sub> and Cd-MT

	Liver toxicity (CdCl <sub>2</sub> )	Renal toxicity (Cd-MT)
MT +/- mice	+++	+++
MT-/- mice	+	+++
effect of Zn pretreatment	protects +/- only	protects +/- and -/-

Chronic toxic effects of Cd in the kidney are likely to occur when tubular cell capacity for producing MT is insufficient to sequester all the Cd ions in the cell cytoplasm.

Chronic Cd administration of CdCl<sub>2</sub> produces renal injury in MT-null mice, indicating that Cd-induced nephrotoxicity is not necessarily mediated through the CdMT complex (Liu et al., 1998; Liu et al., 2000). However, MT protects against chronic CdCl<sub>2</sub> nephropathy, suggesting that intracellular MT is an important adaptive mechanism decreasing CdCl<sub>2</sub> nephrotoxicity (Liu et al., 1999), and that a single injection of CdMT may not be a good model to study chronic Cd nephropathy (Klaassen and Liu, 1998).

There are likely species differences with regard to the capacity of different animals to produce MT in the renal cortex. Therefore, signs of renal toxicity may occur at different total concentrations of Cd. In the case of human exposure, constitutional factors as well as age and simultaneous exposure to other nephrotoxic agents may influence renal MT in production capacity and thus the susceptibility of the kidneys to Cd (CRC, 1986). The exact impact of these possible variations in humans is however not clearly identified.

Zn pretreatment protects against the nephrotoxicity of Cd-MT. Several mechanisms have been suggested (Tang et al., 1998):

- the induction of the synthesis of MT by Zn and sequestration of Cd<sup>++</sup> released from the lysosomal degradation of exogenous Cd-MT by the newly synthesised renal MT. However even MT-null mice are protected by Zn (Liu et al., 1996);
- plasma Zn seems to displace some of the Cd from Cd-MT and thus decreases renal Cd accumulation
- it appears to reduce the pinocytotic uptake of Cd-MT complex by affecting the stability of the renal brush border membrane (Chvapil, 1973)
- more recently, GSH has been proposed as an important factor in regulating Cd-MT nephrotoxicity. Exogenous GSH can reduce Cd-MT nephrotoxicity in MT-null mice, while depletion of GSH severely enhanced the nephrotoxicity of Cd-MT. Although Zn does not require elevation of renal cortex GSH levels for protection against Cd-MT nephrotoxicity, the protection depends on the maintenance of normal intracellular GSH levels. While Zn reduces both Cd and MT accumulation, it does not alter the subcellular distribution of Cd. Zn protection in the MT-null mice appears to be through the reduction of Cd accumulation in the renal cortical epithelial cells to a level where the normal GSH levels are sufficient to prevent toxic interactions of Cd<sup>++</sup> with sensitive intracellular sites (Tang et al., 1998).

Habeebu et al. (2000) have shown that MT also protects against the bone toxicity of Cd. Upon repeated sc injections of CdCl<sub>2</sub> over a wide range of doses for 10 weeks, they found no difference in bone Cd content between wild-type and MT-null mice. Repeated Cd injections produced, however, a dose-dependent loss of bone mass (up to 25%), as shown by analysis of the femur, tibia, and lumbar vertebrae. The loss of bone mass was more marked in MT-null mice than in wild-type mice, as shown by dry bone weight, defatted bone weight, bone ash weight,

and total calcium content. X-ray photography showed decreasing bone density along the entire bone length with increasing dose and time of Cd exposure.

## **Annex C Cadmium exposure and End-Stage Renal Disease (ESRD)**

### **Critical original studies**

#### a) Retrospective mortality studies

##### *Studies from Japan: Jinzu River basin, Toyama Prefecture*

Nakagawa et al. (1990) examined the mortality (20-year follow-up) of Itai-Itai disease patients, patients suspected of having Itai-Itai disease, and control subjects matched for age, gender, and place of residence. Most cases were women (186 out of 190). Control subjects had neither proteinuria nor glucosuria (sulfosalicylic acid method and Benedict's reaction, respectively). Briefly summarised, Itai-Itai patients had the highest mortality and patients suspected of having Itai-Itai disease had a higher mortality than the control subjects. The increased mortality of patients with and suspected of Itai-Itai became statistically significant after three and 18 years of follow-up, respectively. However, some questions remain open. Firstly, the Cd body burden and the values of the renal parameters are not given and it is not known whether there was a relationship between these variables and mortality. Secondly, it is not clear whether the cause of death was due to end-stage renal disease or to another cause. This is an important issue because some observations suggest that the relationship between cadmium exposure and Itai-Itai disease is not univocal as several factors may have influenced cadmium toxicity in humans including nutritional deficiencies in calcium, protein, vitamin D, and iron, or zinc intake (ATSDR, 1999). As most of these factors may reflect unfavourable living conditions (low socio-economic level), it cannot be excluded that they were to some extent responsible for the increased mortality. Thirdly, regarding renal function it would be extremely important to know whether the patients diagnosed with Itai-Itai disease used non-steroidal anti-inflammatory drugs. Indeed, some authors have stressed the potential role of these agents in the progression to chronic renal disease (De Broe and Elseviers, 1998), the use of analgesic therapy for relief of pain due to osteomalacia has been reported in Itai-Itai patients (Kagamimori et al., 1986), and an interaction between acetaminophen and Cd effects has been described in experimental animals (Bernard et al., 1988). In human studies conducted in Belgium also, the use of analgesics was found to significantly influence tubular parameters alone or in interaction with the Cd body burden (Buchet et al., 1990; Hotz et al., 1999).

A last issue is the possible publication bias. Indeed, two other surveys dealing with the mortality of the population from the Jinzu River basin found no increased mortality and were published in Japanese only (abstracts unavailable on Medline), one of them reported that the mortality was low especially in the highly polluted area (Shigematsu et al., 1982; Shigematsu et al., 1980). Similarly, the publication dealing with the possible confounding factors is available in Japanese only (Kawano et al., 1981). Thus, no overall assessment of all these studies can be made. Furthermore, the study by Nakagawa et al. (1990) extends the findings reported by Kawano et al. (1986); both reports can, therefore, not be considered as independent with which consistency can be examined.

To summarise, the aforementioned study (Nakagawa et al., 1990) concludes to an association between Itai-Itai disease and increased "all causes" mortality. However, both the causal role of Cd and its association with end-stage renal disease remain unclear. In particular, it would be interesting to know whether men with a similar Cd body burden had an increased mortality as well. Moreover, the fact that results showing an increased mortality were published in English and in international journals (Nakagawa et al., 1990; Kawano et al., 1986) unlike the results of

the negative study (Shigematsu et al., 1982; Shigematsu et al., 1980) or those of the report on the comparability of the control group (Kawano et al., 1981), may suggest a publication bias.

*Studies from Japan: Kosaka Town, Akita Prefecture*

Iwata et al. (1992) found an increased “all causes” mortality in women (but not in men) with increased urinary  $\beta_2\text{M}$  and/or total amino nitrogen concentration which was attributed to exposure to Cd in the environment. These results were published in English in an international journal whereas a negative study (Ono and Saito, 1985) from the same region is available in Japanese only (a very short abstract could be found in Nakagawa et al., 1990).

Again, only the “all causes” mortality is known, there is no specific data on ESRD, and the publication of the negative study in Japanese only makes an overall evaluation of the results extremely difficult and suggests a publication bias.

*Studies from Japan: Kakehashi River basin, Ishikawa Prefecture*

Nishijo et al. (1995) reported an increased mortality from “nephritis and nephrosis” in persons with tubular dysfunction diagnosed in 1974-1975 (15 year follow-up, 930 deaths or 38.6% of the subjects having participated in the 1974-1975 survey, tubular dysfunction assessed by semi-quantitative urinary RBP concentration) thought to be due to environmental cadmium exposure in the Kakehashi River basin. However, a diagnostic suspicion bias is possible. Indeed, all cases of “urinary tract diseases” were recorded in the group without increased RBP whereas no case with this diagnosis was found in the group with increased RBP. That some persons with “urinary tract diseases” and increased RBP were diagnosed erroneously with “nephritis and nephrosis” is likely because diagnoses were apparently not confirmed objectively. Furthermore, the authors noted that the quality of the death certificates was not very satisfactory (Nishijo et al., 1995).

More importantly, Nishijo et al. (1994) examined the mortality in the population from the same region using  $\beta_2\text{M}$  instead of RBP as an indicator of tubular dysfunction. Although they found an increased mortality in subjects with increased  $\beta_2\text{M}$  “most deaths were due to non-specific cardiac disease such as heart failure and cerebro-vascular diseases”. A further important fact was that cases with increased total urinary protein were overrepresented and total urinary protein concentrations higher in the group with increased  $\beta_2\text{M}$  concentrations (Nakagawa et al., 1993). Further analysis of the results presented by these authors (Nishijo et al., 1994) suggests that the group of subjects with increased  $\beta_2\text{M}$  was not homogenous and included a subgroup of subjects with cardiovascular risk factor (as indicated by increased urinary protein) (Ruggenenti et al., 1998; Grimm et al., 1997) but without increased urinary  $\beta_2\text{M}$ . Therefore, increased cardiovascular risk factors could be considered as associated with but not due to the cadmium exposure. Finally, an association between individual cadmium body burden and mortality from renal disease was not reported. Taken together, these results suggest that patients with cardiovascular risk factors as indicated by an increased urinary protein concentration could have been overrepresented in the subgroup with increased  $\beta_2\text{M}$  and that this finding may not have been associated with cadmium exposure. Indeed, others have found that it is unlikely that Cd exposure could be associated with the risk of cardiovascular diseases in a causal way (Staessen et al., 1991 and 2000). It should also be borne in mind that the association between age and  $\beta_2\text{M}$  excretion has been suggested as a possible source of error (Park, 1991).

In 1999, the same authors published a 15 year follow-up of 3,119 inhabitants living in the same Cd polluted areas of the Kakehashi River basin (1,403 men, and 1,716 women) (Nishijo et al., 1999). The age-specific cumulative survival curves were lower with increasing Cd-U measured

in 1981-82 (< 5, 5-9.9, 10-19.9 and > 20 µg/g creatinine), suggesting a dose-response relationship between Cd exposure and mortality. As this study is an extension of the previous follow-up published by Nakagawa et al. (1993), the same comments hold for the present report.

To summarise, these studies from the Kakehashi River basin are compatible with Cd causing ESRD but other explanations seem plausible as well.

