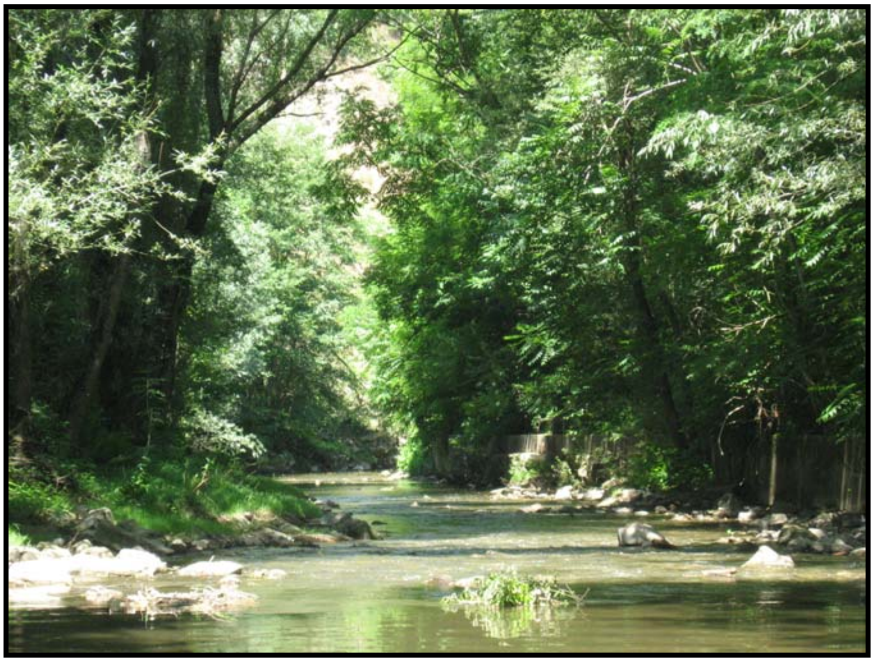
JRC Scientific and Technical Reports

Pollution disaster monitoring and ecological impact prediction

Implications of results of the ECODIS project for aquatic ecosystem disaster management

U. Hansen and D. Sarigiannis (eds.)



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Cover Page
Riou Mort river in France (foto: D. de Beer, MPIMM Bremen, Germany).

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Preface

The document presented here has been prepared within the EU-FP6 funded ECODIS project on "Dynamic Sensing of Chemical Pollution Disasters and Predictive Modelling of their Spread and Ecological Impact". It reflects a substantial part of the project work, i.e. the part focusing on, first, the identification of ECODIS findings with relevance to the management of chemical disasters, and, second, the preparation of an user friendly document summarizing the respective recommendations derived from the work performed within the ECODIS project. The report is mainly based on presentations given during the final meeting of the consortium which was hosted by the JRC and took place on the 27th and 28th of November 2008 in Ispra. References to recent scientific publications are given.

Part A of the document dealing with pollution disaster monitoring and ecological impact prediction is complemented by Annex I giving examples for the application of new sensor techniques and specific ECODIS results with relevance to the prediction of adverse effects of water contamination. Part B summarizes related EU legislation, gives details on monitoring approaches under the Water Framework Directive and provides information on other research projects dealing with chemical pollution and ecosystem impairment. The Major Accident Reporting System of the European Union is described in Part C analysing major water polluting accidents reported to the MARS database.

<u>Part A: Pollution disaster monitoring and ecological impact prediction</u>

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Part C: Major accidents registered in the EC MARS database: A review of water polluting accidents (1986 to 2005)

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ANNEX to Part A: Supporting information: Cadmium related ECODIS results and thresholds set for the protection of the environment and human health

Part B: Related EU legislation, other research activities and River Basin Management

Part C: Major accidents registered in the EC MARS database: A review of water polluting accidents (1986 to 2005)

Executive Summary

Disasters leading to a release of pollutant(s) into rivers, streams or lakes can have severe short and/or long term effects on the chemical status of aquatic ecosystems. The aim of the study presented here is to give recommendations for disaster management based on new methods, recent progress in research and advanced sensor techniques developed within the EU-FP6 funded ECODIS project on "Dynamic Sensing of Chemical Pollution Disasters and Predictive Modelling of their Spread and Ecological Impact".

Part A of this document deals with four important components of disaster management, i.e. the characterization of the release, the collection of available information on the substance specific risk to aquatic ecosystems, the prediction of the pollutant concentration in water and biota and the assessment procedure allowing to decide whether predicted levels of hazardous substances should be regarded as a risk. Information on methods and databases is provided with emphasis on new sensor techniques and their relevance for disaster management. In this context their potential suitability as continuously working alarm systems for the direct detection of the release of contaminants into the water is tackled as well as their application in long term monitoring of the status of ecosystems impaired by disasters. The outcomes of the ECODIS project summarized here are highly relevant to decisions on immediate actions, long-term remediation activities and other measures to minimize the risk attributable to recent or past accidental releases of toxic substances into aquatic ecosystems.

Attempts to assess the adverse effects of a contamination of aquatic ecosystems with hazardous chemicals are generally confronted with three major problems. The first problem is that for many compounds it is unclear which proportion of the total amount of a contaminant present in the water can be assumed to be relevant for toxic effects, as organic pollutants and metals occur in several forms usually differing in bioavailability. Extensive research work has been done on this topic within the ECODIS project. Results on metal speciation and new techniques suitable to assess the bioavailability of organic pollutants are summarized in the report presented here. The second problem is due to exchange processes between the water column and the sediment. Even if predictions and/or monitoring activities reveal no indication for pollutants concentrations above the level of no concern, the conclusion that there is no risk can not be drawn if there is a potentially hazardous pool of toxic substances in the catchment or sediment which might be mobilized due to changed flow characteristics. This document gives a short overview of relevant ECODIS results on water column-sediment exchange processes.

The third problem arises from the fact that chemical disasters are highly dynamic. A considerable part of the research work done within the ECODIS project aimed at increasing the extent to which dynamics are considered in risk assessment procedures for disaster management. Speciation dynamics in terms of stability or lability of the binding of contaminants to soluble or particulate compounds in the water, especially to complexing colloids, has been extensively investigated and respective sensor techniques have been developed. Further emphasis was laid on models used to calculate the time course of pollutant concentrations in biota from fluctuating external concentrations and to predict toxic effects on model populations. Promising results have been achieved with passive sampling techiques as they can mimic uptake characteristics of organisms.

Dynamics of sink source characteristics of ecosystems are of outstanding relevance for disaster management. To be able to manage the sink source function of ecosystems, for example through avoidance of secondary disasters attributable to the remobilisation of contaminants previously buried in the sediment, would be an important achievement in disaster management. The ECODIS findings on pollution disaster monitoring and ecological impact prediction summarized in the report presented here contribute to a better understanding of the processes responsible for changes in the source or sink function of aquatic ecosystems. To further increase the knowledge about these processes and to improve tools for the integrated management of the water/sediment/soil/groundwater system accounting for all important terrestrial and aquatic pools and fluxes of toxics influencing water quality shall be an important task of future research activities. Some integrative approaches for the understanding and managing of multi-component systems have been developed at the river basin scale, as described in Part B of this report informing about other research projects dealing with the impairment of aquatic ecosystems by chemical disasters and the River Basin Mangement Concept. Part B of this report further provides information on related EU legislation, especiallly the Water Framework Directive, and several aspects of monitoring of the chemical status of ecosystems. Part C reports the outcome of a study performed with the aim to derive general characteristics of chemical disasters leading to water pollution by analysing accidents reported to the database of the Major Accidents Reporting System at the Joint Research centre of the European Commission.

Part A: Pollution disaster monitoring and ecological impact prediction

The scope of this guidance is not to provide a comprehensive and detailed guidance on all actions to be taken in case of an accident. Disaster management, emergency plans and respective guidance documents are under the responsibility of local, regional and national authorities[1], as they consider specific ecosystem characteristics and specific threats.

The guidance presented here (Figure 1) summarises both generic information sources and specific implications of the work carried out within the ECODIS project for the important components of chemical disaster management. The first component, the characterisation of the release, is described in section 1 dealing with the information to be collected, e.g. on the substances involved and their amount, and new sensor techniques which might be used continuously for the detection of metals giving an alarm in case of an accident. The second step of disaster management, the collection of information on the potential compound specific hazard for aquatic ecosystems, is described in section 2 of this guidance. The third part of the guidance deals with the next component of disaster management, the prediction of the pollutant concentration in water and biota. Comparing the predicted concentration (section 3) to the substance specific concentration levels of no concern (section 2) allows assessing the potential risk attributable to the accident. Procedures of dynamic risk assessment are described in section 4. Measures to minimise risk are mentioned in section 5 of the guidance.