#### *Studies from Japan: Sasu, Nagasaki Prefecture*

In their historical cohort study, Iwata et al. (1991) examined the mortality of 256 subjects (participation rate over 80%) living in a Cd-polluted area. After a 10-year follow-up, 65 subjects (25.4%) had died. In a subgroup of residents (with a urinary β<sub>2</sub>M concentration greater than 1,000 µg/g creat in 1979), observed deaths were greater than expected. Using a Cox's proportional hazard model, the influence of age, mean blood pressure, Cd-U, and β<sub>2</sub>M on all causes mortality was examined. β<sub>2</sub>M proved to be a predictor of mortality in men (but not in women) whereas Cd-U was not ( $p > 0.4$ ). The association between β<sub>2</sub>M and mortality in men only is surprising because both β<sub>2</sub>M and Cd-U concentrations were higher in women than in men. Cause-specific mortality was not calculated because of "uncertainty of the diagnosis". It is reported that the serum creatinine concentration of the most severe case was 3.2 mg/100 ml (no further details on serum creatinine or GFR measurements).

To summarise, no straightforward relationship between Cd body burden and uraemia was demonstrated in this study.

#### *Mortality studies conducted outside Japan*

The village of Shipham (UK) was contaminated by considerable quantities of toxic metal cadmium from nearby extinct calamine workings. Harvey et al. (1979) have conducted a limited study on 21 adults living in the most heavily polluted areas of the village to measure their liver-cadmium concentration. Their mean age was 53 years (40-62) and they had lived there on the average for more than 20 years, 3 were light smokers and 50% of the vegetables they consumed were of local origin. The mean liver-cadmium concentration in these villagers was 11.0±2.0 ppm which was significantly higher than that of 10 non-Shipham controls (2.2±2.0 ppm) of similar age (Harvey et al., 1979). The results of the survey conducted later in Shipham (Inskip et al., 1982) do neither refute nor support an association between renal diseases and environmental cadmium exposure because of small sample size, crude exposure assessment, and lack of dose-response relationship. A follow-up of the mortality in this cohort has been reported by Elliot et al. (2000). There was an excess mortality from cerebro-vascular disease, hypertension, nephritis and nephrosis (for the latter SMR 128, 95% CI: 99-162). However, it was not possible to separate the diagnoses included in the latter category, so that it remains unclear whether the effect is associated with nephritis or nephrosis (Elliot et al., 2000).

Lauwerys and De Wals (1981) wrote a letter drawing attention to a possible relationship between Cd exposure (environmental) and nephritis and nephrosis. Owing to the limitations of this type of publication, definitive conclusions relative to a causal relationship between Cd exposure and ESRD are not possible.

#### b) Longitudinal morbidity studies

Besides retrospective mortality studies, there are also publications dealing with the renal function in Cd-exposed subjects followed-up for some years.

Kido et al. (1990) assessed the course of glomerular function in members of the same population as Nishijo et al. (1995). These authors concluded that Cd exposure is capable of causing progressive glomerular damage. Although it cannot be excluded on the basis of the available data that long-term and high-level exposure to Cd in the environment causes glomerular dysfunction, several potential sources of error should also be considered. Indeed, although the renal parameters were non-specific for the effects of Cd, other causes of renal dysfunction were not systematically ruled out. Moreover, there was no clear dose-effect relationship, latency time did not show a consistent trend, it seems possible that the definition of the groups was based on criteria defined a posteriori, and it is not clear whether the study population was a representative sample of the whole exposed population.

In the longitudinal study by Kido et al. (1988) only tubular markers were considered and it is not known whether the subjects examined are the same as those included in the publication of 1990.

The frequently cited study of Nogawa et al. (1984) included glomerular markers but was a cross-sectional study, a design that is not very suitable to establish a causal relationship.

### c) Case reports and case series

A case series including four persons exposed to cadmium and diagnosed with uremia is discussed by Tsuchiya (1992) and Kido et al. (1990) reported one case of renal insufficiency attributed to environmental exposure. Nagakawa et al. (1990) described briefly an autopsy series but it is unclear whether Cd-induced renal failure was the main cause of death (original report is available in Japanese only). Although case reports and case series are useful for drawing attention to some problem, they are weak study designs to demonstrate the existence of a causal relationship.

## Annex D Kidney effects

Buchet et al. (1990). Renal effects of cadmium body burden of the general population. Lancet 336:699-702 – Detailed calculations.

In the logistic model, the probability of “elevated” value is:

$$P=1/1+\exp-(a+\beta_1X+\beta_2Y)$$

Table D.1 Parameters of the logistic model

	$\beta$ coefficient	SE on $\beta$	p value
Constant	-1.5793	0.3906	< 0.001
Age	-0.0303	0.0088	< 0.001
U-Cd*	1.6093	0.4087	< 0.001

SE Standard error

\* Cd-U is expressed as log  $\mu\text{mol Cd-U/24h}$  centered on the mean of the group (0.837  $\mu\text{g/24h}$ )

Therefore, at age 47 years and Cd-U=2  $\mu\text{g/24 hours}$  (centered log = 0.378)

$$P=1/1+\exp(-1.5793+1.6093 \cdot 0.378-0.0303 \cdot 47)$$

= 0.084 or about 10% probability of elevated Ca-U

Probability of elevated Ca-U

Table D.2 Probability of elevated Cd-U

	Age 40 years	Age 50 years
Cd-U ( $\mu\text{g/24hours}$ )		
0	0.058	0.045
1	0.065	0.049
2	0.101	0.076

Järup et al. (2000). Low level exposure to cadmium and early kidney damage: the OSCAR study Occup Environ Med 57:668-672 - Detailed recalculations based on the raw data provided by the authors.

### 1) Total population

In a logistic regression analysis the estimated probability (p) can also be expressed as:

$$p = [\exp(a + \beta_1X + \beta_2Y)]/[1 + \exp(a + \beta_1X + \beta_2Y)]$$

Table D.3 Parameters of the logistic model

	$\beta$ coefficient	SE on $\beta$	95% CI	p value
Constant	-5.07	0.428	-5.908 to -4.227	< 0.001
Age	0.056	0.007	0.0425 to 0.070	< 0.001
U-Cd	0.295	0.086	0.125 to 0.464	0.001

CI Confidence intervals

Therefore, at age 53 years and Cd-U=1.2 µg/g creat,

$$p = \exp(-5.07 + 0.056 \cdot 53 + 0.295 \cdot 1.2) / (1 + \exp(-5.07 + 0.056 \cdot 53 + 0.295 \cdot 1.2))$$

$$= 0.147 \text{ or about 15\% probability of elevated HC values.}$$

*Probability of HC proteinuria*

Table D.4 Probability of HC proteinuria

	Age 40 years	Age 53 years
Cd-U (µg/g creatinine)		
0	0.056	0.10
1.2	0.078	0.15
2.62	0.113	0.20

2) Subgroup after exclusion of individuals with occupational exposure

Table D.5 Parameters of the logistic model

	β coefficient	SE on β	p value
constant	-5.02	0.476	< 0.001
Age	0.045	0.007	< 0.001
U-Cd	1.535	0.297	0.0001

*Probability of HC proteinuria*

Table D.6 Probability of HC proteinuria

	Age 52-y
Cd-U (µg/g creatinine)	
0	0.06
0.5	0.13
1.0	0.24

## **Annex E *In vitro* studies**

Some *in vitro* studies were conducted in an attempt to elucidate about the mechanism of the developmental and reproductive effects associated with an exposure to cadmium (generic). These studies were performed with water-soluble cadmium compounds.

No study specifically using cadmium oxide was located. One study using cadmium metal is reported here.

Studies have suggested that Cd accumulates in the placenta and exerts its toxicity either directly by creating placental damage or through perturbation of placental transport of nutrients such as calcium and zinc.

Wier et al. (1990) perfused lobes of placenta from normal-term deliveries of non-smoking women with cadmium (as cadmium chloride) at 0-11 mg/l for up to 12 hours. Cadmium content in the perfused tissue was dose-dependent. Alterations of circulatory parameters appeared at doses of 2.2 and 11 mg/l and were correlated with ultra structural alterations (between 5 and 8 hour perfusion): stromal oedema appeared with microvesicular changes in the endoplasmic reticulum, mitochondrial swelling in the syncytiotrophoblast; followed by subsyncytiotrophoblastic vesiculation and finally necrosis of the trophoblast (occurring between 5 and 8 hours of perfusion). There were no effects reported on glucose consumption or lactate production. However, cadmium (at 1.1 mg/l) reduced the placental transfer of zinc into the foetal circuit (Wier et al., 1990). Page et al. (1992) reported that cadmium at 5-50  $\mu\text{M}$  inhibited zinc uptake by placental microvillous membranes (Page et al., 1992 cited in Lin et al., 1997).

Cadmium may also perturb the placental transport of calcium. To investigate the involved mechanism, Lin et al. (1997) used a human choriocarcinoma cell line, which exhibits trophoblastic properties. Culture medium contained low concentrations (0.04, 0.16, 0.64  $\mu\text{M}$ ) of cadmium as  $\text{CdCl}_2$ . Cadmium treatment at low, physiological doses (0.04  $\mu\text{M}$ ), for 24 hours did not compromise cellular integrity but decreased cellular calcium uptake and transport, calcium ion binding and modified intracellular  $\text{Ca}^{2+}$  profile. Higher doses ( $\geq 16\mu\text{M}$ ) affected cell integrity (as assessed by lactate dehydrogenase release). The 24-hour treatment resulted also in a reduced expression of the trophoblast-specific cytosolic  $\text{Ca}^{2+}$ -binding protein (HcaBP). These results suggested that cadmium exposure compromised the calcium handling ability of trophoblastic cells as a consequence of alterations in subcellular, cytosolic  $\text{Ca}^{2+}$  binding activities (Lin et al., 1997).

Wier et al. (1990) also reported that the perfusion of cadmium (as cadmium chloride) in lobes of placenta decreased the synthesis and the release of human chorionic gonadotropin at all experimental concentrations (0-11 mg/l). This was confirmed by the study of Eisenmann and Miller (1994) that compared the toxicity of cadmium (2.2 mg/l) and selenium in a similar experimental system.

Cadmium induces the synthesis of metallothionein which may exert a protective effect against the toxicity of several heavy metal ions. To illustrate this and also the competition with other elements such as zinc, Lehman and Poisner (1984) used an *in vitro* system and studied the induction of metallothionein in human tissues exposed to Cd or Zn. Human chorionic trophoblast cells were exposed to different concentrations of cadmium (compound not specified): for dose-response experiments, Cd (1-32  $\mu\text{M}$ ) or Zn (5-20  $\mu\text{M}$ ) was added and incubation was continued for 24 hours. For time-course experiments, doses of 0.5-2  $\mu\text{M}$  Cd were applied in medium and incubation was continued for 8, 24 or 48 hours. To determine the effect of simultaneous addition

of Cd and Zn, an experiment was done in which Cd (0.5, 1 $\mu$ M) and Zn (2.5, 5 $\mu$ M) were added separately or together to the cells and incubation was continued for 24 hours.

Concentrations of cadmium as low as 0.5  $\mu$ M significantly increased MT synthesis. Higher concentrations of zinc were required to obtain the same phenomenon (2.5  $\mu$ M). When the cells were exposed to the metals for 24 hours, the increased MT levels remained elevated at least 48 hours after removing Cd or Zn. When Cd and Zn were applied simultaneously to the trophoblasts, the resulting increase in the concentration of MT was similar to the increase in MT found in cells exposed to Cd alone (data reported on histogram).