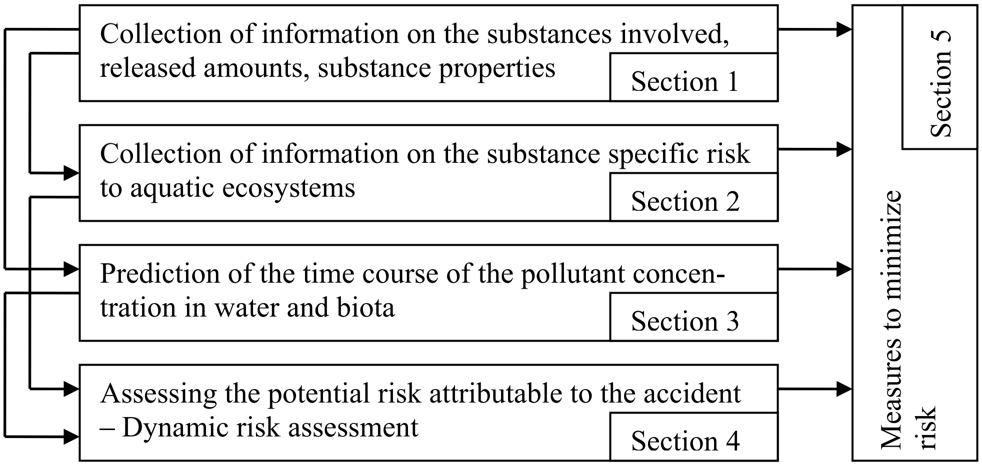

Figure 1 Components of disaster management following the accidental release of pollutant(s) to freshwater ecosystems and structure of the guidance document (arrows indicate a flow of information).

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[1] There is no legislation at the level of the European Union dealing with the management of chemical disasters. The REACH legislation considers water contamination caused by the production and normal use of chemicals. The SEVESO directives deal with the avoidance of accidents. The Water Framework Directive defines a good chemical status of aquatic ecosystems but does not take into account reasons for potential deviations from the good status (for details on related legislation see Part B). The reason might be that EU legislation on disaster management could be in conflict with the "subsidiarity principle" which means that the Union may take action (except on matters for which it alone is responsible) only if EU action is more effective than action taken at national, regional or local level.

1 Characterization of the release

To collect information on the disaster is the first important management step. This step includes the identification of the released substances (section 1.1) and gathering information on physico-chemical properties (section 1.2) of these compounds. Section 1.3 deals with the use of new techniques suitable for the continuous detection of pollutants in water giving an alarm in case of sudden increases in concentration.

1.1 Collection of information on the release

Disasters can lead to the contamination of a multitude of environmental compartments such as soils, ground water, freshwater, sediment and air. The pollution can be due to the accidental emission of the hazardous substances into the respective compartment or to indirect diffuse input, for example due to long term input of contaminants via aerosol deposition. The guidance presented here will focus on the management of disasters leading to the direct discharge of chemicals to freshwater ecosystems such as rivers and streams, i.e. a discharge of a limited duration attributable to a point source leading to the contamination of the whole water body due to diffusion. In case of such accidental releases of substances the first important step of disaster management is to collect all available information on the location of the release, the time and duration, the substance(s) identity, registry numbers, chemical names and synonyms, the pollutants mass flow, the water flow at the release point and other characteristics of the ecosystem.

1.2 Collection of substance specific data on physico-chemical properties

For the substances released into the freshwater ecosystem the available information on relevant physico-chemical properties and data on the environmental fate should be collected, as they allow assessing which compartments of the system might be affected. Substances with low solubility in water and high density can be assumed to contaminate primarily the sediment, those with low density remain at the water surface and for compounds with high vapour pressure the temperature dependent volatilisation should be taken into account. Water soluble compounds can contaminate the whole water body due to diffusion. To which extent soluble pollutants can be expected to be present in the water depends on fate processes leading, for example, to immobilisation, adsorption, remobilisation and degradation (Chapter 3). Whether a substance would be adsorbed to organic matter in water and sediment and thus might accumulate in organisms can be assessed from the octanol/water partition coefficient.

Table 1 shows a selection of relevant physico-chemical properties of substances. For a list of sources of information about physico-chemical property data for a wide range of substances see Table R 7.1-2, Part R 7A (ECHA 2008).

The collected substance specific data on physico-chemical properties[2] are the basis for decisions to be drawn by the disaster management team immediately after the accident concerning, for example, the interruption of the drinking water supply, or, whether barriers should be used to prevent the spread of compounds polluting the water surface, or, specific techniques available to be applied in case of oil spills.

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[2] The physico-chemical properties of Cadmium and Cadmium oxide are given in Table 1 of the Annex to Part A.

Table 1 Selected physico-chemical properties of substances and their significance for risk assessment. Definitions, methods for derivation, examples and further details are given in chapters R.7.1.2 to R.7.1.18 of the REACH guidance document (ECHA 2008).

Physico-chemical property	**Significance for Risk Assessment**
Melting/freezing point	Indicates the state of the substance at ambient temperature and air pressure.
Boiling point, flammability	Allows to assess the risk due to flammability.
Self-ignition temperature	Allows assessing situations in which a substance can spontaneously catch fire.
Relative density	To decide whether a substance my float in water or sinks to the ground and whether water for fire fighting is suitable.
Vapour pressure	Key parameter in determining the fate of the substance in the environment, necessary for the calculation of the predicted environmental concentration (PEC) and for the risk for human health due to inhalation.
Water solubility	Key parameter for assessing the fate of the substance in the environment and for calculating of PEC.
Surface tension	Key parameter in determining the fate of the substance in the environment, modulate the solubility in water and toxic effects on organisms.
Partition coefficient in octanol/water	Substances with high log K_{ow} are hydrophobic and have low water solubilities, substances with negative log K_{ow} values are hydrophilic and show a high solubility in water. Compounds with high log K_{ow} values are assumed to have a high bio-accumulation potential.
Dissociation constant pK_a	This parameter is important for ionisable organic substances and indicates which chemical species will be present at a particular pH.
Granulometry	Information on the particle size spectrum allows assessing the risk for human health due to inhalable, thoracic and respirable fractions of particles in the air.
Explosive Properties	Allows to assess the risk due to explosivity
Viscosity	Influences the velocity of the spread of a substance in water.
Oxidising properties	Some substances can supply oxygen to combustion processes and describing these substance properties allows to assess the risk due to this process.

1.3 Monitoring and sensor techniques providing data on the release

1.3.1 New sensor techniques and alarm systems

Sensors detecting the concentration of hazardous substances in the water continuously with a suitable time resolution are important since they can be applied as a monitoring system sending warning/alarm signals when the concentration of the respective pollutant in the water increases. For the reliable working of such systems, the following features are required: The sensor signal should be specific for the substance or substance class, the sensor signal should be reliable over a wide concentration range, the analysis time should be appropriate for the resolution of peak releases of chemicals (in the hours time range), the system should work over several days without the necessity of maintenance activities, and the system should be configured for remote transfer of data to a central database displaying the real time the changes in the chemical status of the ecosystem and thus permit the fast implementation of remedial actions.

According to a review article published by Tercier-Waeber and Taillefert (2008), submersible voltammetric metal sensors meet the requirements listed above. They can complement continuous measurements of physical and chemical parameters, such as flow rate, pH, temperature and oxygen saturation and could be configured as a net of sensors detecting the variability in concentration with both space and time. A network of sensors set up in a way that sensors are applied upstream and downstream of potential polluters would allow the localization of the release and the identification of certain pollution events.

Table 2 gives an overview of voltammetric devices which have been used for simultaneous *in-situ* monitoring of trace metal species in aquatic systems. The comparison of the performance of several metal sensor systems in the field is one of the major achievements of the ECODIS project (see ECODIS deliverable D29 “Protocol and tools for monitoring of chemical, biological and physical parameters on the site of a pollution”). *In-situ* measurements were carried out in rivers of the Lot-Garonne fluvial system in France under conditions of high and low water flow rate, different water chemistries and metal loads. The rivers have been characterised with respect to metal pollution due to mining and industrial activities in previous studies (Blanc et al. 1999, Grousset et al., 1999 and Coynel et al. 2007).

Table 2 Voltammetric devices which have been used for simultaneous *in-situ* monitoring of trace metal species in freshwater, estuarine and marine ecosystems, metal species they detect, typical total analysis times and lower detection limits (taken from the review article published by Tercier-Waeber and Taillefert, 2008).