Cd has been reported to bind MT approximately 3,000 times more strongly than Zn (see Section 4 of this report in a separate document). It has been reported that Cd may displace zinc, by competing for the same binding site. The results of this study demonstrated the ability of cultured human trophoblasts to synthesise MT in response to Cd or Zn and that lower concentrations of cadmium than zinc are required for this synthesis.

Considering this, authors concluded that MT synthesised in foetal membranes may play a role in protecting the foetus from cadmium-toxicity (Lehman and Poisner, 1984).

In relation to a possible role of cadmium in mechanisms of preterm labour, effects of cadmium on the activity of myometrial strips from term pregnant women were examined by Sipowicz et al. (1995). Cadmium (Cd<sup>2+</sup>) in a concentration of 10<sup>-9</sup> M inhibited spontaneous contractile activity. Responses to Ca<sup>2+</sup> and oxytocin were significantly increased by exposure to cadmium in low concentrations (10<sup>-9</sup> M), whereas higher concentrations (10<sup>-3</sup> M) had inhibitory action. These results suggest that cadmium not only blocks Ca<sup>2+</sup> channels in the human myometrium, but also interferes with intracellular mechanisms involved in excitation-contraction coupling. The increased responses to Ca<sup>2+</sup> and oxytocin in the presence of low amounts of Cd<sup>2+</sup> support a role of cadmium in mechanisms of preterm labour (Sipowicz et al., 1995).

Clough et al. (1990) reported that cultured rat Sertoli cells were more sensitive to cadmium chloride than interstitial (primary Leydig ) cells. Different cell populations within a same tissue differed markedly in susceptibility to the toxicant: the 72-hour LC<sub>50</sub> for Sertoli and interstitial cells were 4.1 and 19.6  $\mu$ M, respectively. Because the Sertoli cell provides support for the seminiferous epithelium, the differential sensitivity of this cell may in part explain cadmium-induced testicular dysfunction, particularly at doses that leave intact the vascular epithelium (Clough et al., 1990).

Laskey and Phelps (1991) also showed a reduction of rat Leydig cell function following *in vitro* exposure to cadmium chloride at concentrations of 1 to 5,000  $\mu$ M for 3 hours (Laskey and Phelps, 1991, cited in IARC 1993).

The toxicity to the human spermatozoa of cadmium metal (200 mm<sup>2</sup> in a flask) was already tested by Holland and White in 1979. Human ejaculates were obtained and motility of the spermatozoa was estimated before to be incubated with the metal for 3 hours under constant shaking. Oxygen uptake, glucose utilisation and oxidation, lactate accumulation were also measured. Cadmium reduced significantly the percentage of motile spermatozoa (73.0  $\pm$  2.5% and 43.0  $\pm$  2.0% at 0 and 3 hours respectively) and decreased the quantity of glucose used by the spermatozoa. As cadmium had a detrimental effect on the motility of the spermatozoa but only moderately depressed glycolysis and had even less effect on oxidative metabolism, authors suggested that cadmium may specifically inhibit the motility apparatus of the spermatozoa (Holland and White, 1979).

Fertility of ejaculates of rabbit sperm after *in vitro* exposure to CdCl<sub>2</sub> (0.02-0.05-0.1 mM) was tested by Foote (1999). Semen was washed to remove seminal plasma and minimise possible bindings of the metal by proteins. Exposure of the sperm was followed by insemination of superovulated does. The concentrations used to treat the sperm *in vitro* were, as reported by the authors, higher than the concentrations found in semen and/or blood of men exposed to heavy metals in occupational studies. The tested concentrations of Cd<sup>2+</sup> did not reduce hyperactivity of the sperm. The fertility tests also resulted in little or no difference, consistent with the findings that Cd did not affect the proportion of hyperactive sperm, a variable often associated with capacitation (required for fertilisation) (Foote, 1999).

*Conclusions: in vitro studies*

Most of the located studies have used water-soluble cadmium compounds and not cadmium metal or cadmium oxide.

Different mechanisms, which may account for reprotoxic effects of cadmium, have been suggested, involving a direct placental damage, an indirect action via a perturbation of the placental transport of other nutrients or an effect on the synthesis or release of human chorionic gonadotropin.

Some cell populations (Sertoli cells) were reported to be more susceptible than others to a toxic effect of cadmium compounds, which could explain the rather specific action of cadmium compounds on the testes in experimental animals when injected.

Cadmium metal appeared to reduce motility of human spermatozoa *in vitro* after 3 hours of incubation. This was not observed with rabbit sperm exposed to cadmium chloride.

Although, some mechanistic explanations are suggested, no definite conclusion can be drawn from these *in vitro* studies about the toxicity of cadmium oxide/metal.

## Annex F The occurrence of cadmium (metal) in products according to the Swedish product register

Trades that use products containing metallic cadmium and product functions.

Trade	Product functions
Paint industry	Activators* Dyestuffs, pigments Fillers (plastic, paint,...)
Industry for rubber products	Activators* Dyestuffs, pigments Fillers (plastic, paint,...)
Industry for ceramic tiles and flags	Activators* Dyestuffs, pigments Fillers (plastic, paint,...)
Treatment and coating of metals; workshops for gen. mech. engin.	Activators* Degreasing agents* Dyestuffs, pigments Fillers (plastic, paint,...)
Retail trade; repair shops	Adhesives, glues* Cast compounds*
Fabricated metal products, except machinery and equipment	Alloy metals* Fillers (plastics, paint, etc)
Soap and detergents, cleaning and polishing preparations	Corrosion inhibitors* pH-regulating agents*
Textile	Dyestuffs, pigments
Pulp, paper and paper products	Dyestuffs, pigments
Other organic basic chemicals	Dyestuffs, pigments
Agricultural establishment and related	Feedstuff/feedstuff additives*
Basic metals industry	Metal surface coating agents*
Glass and glass products industry	Other paints and varnishes, solvent-based*
Whole sale and retail	Paints, varnishes*
Pharmaceutical preparations	Skin protection agents*

\* Less than three products in the product category

In total 35 products (total volume less than 1 ton per year) whereof two consumer products with a cadmium concentration lesser or equal at 10% of the product (Swedish Product Register for the year 1996, 15/09/97). No further details could be identified related to these latter products (KEMI, pers. com 2000/2001)

## Annex G The occurrence of cadmium oxide in products according to the Swedish product register

Trades that use products containing cadmium oxide and product functions.

Trade	Product functions
Industry for radio, television and communication apparatus	Contact agents*
Treatment and coating of metals; workshops for gen. mech. engine.	Electrolytes*
Industry for glass and glass products	Enamels, glazes Paints, varnishes*
Industry for ceramic products, other than non-refractory for construction purposes	Enamels, glazes
Industry for plastic products	Intermediates (plastic manufacture)*
Manufacture of chemicals and chemical products	Metal surface treatment agents*

\* Less than three products in the product category

In total 45 products whereof 37 with a cadmium concentration less than or equal at 10% of the product. Mainly in the Industry for glass and glass products and Industry for ceramic products with the following use/function: enamels, glazes. The Register further mentions seven products with a substance concentration in the range 10-20% and 1 product with a high (80-100%) content. No consumer products have been registered. The overall total volume accounts for less than 1 ton per year. (Swedish Product Register for the year 1996, 15/09/97).

## Annex H Check-list for evaluating epidemiological studies

(check-list established by Professor Philippe Hotz from the Institut für Sozial- und Präventivmedizin der Universität Zürich)



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ABTEILUNG FÜR ARBEITS-  
UND UMWELTMEDIZIN

### **CROSS-SECTIONAL STUDIES.**

#### **1. Other publications on the same population.**

Consider possible overlapping with other studies by quite different authors which included part of the same study population.  
If relevant : on the first page indications about possible redundancy (part of the same authors have already published results on part of this study population). Indicate references for easy retrieval of publications. Briefly comment on differences / similarities between former and latter publications and justify the exclusion of the study not considered.

#### **2. Location.**

Country / region / institution (selection bias !).

#### **3. Purpose**

precisely defined ?

#### **4. Study population**

##### **4.1. and 4.2. Exposed and nonexposed.**

- size of study population, men /women, age. If possible : socioeconomic class, smoking, alcohol, and other relevant factors in that context.

- is the study population young ?  
- definition of the study population :  
a) beginning of work at...

b) end of work at ...; b) if sequential cross-sectional study or inclusion of retired workers  
c) minimal duration;

d) all workers presently working and exposed ? Retired and currently nonexposed workers ?  
Time since last exposure ?

Are workers previously diagnosed with poisoning included ?

##### **4.3. Final study population.**

- initial vs final study population (as a summary showing the lost cases and controls at each step of constitution of study population with the most important data on age, sex, employability, and other important variables in that context).

- comparability of cases and controls as for : age, sex, socioeconomic group, education, and other important variables in that context.

Are workers previously diagnosed with poisoning included ?

IMPORTANT : considerable differences may be found between initial and final study population. A presentation of the results (for example in tables) should take this issue into account.

##### **5. Selection, participation rate, representativeness.**

- selection of the study population  
- selection of the study sample  
- participation rate  
- representative sample ?

If sequential cross-sectional study : are the samples comparable ?

##### **6. Exposure.**

###### **6.1. Specific aspects : exposed workers**

Is the word "exposed" clearly defined (with respect to type, minimal intensity, duration, frequency?). Observational period (if not mentioned under 4.; important because of time-related changes of exposure intensity)? Previous poisonings?

- type :

== general population or industry ?

== type of industry (for example Cd exposure : cadmium production, alloys, soldering and/or cutting, Cd-Ni battery, etc.) ?

== is "exposure" defined by occupation and/or industry, group of agents, agent ? Are the groups specific or very broad (= how specific if this definition ?) ? Are concomitant exposures possible (for example : heavy metals vs Cd + As inorg or Pb or Ni vs Cd only ? Benzene in garages, oil refineries, printing plants represent three quite different exposure conditions).

- information on exposure frequency, duration, and intensity :

== yes/no

== only present exposure (strictly cross-sectional) or information on previous exposure (in this plant, in the same occupation but in other plants, in all occupations for the lifetime)

== minimal intensity, duration, frequency : based on exposure reconstruction or objective measures ?

== if exposure reconstruction : type of variable (dichotomous if exposed vs nonexposed, ordinal, exposure score, etc.) ?

== if dichotomous classifications : is the cut-off clearly described, credible, arbitrary ? Are minimal intensity, duration, frequency taken into account to define the word "exposed" ?

== if ordinal categories or of exposure score : is the classification / score credible, consistent ? Is there any indication of the validity of the classification / score ?

== objective measures available ? air sampling (area vs. personal, total vs respirable dust); biol.monitoring (blood/urine/neutron activation analysis/x-ray fluorescence, etc.)

samples from controls and exposed workers examined in the same series ?

quality control (exposure assessment) ?