Sensor/probe	**Metal species measured**	**Typical total analysis time**	**Lower detection limit[c] [µg l^{-1}]**
GIME (VIP[a] or MPCP[b]**)** Gel Integrated Micro-Electrode	Cu, Pb, Cd and Zn free ions and dynamic complexes with a size of a few nm	10 to 40 min	Cu: 0.013 Pb: 0.006 Cd: 0.006 Zn: 0.020
CGIME (MPCP[b]) Complexing Gel Integrated Micro-Electrode	Cu, Pb and Cd free ions	70 – 130 min	Cu: 0.0013 Pb: 0.002 Cd: 0.007
FIA-GIME (MPCP[b]) Flow Injection Analysis[d] Gel Integrated Micro-Electrode	Cu, Pb and Cd total extractable concentration	20 to 30 min	Cu: 0.051 Pb: 0.031 Cd: 0.023

[a] The VIP (Voltammetric *in-situ* profiling system) is a submersible probe (Tercier et al. 1998) based on a GIME sensor developed for measuring depth profiles and surface concentrations of the dynamic metal species (i.e. the fraction of metal potentially bioavailable).

[b] The MPCP is a multi physical chemical profiler (Tercier –Waeber et al. 2005) based on: i) three independent voltammetric measuring channels equipped with one CGIME and two GIME sensors and, ii), an integrated multiparameter probe for *in-situ* surface end depth profiles of trace metal speciation coupled to master variables (pressure, temperature, pH, oxygen content, conductivity, salinity, redox potential, turbidity and chlorophyll fluorescence) respectively. Concentrations close to the detection limit may require higher total analysis times.

[c] Concentrations close to the detection limit may require higher total analysis times.

[d] Extraction of metals with an automatic sample pre-treatment consisting of a complexation step, acidification and heating of the solution.

The ECODIS field measurements revealed a high similarity of the day to day variation pattern between Cd and Cu concentrations measured using the FIA-GIME (Flow Injection Analysis Gel Integrated Micro-Electrode) and concentration data determined using ICP-MS with water samples analysed in the lab. The total metal concentration extractable with the automatic extraction system of the FIA-GIME was in most cases similar to or slightly lower than the amount of Cd and Cu extracted with wet chemical analysis using ICP-MS. The voltammetric sensor appears to be suitable for use for the detection of the concentration time courses displaying the appropriate time resolution irrespective of slight deviations in the fractions of the total metal detected (Figure 2).

It should be noted that accidental releases of contaminants into the water are not necessarily linked to increased concentrations in the water. A high pollutant mass flow can be masked when the water flow rate is correspondingly increased as well. Continuous concentration monitoring should therefore be complemented by flow rate detection so that accidental releases of pollutants can be identified even at a constant concentration of the hazardous compound.

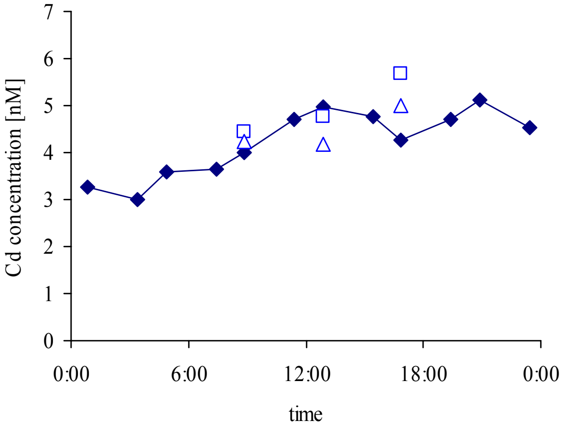

Figure 2 Variation of the Cadmium concentration detected *in-situ* using the FIA-GIME system (see Table 2) in the Lot river, France, at the measuring station Bouillac on the 29th April 2007 (closed symbols). Open symbols: Cd concentration determined using ICP-MS with samples transported to the lab, squares: total Cd, triangles: total dissolved Cd fraction.

1.3.2 Rules assuring the quality of monitoring data

Monitoring of pollutant concentrations requires sufficiently reliable methods of sampling, analysis, traceability and data treatment. Several guidance documents giving details on monitoring of the chemical status of aquatic ecosystems are available as listed in section 3.3.1. The accepted generic rules regarding the quality of WFD monitoring data should be applied when measured data are used to characterize the accidental pollution of freshwater ecosystems. But, it should be noted that monitoring within the WFD aims at the description of the ecosystems status by averaging over a prolonged period. The use of monitoring techniques for the characterisation of accidental pollutant releases requires, in contrast, adjusted monitoring strategies, e.g. measurements with a higher time resolution, the application of sensors providing reliable data over a wide range of concentrations and being specific for certain pollutants.

Guidance on the use of measured data for release estimation is given in chapter R16.3.2 of part R16 of the REACH implementation document (ECHA 2008). Since the described procedures refer to continuous

releases of chemicals due to identified uses of the substances and not to accidental spills they are not directly applicable for the characterisation of the accidental pollution of freshwater ecosystems.
One of the ECODIS findings with high relevance for continuous or high-time-resolution monitoring being the basis for the immediate detection of sudden releases of chemicals due to disasters is the diurnal variation in the total dissolved (Beck et al. 2009) and dynamic (Tercier-Waeber et al. 2009) metal concentration in water. Metal cycling can be assumed to play a role in all freshwater ecosystems subjected to diurnal variations in pH. A short description of the experimental evidence is given in Annex I, section 3.3 and details are available in the ECODIS deliverable D26 "Influence of microbial processes on pollutant exchange".

The total dissolved Cd concentration detected during the night made up the 1.3-fold of the afternoon concentration (Annex I, Figure 3). Thus, taking a single water sample during the day and analysing the total dissolved Cd concentration after filtration in the lab may not be sufficient to characterise the toxicologically relevant Cd level, at least if ecosystem characteristics allow fast pH changes. Such pH changes occur when the light absorption of the water column is low and photosynthetically active biofilms and/or submersed macrophytes are present with a biomass high enough to influence water chemistry[3]. These conditions were met when the respective measurements were carried out at the Riou Mort in France in June 2008.

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[3] Photosynthesis consumes the carbon dioxide of dissociated H_2CO_3. Because in the water H_2CO_3 and insoluble $CaCO_3$ on one side are in equlibrium with soluble $Ca(HCO_3)_2$ on the other side, the consumption of CO_2 due to photosynthesis leads to a shift of the equlibrium towards H_2CO_3 and $CaCO_3$. This is related to a higher pH due to H_2CO_3 elimination and the precipitation of calcite (travertine). High temperatures have the same effect as photosynthesis due to the lower capacity of the water to contain the soluble gas CO_2. A part of the precipitated calcite may be redissolved at lower pH.

2 Collection of available information on the substance specific risk to aquatic ecosystems

2.1 Collection of literature and modelling data

Gathering of available information on the ecotoxicity and environmental fate of the substances released into the water is the next important step of disaster management.

In the ecological risk assessment process the hazard of chemicals to organisms in the environment is often estimated based on effect concentrations measured in the laboratory for a very limited number of organisms. Most often three organisms are tested (algae, crustaceans and fish) and LC50's (concentrations leading to 50 % mortality) or NOECs (no observed effect concentrations) for sublethal effects are generated. The "safe concentration" or PNEC (predicted no-effect concentration) is then derived with assessment factors.

The main input parameters in the risk assessment process are:
- Partitioning air-water
- Sorption to sediment and soil
- Degradation
- Bioaccumulation and biomagnification
- No-effect concentrations to algae, *Daphnia magna* and fish

Within the new Water Framework Directive (WFD 2008) levels of no concern, i.e. substance concentrations in water most probably not leading to adverse effects, are given for 33 priority substances and 8 other pollutants. These Environmental Quality Standards (EQS) have been set for annual average concentrtions and maximum levels, which should not be exceeded. Related information and, especially, the data being the basis for the threshold setting, is provided in EQS data sheets available for each substance via http://circa.europa.eu/Public/irc/env/wfd/home.

Further details on sources for substance specific information are given in the "Guidance for Implementation of REACH" (ECHA 2008), Part R 3 on "Information gathering", including a list of available databanks and databases (Table 3).

Similarity of structure approaches, e.g. quantitative structure-activity relationships (Q)SAR[4] models have to be used when no information is available on the toxicity of the released substance. (Q)SARs are theoretical models used to predict physico-chemical, biological (e.g. toxicological) and environmental fate properties of compounds from knowledge of their chemical structure. Within the ECODIS project a short overview has been prepared[5] summarizing (Q)SAR tools and existing databases provided by the European Union and the US-EPA[6]. Because experimental data for these parameters are only available for a limited number of chemicals, several estimation methodologies have been developed. Quantitative structure-activity relationship models (QSARs) represent the most important estimation method. During the last decade, several programs and databases have been developed and several reports have been published with overviews of QSAR models. Some of these reports also pay attention to the validation of QSARs.

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[4] (Q)SARS refers to SARs (structure-activity relationships) and QSARS (quantitative structure-activity relationships).