## **6.2. Specific aspects : control workers**

### **6.3. Summary**

## **7. Diagnosis.**

Is the endpoint clinically relevant (predictive value) ? Methods ? Quality control ?

If relevant :

Classification scheme

Are there objective criteria required for ascertaining diagnosis (example : FAB, SLE) ?

Blind review of medical records, slides, if any ?

Panel review ?

Other important methodologic aspects (example : biopsy for kidney diseases, immunofluorescence for glomerulonephritis, histological confirmation for cancer).

## **8. Bias.**

- preplacement examination

- healthy worker effect

- is it clear that the endpoint is really an effect of the exposure (cross-sectional design !)

## **9. Interview and coding. laboratory.**

Blind interview / interview procedure / structure and content of the interview.

Blind coding of the answers / coding according to .... (are criteria mentioned, credible, arbitrary).

samples from controls and exposed workers examined in the same series and quality control (exposure assessment : see exposure). Are these units adequate and do they consider age- or sex-related differences (mg/l, mg/g, mg/24h for metabolite; ml/mn or ml/mn/1.76m<sup>2</sup> for clearance)

#### **10. Design and statistics.**

- design
- control population : regional, other industrial workers, office workers, low vs high exposure (definition of control group : see 4.2.; exposure assessment in the control group : see 6.2.)
- statistical methods

#### **11. Confounding factors**

Age, sex, hospital, smoking, alcohol ?

If relevant : socioeconomic group, residence, genetic / familial factors, ethnicity, race. Are these factors clearly defined (nationality may change after wedding) ? If subgroups are used are these subgroups relevant ?

Considerable sources of misclassification ? (for exposure and disease see 6. and 7., respectively)

IMPORTANT : were the confounding factors taken into account in the analysis or were they only mentioned as items in the interview and not considered in the statistical analysis ?

#### **12. Results.**

##### **12.1. Results**

##### **12.2. What about power ?**

#### **13. Identification, latency, DRC.**

Identification : of a specific causal agent, specific causal occupation ?

Latency time (lagging of some years) : yes / no ? biologically credible ?

Dose - response curve : was it examined ?

#### **14. Physiopathology.**

Physiopathological mechanisms

#### **15. Miscellaneous.**

26.9.1997



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UND UMWELTMEDIZIN

## **RETROSPECTIVE COHORT STUDIES, MORTALITY.**

### **1. Other publications on the same population.**

. Consider possible overlapping with other studies by quite different authors which included part of the same study population. If relevant : on the first page indications about possible redundancy (part of the same authors have already published results on part of this study population). Indicate references for easy retrieval of publications. Briefly comment on differences / similarities between former and latter publications and justify the exclusion of the study not considered.

### **2. Location.**

Country / region / institution.

### **3. Purpose**

precisely defined / hypotheses - generating

### **4. Study population**

#### **4.1. and 4.2. Exposed and nonexposed.**

- cohort size, men /women, age, number / percentage of deaths (obs. /exp. numbers of deaths). If possible : socioeconomic class, smoking, alcohol, and other relevant factors in that context.

- is the percentage of deaths higher than 10 % ?

- is the cohort young ?

- definition of the cohort :

a) begin of work at...

b) end of work at ...

c) minimal duration

d) other characteristics

Definition of follow - up : begin / end of follow - up

Are workers previously diagnosed with poisoning included ?

#### **4.3. Final study population.**

- initial vs final study population (as a summary showing the lost cases and controls at each step of constitution of study population with the most important data on age, sex, employability, and other important variables in that context).

- comparability of cases and controls as for : age, sex, socioeconomic group, education, and other important variables in that context.

Are workers previously diagnosed with poisoning included ?

IMPORTANT : considerable differences may be found between initial and final study population. A presentation of the results (for example in tables) should take this issue into account.

### **5. Selection, participation rate, representativeness.**

- selection

- participation rate

- representative sample

If register : is the coverage good ?

If morbidity / mortality statistics : data quality ?

### **6. Exposure.**

#### **6.1. Specific aspects.**

Is the word "exposed" clearly defined (with respect to type, minimal intensity, duration, frequency?). Observational period (if not mentioned under 2.; important because of time-related changes of exposure intensity)? Previous poisonings?

- type :

== general population or industry ?

== type of industry (for example : exposure to heavy metals/to Cd + As inorg or Pb or Ni/or to Cd only ? Benzene in garages, oil refineries, printing plants represents three quite different exposure situations).

== is "exposure" defined by occupation and/or industry, group of agents, agent ? Are the groups specific or very broad (= how specific if this definition ?) ? Are concomitant exposures possible (for example : heavy metals vs Cd + As inorg or Pb or Ni vs Cd only ? Benzene in garages, oil refineries, printing plants represent three quite different exposure conditions).

== if coding of occupations : clearly standardized ? Based on which coding system (for example : Dictionary of Occupational Titles of the Census) ? Blind ?

- information on exposure frequency, duration, and intensity :

== yes/no

== minimal intensity, duration, frequency : based on exposure reconstruction or objective measures ?

== if exposure reconstruction : type of variable (dichotomous if exposed vs nonexposed, ordinal, exposure score, etc.) ?

== if dichotomous and based on death certificates, registers, or similar sources of information : longest, usual, current, last occupation or occupation at diagnosis ?

== if other dichotomous classifications : is the cut-off clearly described, credible, arbitrary ?

Are minimal intensity, duration, frequency taken into account to define the word "exposed" ?

== if ordinal categories or of exposure score : is the classification / score credible, consistent ? Is there any indication of the validity of the classification / score ?

== objective measures available ? air sampling (area vs. personal, total vs respirable dust); biol.monitoring (blood/urine/neutron activation analysis/x-ray fluorescence, etc.)

### **7. Diagnosis.**

Classification scheme (ICD, ICD - O, etc.)

Are there objective criteria required for ascertaining diagnosis (example : FAB, SLE) ?

Blind review of medical records, slides, if any ?

Panel review ?

Other important methodologic aspects (example : biopsy for kidney diseases, immunofluorescence for glomerulonephritis, histological confirmation for cancer).

If death certificates : underlying vs. contributing cause of death.

- high / low mortality rate ?

### **8. Bias.**

- surveillance bias

- changes in the course of the study (for example : job changes in comparison to the job used as exposure surrogate)

- diagnostic access bias

- diagnostic suspicion bias

### **9. Interview and coding.**

Blind interview / interview procedure / structure and content of the interview.

Blind coding of the answers / coding according to .... (are criteria mentioned, credible, arbitrary).

### **10. Design and statistics.**

- design
- SIR, SMR, PMR
- reference population : national, regional, other industrial workers, low vs high exposure
- statistical methods

#### **11. Confounding factors**

Age, sex, hospital, smoking, alcohol ?

If relevant : socioeconomic group, residence, genetic / familial factors, race, ethnicity

Considerable sources of misclassification ? (for exposure and disease see 6. and 7., respectively)

Sensitivity analysis ?

IMPORTANT : were the confounding factors taken into account in the analysis or were they only mentioned as items in the interview and not considered in the statistical analysis ? Are these factors clearly defined (nationality may change after wedding) ? If subgroups are used are these subgroups relevant ?

#### **12. Results.**

##### **12.1. Results**

##### **12.2. What about power ?**

#### **13. Identification, latency, DRG.**

Identification : of a specific causal agent, specific causal occupation ?

Latency time (lagging of some years) : yes / no ? biologically credible ?

Dose - response curve : was it examined ?

#### **14. Physiopathology.**

Physiopathological mechanisms (plausibility)

#### **15. Miscellaneous.**

26.9.1997

**Annex I EUSES output related to the calculations of regional and continental PECs**

EUSES Full report

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Study  
Substance  
Defaults  
Assessment types  
Base set complete

Explanation status column

Name

STUDY  
STUDY IDENTIFICATION  
Study name  
Study description  
Author  
Institute  
Address  
Zip code  
City  
Country  
Telephone  
Telefax  
Email  
Calculations checksum

Single substance

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Cd  
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1A, 1B, 2, 3A, 3B  
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'O' = Output; 'D' = Default; 'S' = Set; 'I' =  
Imported

Value

Units

Status

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version 2003, Kp 130000

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Substance

Cd

Defaults

Standard

Assessment types

1A, 1B, 2, 3A, 3B

Base set complete

No

Name	Value	Units	Status
<b>DEFAULTS</b>			
<b>DEFAULT IDENTIFICATION</b>			
General name	Standard		D
Description	According to TGDs		D
<b>RELEASE ESTIMATION</b>			
Fraction of EU production volume for region	0.1	[-]	D
Fraction connected to sewer systems	0.7	[-]	D
<b>CHARACTERISTICS OF COMPARTMENTS</b>			
<b>GENERAL</b>			
Density of solid phase	2.5	[kg.l-1]	D
Density of water phase	1	[kg.l-1]	D
Density of air phase	1.3E-03	[kg.l-1]	D
Environmental temperature	12	[°C]	D
Constant of Junge equation	0.01	[Pa.m]	D
Surface area of aerosol particles	0.01	[m2.m-3]	D
Gas constant (8.314)		8.314 [Pa.m3.mol-1.K-1]	D
<b>SUSPENDED MATTER</b>			
Volume fraction solids in suspended matter	0.1	[m3.m-3]	D
Volume fraction water in suspended matter	0.9	[m3.m-3]	D
Weight fraction of organic carbon in suspended matter	0.1	[kg.kg-1]	D
Wet bulk density of suspended matter	1.15E+03	[kg.m-3]	O
<b>SEDIMENT</b>			
Volume fraction solids in sediment	0.2	[m3.m-3]	D
Volume fraction water in sediment	0.8	[m3.m-3]	D
Weight fraction of organic carbon in sediment	0.05	[kg.kg-1]	D
Bulk density of sediment	1.3E+03	[kgwwt.m-3]	O
Conversion factor wet-dry sediment	2.6	[kgwwt.kgdwt-1]	O
<b>SOIL</b>			
Volume fraction solids in soil	0.6	[m3.m-3]	D
Volume fraction water in soil	0.2	[m3.m-3]	D
Volume fraction air in soil	0.2	[m3.m-3]	D
Weight fraction of organic carbon in soil	0.02	[kg.kg-1]	D
Bulk density of soil	1.7E+03	[kgwwt.m-3]	O
Conversion factor wet-dry soil	1.13	[kgwwt.kgdwt-1]	O
<b>STP SLUDGE</b>			
Fraction of organic carbon in raw sewage sludge	0.3	[kg.kg-1]	D
Fraction of organic carbon in settled sewage sludge	0.3	[kg.kg-1]	D
Fraction of organic carbon in activated sewage sludge	0.37	[kg.kg-1]	D
Fraction of organic carbon in effluent sewage sludge	0.37	[kg.kg-1]	DUSES

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Assessment types

1A, 1B, 2, 3A, 3B

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No

Name	Value	Units	Status
<b>DEGRADATION AND TRANSFORMATION RATES</b>			
Concentration of OH-radicals in atmosphere		5,00E+05 [molec.cm-3]	D
Rate constant for abiotic degradation in STP		0 [d-1]	D
Rate constant for abiotic degradation in bulk soil		0 [d-1]	D
Rate constant for abiotic degradation in bulk sediment		0 [d-1]	D
Rate constant for anaerobic biodegradation in sediment		0 [d-1]	D
Fraction of sediment compartment that is aerated	0.1	[m3.m-3]	D
<b>SEWAGE TREATMENT</b>			
<b>GENERAL</b>			
Number of inhabitants feeding one STP		1,00E+04 [eq]	D
Sewage flow		200 [l.eq-1.d-1]	D
Effluent discharge rate of local STP		2,00E+06 [l.d-1]	O
Temperature dependency correction	No		D
Temperature of air above aeration tank		15 [oC]	D
Temperature of water in aeration tank		15 [oC]	D
Height of air column above STP		10 [m]	D
Number of inhabitants of region		2,00E+07 [eq]	D
Number of inhabitants of continental system	3.5E+08	[eq]	O
Windspeed in the system		3 [m.s-1]	D
<b>RAW SEWAGE</b>			
Mass of O2 binding material per person per day		54 [g.eq-1.d-1]	D
Dry weight solids produced per person per day	0.09	[kg.eq-1.d-1]	D
Density solids in raw sewage	1.5	[kg.l-1]	D
Fraction of organic carbon in raw sewage sludge	0.3	[kg.kg-1]	D
<b>PRIMARY SETTLER</b>			
Depth of primary settler		4 [m]	D
Hydraulic retention time of primary settler		2 [hr]	D
Density suspended and settled solids in primary settler	1.5	[kg.l-1]	D
Fraction of organic carbon in settled sewage sludge	0.3	[kg.kg-1]	D
<b>ACTIVATED SLUDGE TANK</b>			
Depth of aeration tank		3 [m]	D
Density solids of activated sludge	1.3	[kg.l-1]	D
Concentration solids of activated sludge		4 [kg.m-3]	D
Steady state O2 concentration in activated sludge		2,00E-03 [kg.m-3]	D
Mode of aeration	Surface		D
Aeration rate of bubble aeration	1.31E-05	[m3.s-1.eq-1]	D
Fraction of organic carbon in activated sewage sludge	0.37	[kg.kg-1]	D
Sludge loading rate	0.15	[kg.kg-1.d-1]	D
Hydraulic retention time in aerator (9-box STP)	6.9	[hr]	O
Hydraulic retention time in aerator (6-box STP)	10.8	[hr]	O
Sludge retention time of aeration tank	9.2	[d]	OSSES

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21/02/2003 12:20

Name	Value	Units	Status
<b>SOLIDS-LIQUIDS SEPARATOR</b>			
Depth of solids-liquid separator		3 [m]	D
Density suspended and settled solids in solids-liquid separator	1.3	[kg.l-1]	D
Concentration solids in effluent		30 [mg.l-1]	D
Hydraulic retention time of solids-liquid separator		6 [hr]	D
Fraction of organic carbon in effluent sewage sludge	0.37	[kg.kg-1]	D
<b>REGIONAL AND CONTINENTAL DISTRIBUTION</b>			
<b>CONTINENTAL</b>			
Area of EU	3.56E+06	[km2]	D
Area of continental system	3.52E+08	[km2]	O
Number of inhabitants in the EU	3.7E+08	[eq]	D
Number of inhabitants of continental system	3.5E+08	[eq]	O
Area fraction of water of the continental system	0.03	[-]	D
Area fraction of natural soil	0.6	[-]	D
Area fraction of agricultural soil	0.27	[-]	D
Area fraction of industrial/urban soil	0.1	[-]	D
Fraction of water flow from global scale to continent		0 [-]	D
Water depth of system		3 [m]	D
Suspended solids concentration of continental system		15 [mg.l-1]	S
Residence time of water in system		166 [d]	O
Residence time of air in system	6.41	[d]	O
Net sedimentation rate	2.72	[mm.yr-1]	O
<b>REGIONAL</b>			
Area of regional system		4,00E+04 [km2]	D
Number of inhabitants of region		2,00E+07 [eq]	D
Area fraction of water of the regional system	0.03	[-]	D
Area fraction of natural soil	0.6	[-]	D
Area fraction of agricultural soil	0.27	[-]	D
Area fraction of industrial/urban soil	0.1	[-]	D
Fraction of water flow from continental scale to region	0.034	[-]	D
Water depth of system		3 [m]	D
Suspended solids concentration of regional system		15 [mg.l-1]	D
Residence time of water in system	40.1	[d]	O
Residence time of air in system	0.684	[d]	O
Net sedimentation rate	2.73	[mm.yr-1]	O
<b>AIR</b>			
Atmospheric mixing height		1000 [m]	D
Windspeed in the system		3 [m.s-1]	D
Aerosol deposition velocity		1,00E-03 [m.s-1]	D
Aerosol collection efficiency		2,00E+05 [-]	D
Average annual precipitation		700 [mm.yr-1]	D
<b>WATER AND SEDIMENT</b>			
Concentration biota		1 [mg.l-1]	DES

EUSES Full report

Single substance

21/02/2003 12:20

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Study

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Standard

Assessment types

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Base set complete

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Name	Value	Units	Status
<b>WATER AND SEDIMENT ( Continued )</b>			
Sediment mixing depth	0.03	[m]	D
Settling velocity of suspended solids	2.5	[m.d-1]	D
(biogenic) production of suspended solids in water		0 [kg.d-1]	D
Sewage flow		200 [l.eq-1.d-1]	D
Concentration solids in effluent		30 [mg.l-1]	D
Fraction connected to sewer systems	0.7	[-]	D
<b>SOIL</b>			
Mixing depth natural soil	0.05	[m]	D
Mixing depth agricultural soil	0.2	[m]	D
Mixing depth industrial/urban soil	0.05	[m]	D
Fraction of rain water infiltrating soil	0.25	[-]	D
Fraction of rain water running off soil	0.25	[-]	D
Soil erosion rate of regional system	0.03	[mm.yr-1]	D
<b>MASS TRANSFER</b>			
Air-film PMTC (air-water interface)	1.39E-03	[m.s-1]	D
Water-film PMTC (air-water interface)	1.39E-05	[m.s-1]	D
Air-film PMTC (air-soil interface)	1.39E-03	[m.s-1]	D
Soil-air PMTC (air-soil interface)	5.56E-06	[m.s-1]	D
Soil-water film PMTC (air-soil interface)	5.56E-10	[m.s-1]	D
Water-film PMTC (sediment-water interface)	2.78E-06	[m.s-1]	D
Pore water PMTC (sediment-water interface)	2.78E-08	[m.s-1]	D
<b>LOCAL DISTRIBUTION</b>			
<b>AIR AND SURFACE WATER</b>			
Concentration in air at source strength 1 [kg.d-1]	2.78E-04	[mg.m-3]	D
Standard deposition flux of aerosol-bound compounds	0.01	[mg.m-2.d-1]	D
Standard deposition flux of gaseous compounds	??	[mg.m-2.d-1]	D
Suspended solids concentration of regional system		15 [mg.l-1]	D
Dilution factor		10 [-]	D
Flow rate of the river	1.8E+04	[m3.d-1]	D
Calculate dilution from river flow rate	No		D
<b>SOIL</b>			
Mixing depth of grassland soil	0.1	[m]	D
Dry sludge application rate on agricultural soil		5,00E+03 [kg.ha-1.yr-1]	D
Dry sludge application rate on grassland		1000 [kg.ha-1.yr-1]	D
Averaging time soil (for terrestrial ecosystem)		30 [d]	D
Averaging time agricultural soil		180 [d]	D
Averaging time grassland		180 [d]	D
Air-film PMTC (air-soil interface)	1.39E-03	[m.s-1]	D
Soil-air PMTC (air-soil interface)	5.56E-06	[m.s-1]	D
Soil-water film PMTC (air-soil interface)	5.56E-10	[m.s-1]	D
Mixing depth agricultural soil	0.2	[m]	D
Fraction of rain water infiltrating soil	0.25	[-]	DUSES

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No

Name	Value	Units	Status
SOIL ( Continued )			
Average annual precipitation		700 [mm.yr-1]	D
<b>CHARACTERISTICS OF PLANTS AND CATTLE</b>			
<b>PLANTS</b>			
Volume fraction of water in plant tissue	0.65	[m3.m-3]	D
Volume fraction of lipids in plant tissue	0.01	[m3.m-3]	D
Volume fraction of air in plant tissue	0.3	[m3.m-3]	D
Correction for differences between plant lipids and octanol	0.95	[-]	D
Bulk density of plant tissue (wet weight)	0.7	[kg.l-1]	D
Rate constant for metabolism in plants		0 [d-1]	D
Rate constant for photolysis in plants		0 [d-1]	D
Leaf surface area		5 [m2]	D
Conductance		1,00E-03 [m.s-1]	D
Shoot volume		2 [l]	D
Rate constant for dilution by growth	0.035	[d-1]	D
Transpiration stream		1 [l.d-1]	D
<b>CATTLE</b>			
Daily intake for cattle of grass (dryweight)	16.9	[kg.d-1]	D
Conversion factor grass from dryweight to wetweight		4 [kg.kg-1]	D
Daily intake of soil (dryweight)	0.41	[kg.d-1]	D
Daily inhalation rate for cattle		122 [m3.d-1]	D
Daily intake of drinking water for cattle		55 [l.d-1]	D
<b>CHARACTERISTICS OF HUMANS</b>			
Daily intake of drinking water		2 [l.d-1]	D
Daily intake of fish	0.115	[kg.d-1]	D
Daily intake of leaf crops (incl. fruit and cereals)	1.2	[kg.d-1]	D
Daily intake of root crops	0.384	[kg.d-1]	D
Daily intake of meat	0.301	[kg.d-1]	D
Daily intake of dairy products	0.561	[kg.d-1]	D
Inhalation rate for humans		20 [m3.d-1]	D
Bioavailability for oral uptake		1 [-]	D
Bioavailability for inhalation	0.75	[-]	D
Bioavailability for dermal uptake		1 [-]	D
Bodyweight of the human considered		70 [kg]	D
Oral to inhalatory extrapolation	Using adsorption rates		

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Single substance

Printed on  
Study  
Substance  
Defaults  
Assessment types  
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21/02/2003 12:20

Cd RAR 2003  
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Standard  
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No

Name	Value	Units	Status
<b>SUBSTANCE IDENTIFICATION</b>			
General name	Cd		S
Description			D
CAS-No			D
EC-notification no.			D
EINECS no.			D
<b>PHYSICO-CHEMICAL PROPERTIES</b>			
Molecular weight		112 [g.mol-1]	S
Melting point	??	[oC]	D
Boiling point	??	[oC]	D
Vapour pressure at 25 [oC]		1,00E-10 [Pa]	S
Octanol-water partition coefficient.		-1 [log10]	S
Water solubility		5,00E-03 [mg.l-1]	SSES