[5] Deliverable D23: "Validated QSAR models for pollution disaster conditions"

[6] United States Environmental Protection Agency

US-EPA

The EPIsuite program is a suite of programs, developed by the Office of Pollution Prevention Toxics and Syracuse Research Corporation (SRC). The whole suite of programs can be downloaded from http://www.epa.gov/opptintr/exposure/pubs/episuite.htm.
It has separate estimation routines for:
- the octanol-water partition coefficient
- water solubility
- Henry's law constant
- bioaccumulation
- sorption to sediment and soil
- aquatic toxicity

The EPISUITE program is presently the most user friendly program for the application of QSARs in estimation of relevant parameters in the ecological risk assessment. It will supply estimates for almost each organic compound. This program is very useful for a first, initial, screening. On the other hand, drawbacks are that it does not supply transparent information about the accuracy of the estimates and the domains of applicability of the models. The EPI Suite program was recently evaluated by the US EPA Science Advisory Board (SAB) and this report is available from http://www.epa.gov/sab.

European Union

Detailed information on the approach and a comprehensive overview of QSARs which can be applied in ecological risk assessment is given in sections R 4.3.2 and R 6 of the REACH guidance documents (ECHA 2008). During an earlier EU funded project, a critical review and overview of existing QSARs has been prepared for physico-chemical properties, fate properties and ecotoxicity (Utrecht University, 1995). In this overview, specific information was given about the reliability of predictions as well as the domain of applicability of the QSAR models.

More recent developments in the application of QSARs within the European Union are summarized by the EU European Chemicals Bureau (Worth, 2007). A complete overview of activities within the European Union can also be found on the ECB website (http://ecb.jrc.ec.europa.eu/qsar/qsar-tools/). This same website also gives information about relevant programs and databases developed within the European Union and member countries as well as several documents about activities related to the validation of QSAR models.

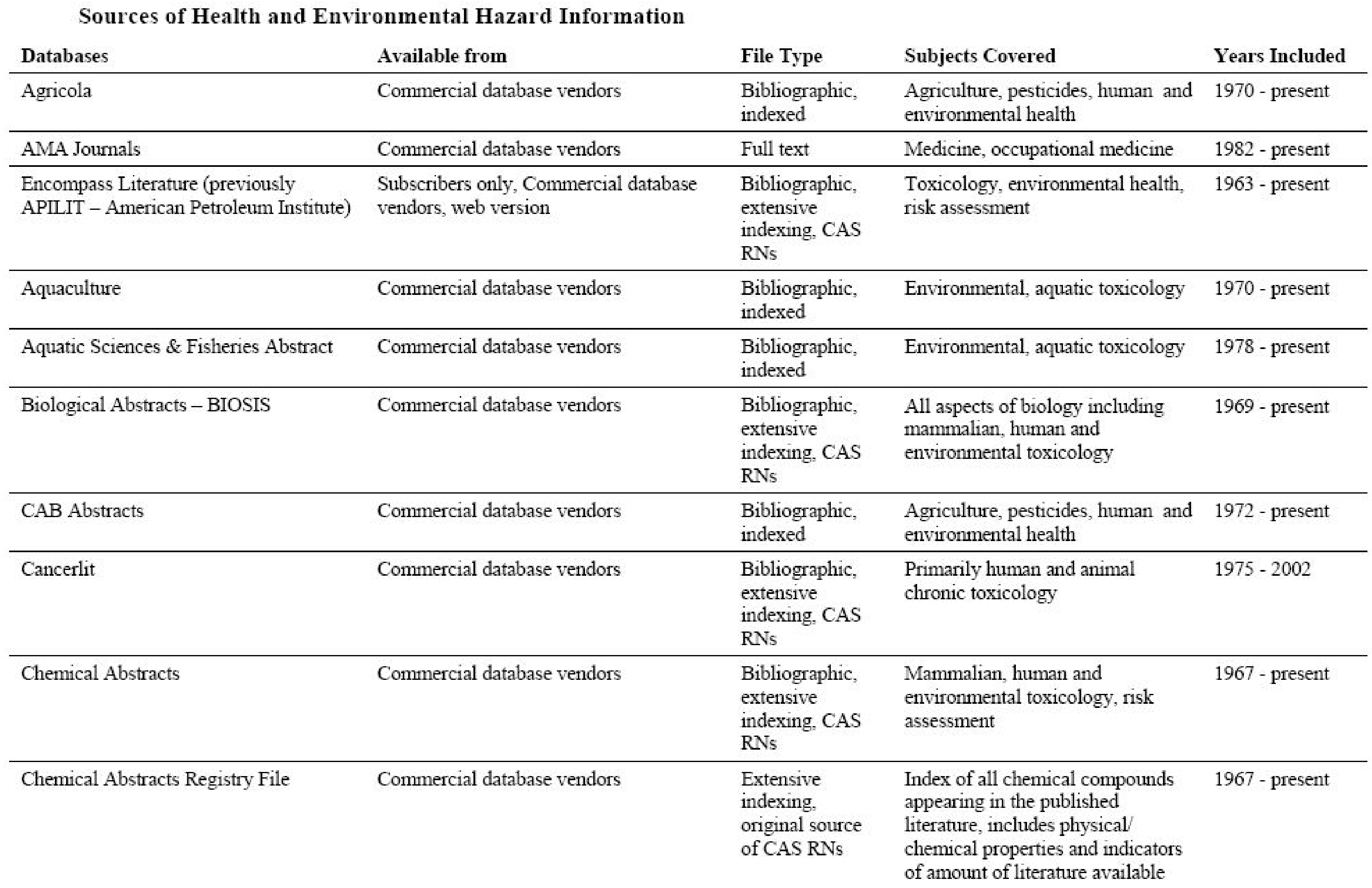
Table 3 Indicative list of major available databases and databanks for gathering of available information on the ecotoxicity and environmental fate of substances taken from (ECHA 2008), Part R 3.4.