EUSES Full report	Single substance		
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Study	Cd RAR 2003		
Substance	Cd		
Defaults	Standard		
Assessment types	1A, 1B, 2, 3A, 3B		
Base set complete	No		
Name	Value	Units	Status
<b>RELEASE ESTIMATION</b>			
<b>CHARACTERIZATION AND TONNAGE</b>			
High Production Volume Chemical	No		D
Production volume of chemical in EU		0 [tonnes.yr-1]	D
Volume of chemical imported to EU		0 [tonnes.yr-1]	D
Volume of chemical exported from EU		0 [tonnes.yr-1]	D
Intermittent release	No		D
<b>INTERMEDIATE RESULTS PRODUCTION VOLUMES</b>			
Tonnage of substance in Europe		0 [tonnes.yr-1]	O
Regional production volume of substance		0 [tonnes.yr-1]	O
Continental production volume of substance		0 [tonnes.yr-1]	O
<b>USE PATTERNS</b>			
<b>EMISSION INPUT DATA</b>			
Industry category	15/0 Others		D
Use category	55/0 Others		D
Emission scenario document available	No		O
Extra details on use category	No extra details necessary		D
Extra details on use category	No extra details necessary		D
Fraction of tonnage for application		1 [-]	O
Fraction of chemical in formulation		1 [-]	D
Production	Yes		D
Formulation	Yes		D
Processing	Yes		D
Private use	Yes		D
Recovery	Yes		D
Main category production	III Multi-purpose equipment		D
Main category formulation	III Multi-purpose equipment		D
Main category processing	III Non-dispersive use		D
<b>INTERMEDIATE RESULTS</b>			
<b>USE PATTERN 1</b>			
<b>INTERMEDIATE RESULTS TONNAGES PER USE PATTERN</b>			
Relevant tonnage for application		0 [tonnes.yr-1]	O
Regional tonnage of substance		0 [tonnes.yr-1]	O
Continental tonnage of substance		0 [tonnes.yr-1]	O
<b>RELEASE FRACTIONS AND EMISSION DAYS</b>			
<b>[PRODUCTION]</b>			
Fraction of tonnage released to air		1,00E-05 [-]	O
Fraction of tonnage released to waste water	0.02	[-]	O
Fraction of tonnage released to surfacewater		0 [-]	O
Fraction of tonnage released to industrial soil		1,00E-04 [-]	O
Source of A-table data	General table		OUSES

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Assessment types  
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21/02/2003 12:20

Cd RAR 2003  
Cd  
Standard  
1A, 1B, 2, 3A, 3B  
No

Name	Value	Units	Status
<b>RELEASE FRACTIONS AND EMISSION DAYS ( Continued )</b>			
<b>[PRODUCTION]</b>			
Fraction of the main local source		1 [-]	O
Number of emission days per year		1 [-]	O
Source of B-table data	General table		O
<b>[FORMULATION]</b>			
Fraction of tonnage released to air	2.5E-03	[-]	O
Fraction of tonnage released to waste water	0.02	[-]	O
Fraction of tonnage released to surfacewater		0 [-]	O
Fraction of tonnage released to industrial soil		1,00E-04 [-]	O
Source of A-table data	General table		O
Fraction of the main local source		1 [-]	O
Number of emission days per year		20 [-]	O
Source of B-table data	General table		O
<b>[PROCESSING]</b>			
Fraction of tonnage released to air		1,00E-03 [-]	O
Fraction of tonnage released to waste water	0.1	[-]	O
Fraction of tonnage released to surfacewater		0 [-]	O
Fraction of tonnage released to industrial soil		1,00E-02 [-]	O
Source of A-table data	General table		O
Fraction of the main local source		1 [-]	O
Number of emission days per year		1 [-]	O
Source of B-table data	General table		O
<b>[PRIVATE USE]</b>			
Fraction of tonnage released to air		0 [-]	O
Fraction of tonnage released to waste water		0 [-]	O
Fraction of tonnage released to surfacewater		0 [-]	O
Fraction of tonnage released to industrial soil		0 [-]	O
Source of A-table data	No applicable data found		O
Fraction of the main local source		0 [-]	O
Number of emission days per year		1 [-]	O
Source of B-table data	General table		O
<b>[RECOVERY]</b>			
Fraction of tonnage released to air		0 [-]	O
Fraction of tonnage released to waste water		0 [-]	O
Fraction of tonnage released to surfacewater		0 [-]	O
Fraction of tonnage released to industrial soil		0 [-]	O
Source of A-table data	No applicable data found		O
Fraction of the main local source	0.5	[-]	O
Number of emission days per year		150 [-]	O
Source of B-table data	General table		OUSES

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Single substance

21/02/2003 12:20

Printed on

Study

Substance

Defaults

Assessment types

Base set complete

Cd RAR 2003

Cd

Standard

1A, 1B, 2, 3A, 3B

No

Name	Value	Units	Status
<b>CONTINENTAL</b>			
<b>[PRODUCTION]</b>			
Continental release to air	0	[kg.d-1]	O
Continental release to waste water	0	[kg.d-1]	O
Continental release to surface water	0	[kg.d-1]	O
Continental release to industrial soil	0	[kg.d-1]	O
<b>[FORMULATION]</b>			
Continental release to air	0	[kg.d-1]	O
Continental release to waste water	0	[kg.d-1]	O
Continental release to surface water	0	[kg.d-1]	O
Continental release to industrial soil	0	[kg.d-1]	O
<b>[PROCESSING]</b>			
Continental release to air	0	[kg.d-1]	O
Continental release to waste water	0	[kg.d-1]	O
Continental release to surface water	0	[kg.d-1]	O
Continental release to industrial soil	0	[kg.d-1]	O
<b>[PRIVATE USE]</b>			
Continental release to air	0	[kg.d-1]	O
Continental release to waste water	0	[kg.d-1]	O
Continental release to surface water	0	[kg.d-1]	O
Continental release to industrial soil	0	[kg.d-1]	O
<b>[RECOVERY]</b>			
Continental release to air	0	[kg.d-1]	O
Continental release to waste water	0	[kg.d-1]	O
Continental release to surface water	0	[kg.d-1]	O
Continental release to industrial soil	0	[kg.d-1]	O
<b>REGIONAL</b>			
<b>[PRODUCTION]</b>			
Regional release to air	0	[kg.d-1]	O
Regional release to waste water	0	[kg.d-1]	O
Regional release to surface water	0	[kg.d-1]	O
Regional release to industrial soil	0	[kg.d-1]	O
<b>[FORMULATION]</b>			
Regional release to air	0	[kg.d-1]	O
Regional release to waste water	0	[kg.d-1]	O
Regional release to surface water	0	[kg.d-1]	O
Regional release to industrial soil	0	[kg.d-1]	O
<b>[PROCESSING]</b>			
Regional release to air	0	[kg.d-1]	O
Regional release to waste water	0	[kg.d-1]	OUSES

EUSES Full report

Single substance

Printed on  
Study  
Substance  
Defaults  
Assessment types  
Base set complete

Cd RAR 2003  
Cd  
Standard  
1A, 1B, 2, 3A, 3B  
No

21/02/2003 12:20

Name	Value	Units	Status
[PROCESSING] ( Continued )			
Regional release to surface water		0 [kg.d-1]	O
Regional release to industrial soil		0 [kg.d-1]	O
[PRIVATE USE]			
Regional release to air		0 [kg.d-1]	O
Regional release to waste water		0 [kg.d-1]	O
Regional release to surface water		0 [kg.d-1]	O
Regional release to industrial soil		0 [kg.d-1]	O
[RECOVERY]			
Regional release to air		0 [kg.d-1]	O
Regional release to waste water		0 [kg.d-1]	O
Regional release to surface water		0 [kg.d-1]	O
Regional release to industrial soil		0 [kg.d-1]	O
CONTINENTAL			
Total continental emission to air	113.1	[tonnes.yr-1]	S
Total continental emission to wastewater		0 [kg.d-1]	O
Total continental emission to surface water	35.2	[tonnes.yr-1]	S
Total continental emission to industrial soil		0 [tonnes.yr-1]	S
Total continental emission to agricultural soil	220.1	[tonnes.yr-1]	S
REGIONAL			
Total regional emission to air	12.6	[tonnes.yr-1]	S
Total regional emission to wastewater		0 [kg.d-1]	O
Total regional emission to surface water	3.9	[tonnes.yr-1]	S
Total regional emission to industrial soil		0 [tonnes.yr-1]	S
Total regional emission to agricultural soil	24.5	[tonnes.yr-1]	S
LOCAL			
[PRODUCTION]			
Local emission to air during episode		0 [kg.d-1]	O
Local emission to wastewater during episode		0 [kg.d-1]	O
Show this step in further calculations	No		O
Intermittent release	No		D
[FORMULATION]			
Local emission to air during episode		0 [kg.d-1]	O
Local emission to wastewater during episode		0 [kg.d-1]	O
Show this step in further calculations	No		O
Intermittent release	No		D
[PROCESSING]			
Local emission to air during episode		0 [kg.d-1]	O
Local emission to wastewater during episode		0 [kg.d-1]	O
Show this step in further calculations	No		OUSES

EUSES Full report

Single substance

Printed on  
Study  
Substance  
Defaults  
Assessment types  
Base set complete

21/02/2003 12:20

Cd RAR 2003  
Cd  
Standard  
1A, 1B, 2, 3A, 3B  
No

Name	Value	Units	Status
[PROCESSING] ( Continued )			
Intermittent release	No		D
[PRIVATE USE]			
Local emission to air during episode		0 [kg.d-1]	O
Local emission to wastewater during episode		0 [kg.d-1]	O
Show this step in further calculations	No		O
Intermittent release	No		D
[RECOVERY]			
Local emission to air during episode		0 [kg.d-1]	O
Local emission to wastewater during episode		0 [kg.d-1]	O
Show this step in further calculations	No		O
Intermittent release	No		DUSES

EUSES Full report

Single substance

Printed on

21/02/2003 12:20

Study

Cd RAR 2003

Substance

Cd

Defaults

Standard

Assessment types

1A, 1B, 2, 3A, 3B

Base set complete

No

Name	Value	Units	Status
<b>DISTRIBUTION</b>			
<b>PARTITION COEFFICIENTS</b>			
<b>SOLIDS WATER PARTITIONING</b>			
Organic carbon-water partition coefficient	0.195	[l.kg-1]	O
Solids-water partition coefficient in soil		280 [l.kg-1]	S
Solids-water partition coefficient in sediment	1.3E+05	[l.kg-1]	S
Solids-water partition coefficient suspended matter	1.3E+05	[l.kg-1]	S
Solids-water partition coefficient in raw sewage sludge	0.0585	[l.kg-1]	O
Solids-water partition coefficient in settled sewage sludge	0.0585	[l.kg-1]	O
Solids-water partition coefficient in activated sewage sludge	0.0722	[l.kg-1]	O
Solids-water partition coefficient in effluent sewage sludge	0.0722	[l.kg-1]	O
Suspended matter-water partition coefficient	3.25E+04	[m3.m-3]	O
Soil-water partition coefficient		420 [m3.m-3]	O
Sediment-water partition coefficient	6.5E+04	[m3.m-3]	O
<b>AIR-WATER PARTITIONING AND ADSORPTION TO AEROSOL PARTICLES</b>			
Sub-cooled liquid vapour pressure		1,00E-10 [Pa]	O
Fraction of chemical associated with aerosol particles		1 [-]	O
Henry's law constant		0 [Pa.m3.mol-1]	S
Air-water partitioning coefficient		0 [m3.m-3]	O
<b>BIOTA-WATER</b>			
Bioconcentration factor for aquatic biota	1.41	[l.kg-1]	O
<b>DEGRADATION AND TRANSFORMATION RATES</b>			
<b>CHARACTERIZATION AND STP</b>			
Characterization of biodegradability	Not biodegradable		D
Degradation calculation method in STP	First order, standard OECD/EU tests		D
Rate constant for biodegradation in STP		0 [d-1]	O
Total rate constant for degradation in STP		0 [d-1]	O
Maximum growth rate of specific microorganisms		2 [d-1]	D
Half saturation concentration	0.5	[g.m-3]	D
<b>ENVIRONMENTAL</b>			
Specific degradation rate constant with OH-radicals		0 [cm3.molec-1.s-1]	D
Rate constant for degradation in air		0 [d-1]	O
Rate constant for hydrolysis in surface water		0 [d-1]	S
Rate constant for photolysis in surface water		0 [d-1]	S
Rate constant for biodegradation in surface water		0 [d-1]	O
Total rate constant for degradation in bulk surface water		0 [d-1]	O
Rate constant for biodegradation in bulk soil		0 [d-1]	S
Total rate constant for degradation in bulk soil		0 [d-1]	O
Rate constant for biodegradation in aerated sediment		0 [d-1]	S
Total rate constant for degradation in bulk sediment		0 [d-1]	OUSES

EUSES Full report

Single substance

Printed on  
Study  
Substance  
Defaults  
Assessment types  
Base set complete

Cd RAR 2003  
Cd  
Standard  
1A, 1B, 2, 3A, 3B  
No

21/02/2003 12:20

Name	Value	Units	Status
<b>SEWAGE TREATMENT</b>			
<b>CONTINENTAL</b>			
Fraction of emission directed to air		0 [-]	O
Fraction of emission directed to water		0 [-]	O
Fraction of emission directed to sludge		0 [-]	O
Fraction of the emission degraded		0 [-]	O
Total of fractions		0 [-]	O
Indirect emission to air		0 [kg.d-1]	O
Indirect emission to surface water		0 [kg.d-1]	O
Indirect emission to agricultural soil		0 [kg.d-1]	O
<b>REGIONAL</b>			
Fraction of emission directed to air		0 [-]	O
Fraction of emission directed to water		0 [-]	O
Fraction of emission directed to sludge		0 [-]	O
Fraction of the emission degraded		0 [-]	O
Total of fractions		0 [-]	O
Indirect emission to air		0 [kg.d-1]	O
Indirect emission to surface water		0 [kg.d-1]	O
Indirect emission to agricultural soil		0 [kg.d-1]	O
<b>CONTINENTAL AND REGIONAL</b>			
<b>CONTINENTAL</b>			
Continental PEC in surface water (total)	0.0281	[ug.l-1]	O
Continental PEC in surface water (dissolved)	9.53E-03	[ug.l-1]	O
Continental PEC in air (total)	1.52E-04	[ug.m-3]	O
Continental PEC in agricultural soil (total)	0.176	[mg.kgwwt-1]	O
Continental PEC in pore water of agricultural soils	7.1E-04	[mg.l-1]	O
Continental PEC in natural soil (total)	0.0177	[mg.kgwwt-1]	O
Continental PEC in industrial soil (total)	0.0177	[mg.kgwwt-1]	O
Continental PEC in sediment (total)	0.477	[mg.kgwwt-1]	O
<b>REGIONAL</b>			
Regional PEC in surface water (total)	1.84E-04	[mg.l-1]	O
Regional PEC in surface water (dissolved)	0.0622	[ug.l-1]	O
Regional PEC in air (total)	5.61E-04	[ug.m-3]	O
Regional PEC in agricultural soil (total)	1.61	[mg.kgwwt-1]	O
Regional PEC in pore water of agricultural soils	6.52E-03	[mg.l-1]	O
Regional PEC in natural soil (total)	0.0656	[mg.kgwwt-1]	O
Regional PEC in industrial soil (total)	0.0656	[mg.kgwwt-1]	O
Regional PEC in sediment (total)	3.11	[mg.kgwwt-1]	OSSES

EUSES Full report

Single substance

Printed on

21/02/2003 12:20

Study

Cd RAR 2003

Substance

Cd

Defaults

Standard

Assessment types

1A, 1B, 2, 3A, 3B

Base set complete

No

Name	Value	Units	Status
<b>EXPOSURE</b>			
<b>BIOCONCENTRATION FACTORS</b>			
Partition coefficient worm-porewater	0.4	[l.kg-1]	O
Bioconcentration factor for earthworms	1.62E-03	[kg.kg-1]	O
Bioconcentration factor for fish	1.41	[l.kg-1]	O
Partition coefficient between plant tissue and water	0.651	[m3.m-3]	O
Partition coefficient between leaves and air	??	[m3.m-3]	O
Transpiration-stream concentration factor	0.033	[-]	O
Bioaccumulation factor for meat	7.94E-07	[d.kg-1]	O
Bioaccumulation factor for milk	7.94E-06	[d.kg-1]	O
Purification factor for surface water		1 [-]	O
<b>HUMANS EXPOSED TO OR VIA THE ENVIRONMENT</b>			
<b>REGIONAL</b>			
<b>CONCENTRATIONS IN FISH, PLANTS AND DRINKING WATER</b>			
Regional concentration in wet fish	8.79E-05	[mg.kg-1]	O
Regional concentration in root tissue of plant	6.07E-03	[mg.kg-1]	O
Regional concentration in leaves of plant	??	[mg.kg-1]	O
Regional concentration in grass (wet weight)	??	[mg.kg-1]	O
Fraction of total uptake by crops from pore water		1 [-]	O
Fraction of total uptake by crops from air	1.13E-06	[-]	O
Fraction of total uptake by grass from pore water		1 [-]	O
Fraction of total uptake by grass from air	1.13E-06	[-]	O
Regional concentration in drinking water	6.52E-03	[mg.l-1]	O
<b>CONCENTRATIONS IN MEAT AND MILK</b>			
Regional concentration in meat (wet weight)	??	[mg.kg-1]	O
Regional concentration in milk (wet weight)	??	[mg.kg-1]	O
Fraction of total intake by cattle through grass	??	[-]	O
Fraction of total intake by cattle through drinking water	??	[-]	O
Fraction of total intake by cattle through air	??	[-]	O
Fraction of total intake by cattle through soil	??	[-]	O
<b>DAILY HUMAN DOSES</b>			
Daily dose through intake of drinking water	1.86E-04	[mg.kg-1.d-1]	O
Fraction of total dose through intake of drinking water	??	[-]	O
Daily dose through intake of fish	1.44E-07	[mg.kg-1.d-1]	O
Fraction of total dose through intake of fish	??	[-]	O
Daily dose through intake of leaf crops	??	[mg.kg-1.d-1]	O
Fraction of total dose through intake of leaf crops	??	[-]	O
Daily dose through intake of root crops	3.33E-05	[mg.kg-1.d-1]	O
Fraction of total dose through intake of root crops	??	[-]	O
Daily dose through intake of meat	??	[mg.kg-1.d-1]	O
Fraction of total dose through intake of meat	??	[-]	O
Daily dose through intake of milk	??	[mg.kg-1.d-1]	O
Fraction of total dose through intake of milk	??	[-]	O
Daily dose through intake of air	1.2E-07	[mg.kg-1.d-1]	OUSES

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Study  
Substance  
Defaults  
Assessment types  
Base set complete

21/02/2003 12:20

Cd RAR 2003  
Cd  
Standard  
1A, 1B, 2, 3A, 3B  
No

Name

Value

Units

Status

DAILY HUMAN DOSES ( Continued )  
Fraction of total dose through intake of air  
Regional total daily intake for humans

??  
??

[-]  
[mg.kg-1.d-1]

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O1/02/2003

EUSES Full report

Single substance

Printed on  
Study  
Substance  
Defaults  
Assessment types  
Base set complete

21/02/2003 12:20

Cd RAR 2003  
Cd  
Standard  
1A, 1B, 2, 3A, 3B  
No

Name	Value	Units	Status
<b>EFFECTS</b>			
<b>INPUT OF EFFECTS DATA</b>			
<b>MICRO-ORGANISMS</b>			
EC50 for micro-organisms in a STP	??	[mg.l-1]	D
Specific bacterial population?	No		D
EC10 for micro-organisms in a STP	??	[mg.l-1]	D
Specific bacterial population?	No		D
NOEC for micro-organisms in a STP	??	[mg.l-1]	D
Specific bacterial population?	No		D
<b>AQUATIC ORGANISMS</b>			
LC50 for fish	??	[mg.l-1]	D
L(E)C50 for Daphnia	??	[mg.l-1]	D
EC50 for algae	??	[mg.l-1]	D
LC50 for other aquatic species	??	[mg.l-1]	D
Species	other		D
NOEC for fish	??	[mg.l-1]	D
NOEC for Daphnia	??	[mg.l-1]	D
NOEC for algae	??	[mg.l-1]	D
NOEC for other aquatic species	??	[mg.l-1]	D
Additional aquatic NOEC	??	[mg.l-1]	D
Additional aquatic NOEC	??	[mg.l-1]	D
Additional aquatic NOEC	??	[mg.l-1]	D
Additional aquatic NOEC	??	[mg.l-1]	D
Additional aquatic NOEC	??	[mg.l-1]	D
Additional aquatic NOEC	??	[mg.l-1]	D
<b>TERRESTRIAL ORGANISMS</b>			
LC50 for plants	??	[mg.kgwwt-1]	D
LC50 for earthworms	??	[mg.kgwwt-1]	D
EC50 for microorganisms	??	[mg.kgwwt-1]	D
LC50 for other terrestrial species	??	[mg.kgwwt-1]	D
Species	other		D
NOEC for plants	??	[mg.kgwwt-1]	D
NOEC for earthworms	??	[mg.kgwwt-1]	D
NOEC for microorganisms	??	[mg.kgwwt-1]	D
NOEC for other terrestrial species	??	[mg.kgwwt-1]	D
NOEC for other terrestrial species	??	[mg.kgwwt-1]	D
Additional terrestrial NOEC	??	[mg.kgwwt-1]	D
Additional terrestrial NOEC	??	[mg.kgwwt-1]	D
Additional terrestrial NOEC	??	[mg.kgwwt-1]	D
Additional terrestrial NOEC	??	[mg.kgwwt-1]	D
Additional terrestrial NOEC	??	[mg.kgwwt-1]	D
Additional terrestrial NOEC	??	[mg.kgwwt-1]	D
<b>BIRDS</b>			
LC50 in avian dietary study (5 days)	??	[mg.kg-1]	DES

EUSES Full report

Single substance

21/02/2003 12:20

Printed on

Study

Cd RAR 2003

Substance

Cd

Defaults

Standard

Assessment types

1A, 1B, 2, 3A, 3B

Base set complete

No

Name	Value	Units	Status
<b>BIRDS ( Continued )</b>			
NOAEL	??	[mg.kg-1.d-1]	D
NOEC via food	??	[mg.kg-1]	O
Duration of (sub-)chronic oral test	Chronic		D
Conversion factor NOAEL to NOEC		8 [kg.d.kg-1]	D
<b>MAMMALS</b>			
<b>ACUTE</b>			
Oral LD50	??	[mg.kg-1]	D
Oral Discriminatory Dose	??	[mg.kg-1]	D
Dermal LD50	??	[mg.kg-1]	O
Inhalatory LC50	??	[mg.m-3]	O
<b>(SUB)CHRONIC</b>			
Oral NOAEL	??	[mg.kg-1.d-1]	O
Oral LOAEL	??	[mg.kg-1.d-1]	O
Inhalatory NOAEL	??	[mg.m-3]	O
Inhalatory LOAEL	??	[mg.m-3]	O
Dermal NOAEL	??	[mg.kg-1.d-1]	O
Dermal LOAEL	??	[mg.kg-1.d-1]	O
NOEC via food	??	[mg.kg-1]	O
LOEC via food	??	[mg.kg-1]	D
Duration of (sub-)chronic oral test	28 days		D
Species for conversion of NOAEL to NOEC	Rattus norvegicus (<6 weeks)		D
Conversion factor NOAEL to NOEC		10 [kg.d.kg-1]	O
<b>HUMANS</b>			
<b>(SUB)CHRONIC</b>			
Oral NOAEL	??	[mg.kg-1.d-1]	D
Oral LOAEL	??	[mg.kg-1.d-1]	D
Dermal NOEC in a medium	??	[mg.cm-3]	D
Dermal LOEC in a medium	??	[mg.cm-3]	D
Inhalatory (fibre) NOAEL	??	[fibres.m-3]	D
Inhalatory (fibre) LOAEL	??	[fibres.m-3]	D
Dermal LOAEL	??	[mg.kg-1.d-1]	O
Dermal NOAEL	??	[mg.kg-1.d-1]	O
Inhalatory LOAEL	??	[mg.m-3]	O
Inhalatory NOAEL	??	[mg.m-3]	O
<b>CURRENT CLASSIFICATION</b>			
Corrosive (C, R34 or R35)	No		D
Irritating to skin (Xi, R38)	No		D
Irritating to eyes (Xi, R36)	No		D
Risk of serious damage to eyes (Xi, R41)	No		D
Irritating to respiratory system (Xi, R37)	No		D
May cause sensitisation by inhalation (Xn, R42)	No		DES

EUSES Full report

Single substance

Printed on

21/02/2003 12:20

Study

Cd RAR 2003

Substance

Cd

Defaults

Standard

Assessment types

1A, 1B, 2, 3A, 3B

Base set complete

No

Name

Value

Units

Status

CURRENT CLASSIFICATION ( Continued )

May cause sensitisation by skin contact (Xi, R43)

No

D

May cause cancer (T, R45)

No

D

May cause cancer by inhalation (T, R49)

No

D

Possible risk of irreversible effects (Xn, R40)

No

D

ENVIRONMENTAL EFFECTS ASSESSMENT

INTERMEDIATE RESULTS AQUATIC ORGANISMS, MICRO-ORGANISMS AND PREDATORS

Toxicological data used for extrapolation to PNEC Aqua

??

[mg.l-1]

O

Assessment factor applied in extrapolation to PNEC Aqua

??

[-]

O

Toxicological data used for extrapolation to PNEC Aqua

??

[mg.l-1]

O

Assessment factor applied in extrapolation to PNEC Aqua

??

[-]

O

Toxicological data used for extrapolation to PNEC micro

??

[mg.l-1]

O

Assessment factor applied in extrapolation to PNEC micro

??

[-]

O

Toxicological data used for extrapolation to PNEC oral

??

[mg.kg-1]

O

Assessment factor applied in extrapolation to PNEC oral

??

[-]

O

INTERMEDIATE RESULTS TERRESTRIAL AND SEDIMENT ORGANISMS

Toxicological data used for extrapolation to PNEC Terr

??

[mg.kgwwt-1]

O

Assessment factor applied in extrapolation to PNEC Terr

??

[-]

O

Equilibrium partitioning used for PNEC in soil?

Yes

O

Equilibrium partitioning used for PNEC in sediment?

Yes

O

PNECS FOR AQUATIC ORGANISMS, MICRO-ORGANISMS AND PREDATORS

PNEC for aquatic organisms

??

[mg.l-1]

O

PNEC for aquatic organisms, intermittent releases

??

[mg.l-1]

O

PNEC for micro-organisms in a STP

??

[mg.l-1]

O

PNEC for secondary poisoning of birds and mammals

??

[mg.kg-1]

O

PNEC for aquatic organisms with statistical method

??

[mg.l-1]

O

PNECS FOR TERRESTRIAL AND SEDIMENT ORGANISMS

PNEC for terrestrial organisms

??

[mg.kgwwt-1]

O

PNEC for terrestrial organisms with statistical method

??

[mg.kgwwt-1]

O

PNEC for sediment-dwelling organisms

??

[mg.kgwwt-1]

OES

EUSES Full report

Single substance

Printed on  
Study  
Substance  
Defaults  
Assessment types  
Base set complete

21/02/2003 12:20

Cd RAR 2003  
Cd  
Standard  
1A, 1B, 2, 3A, 3B  
No

Name	Value	Units	Status
RISK CHARACTERIZATION			
ENVIRONMENTAL EXPOSURE			
REGIONAL			
ENVIRONMENT			
RCR for the regional water compartment	??	[-]	O
RCR for the regional soil compartment	??	[-]	O
Extra factor 10 applied to PEC	No		O
RCR for the regional sediment compartment	??	[-]	O
Extra factor 10 applied to PEC	No		O
HUMANS			
MOS regional, total exposure via all media	??	[-]	O
MOS regional, exposure via air	??	[-]	OS

## Annex J Temporal trends in measured Cd concentrations in the environment

**Table A** Temporal trends in measured local Cd concentrations in the effluent receiving water and ambient air for Cd-producing and – processing plants in the EU-16

Use category	Plant n°	Annual average Cd concentrations in water ( $\mu\text{g L}^{-1}$ )			Annual average Cd concentrations in ambient air ( $\text{ng m}^{-3}$ )					
		1994	1995	1996	1993	1994	1995	1996	1997	1998
Cd-producers	1	1.9	0.9	1.0						
	2					75	84	78		
	4				4.85	3.95				
	5				30	30	30	30		
	6					1	1	1		
	8					8.4		10.7		
	10					<40	<40	<40		
CdOproducers	12				7.6	5.4				

**Table B** Temporal trends in regional measured cadmium concentrations in Dutch freshwaters (total concentrations; 90 percentile; source: Milieucompendium, 2001)

	Total Cd concentrations ( $\mu\text{g L}^{-1}$ )					
	1985	1990	1995	1998	1999	2000
The Netherlands: Rhine	0.42	0.18	0.24	0.15	0.13	0.09
The Netherlands: Schelde	2.80	0.76	0.71	7.95*	1.25	0.50
The Netherlands: IJsselmeer	0.16	0.17	0.08	0.12	0.09	0.10
The Netherlands: Rijkswateren	0.47	0.36	0.30	0.86	0.29	0.17
The Netherlands: Regionale wateren	0.56	0.57	0.37	0.31	0.69	-

\* This value is misquoted in Milieucompendium 2001 and should read 0.79 (Vlaamse Milieu Maatschappij personal communication)

**Table C** Temporal trends in regional measured Cd concentrations in suspended matter of Dutch freshwaters source: Milieucompendium, 2001)

	Cd concentrations in suspended matter ( $\text{mg kg}^{-1} \text{ dw}$ )					
	1988	1990	1995	1998	1999	2000
The Netherlands: Rhine	9.2	5.3	3.8	3.5	3.0	7.5
The Netherlands: Maas	649	57	37	12.3	11.9	19.1
The Netherlands: Schelde	20.4	12.2	9.7	7.4	7.8	8.1
The Netherlands: IJsselmeer	2.2	3.2	2.4	1.2	1.5	1.9
The Netherlands: Rijkswateren	117	12.2	11.3	5.6	5.5	8.5

**Table D** Temporal trends in regional measured Cd concentrations in air (source: Milieucompendium, 2001)

	Cd concentrations in air (ng m <sup>-3</sup> )					
	1990	1992	1994	1996	1998	2000
The Netherlands	0.5	0.6	0.5	0.4	0.3	0.2

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**EU 22919 EN          European Union Risk Assessment Report**

**Cadmium oxide and cadmium metal, Part I – Environment,  
Volume 72**

*Editors: S.J. Munn, K. Aschberger, O. Cosgrove, W. de Coen, S. Pakalin, A. Paya-Perez,  
B. Schwarz-Schulz, S. Vegro.*

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The report provides the comprehensive risk assessment of the substance cadmium metal and cadmium oxide. It has been prepared by Belgium in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to humans and the environment, laid down in Commission Regulation (EC) No. 1488/94.

#### Part I - Environment

This part of the evaluation considers the emissions and the resulting exposure to the environment in the production of cadmium metal and cadmium oxide, the use of these substances in the production of stabilisers, pigments, alloys and plated products. Further downstream uses are not or only limitedly included. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic and terrestrial compartment has been determined. No risk assessment was performed for the atmosphere or the marine environment.

The environmental risk assessment concludes that there is concern for the aquatic ecosystem at certain metal production, processing and NiCd batteries recycling sites. For the terrestrial compartment a risk is identified at cadmium plating and alloy production sites. A borderline risk is found for soil cadmium concentrations leading to secondary poisoning. Furthermore, there is concern for micro-organisms of the wastewater treatment plants of certain NiCd battery recycling plants. In addition, a need for better information regarding the toxic effects of cadmium to aquatic organisms under low water hardness conditions is identified. Furthermore, for sediments there is a need for further information regarding the bioavailability of cadmium in order to possibly refine the assessment.

#### Part II - Human Health

This part of the evaluation is published in a separate document.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commission's committee on risk reduction strategies set up in support of Council Regulation (EEC) N. 793/93.

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European Union Risk Assessment Report

**cadmium oxide and cadmium metal**

**Part I - environment**

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