No fee sources

Source	**Database**	**Description**
European Chemicals Bureau (ECB) European Chemical Substances Information System (ESIS) http://ecb.jrc.it/esis-pgm/esis_reponse_self.php?		Provides information on chemicals, related to: EINECS (European Inventory of Existing Commercial chemical Substances), ELINCS (European List of Notified Chemical Substances), NLP (No-Longer Polymers), HPVCs (High Production Volume Chemicals) and LPVCs (Low Production Volume Chemicals), including EU Producers/Importers lists, C&L (Classification and Labelling), Risk and Safety Phrases, Danger etc..., IUCLID Chemical Data Sheets, IUCLID Export Files, OECD-IUCLID Export Files, EUSES Export Files, Priority Lists, Risk Assessment process and tracking system in relation to Council Regulation (EEC) 793/93 also known as Existing Substances Regulation (ESR).
US National Library of Medicine (NLM), Specialized Information Sources (SIS)		Provides access to many excellent databases, see individual descriptions below
http://sis.nlm.nih.gov/enviro.html	ITER - - International Toxicity Estimates for Risk Assessment	Risk information for over 600 chemicals from authoritative groups worldwide
	IRIS - Integrated Risk Information System	Hazard identification and dose-response assessments for over 500 chemicals
	HSDB - Hazardous Substances Data Bank	Comprehensive, peer-reviewed toxicological data for over 5,000 chemicals Excerpts from published literature on: Human Health Effects and Emergency Medicine Treatment Animal Toxicity Studies Ecotoxicology Studies Environmental Fate and Exposure Chemical and Physical Properties Chemical Safety and Handling Environmental and Occupational Standards and Regulations Manufacturing and Use Information

Source	Database	Description
	TOXLINE - Toxicology Literature Online	Over three million references from the toxicology literature, including MEDLINE/ PubMed, research in progress, and meeting abstracts
	ChemIDplus - Chemical Identification Plus	Dictionary of over 380,000 chemicals (names, synonyms, structures). Includes links to NLM databases and other resources such as ATSDR Medical Management Guidelines and Public Health Statements
	ChemIDplus - advanced	Provides structure search and display for over 260,000 chemicals Includes links to NLM databases and other resources
	SuperList:	Lists of chemicals of interest to government agencies
	CCRIS - Chemical Carcinogenesis Research Information System	Carcinogenicity, mutagenicity, tumour promotion, and tumour inhibition test results for over 9,000 chemicals
	DART - Developmental and Reproductive Toxicology Database	Over 200,000 references to teratology, developmental and reproductive toxicology literature
	GENE-TOX - Genetic Toxicology Data Bank	Peer-reviewed genetic toxicology test data for over 3,000 chemicals
	Haz-Map	Links jobs and hazardous tasks with occupational diseases and their symptoms
	LactMed	Database of drugs to which breastfeeding mothers may be exposed. Covers maternal and infant drug levels possible effects on infants alternate drugs to consider
	Household Products	Potential health effects of chemicals for over 6000 common household products. Information in the Household Products Database is taken from a variety of publicly available sources, including brand-specific labels and Material Safety Data Sheets (MSDS) prepared by manufacturers
	TRI - Toxics Release Inventory	Annual environmental releases on over 600 toxic chemicals by U.S. facilities
	TOXMAP	Geographic representation of TRI (US chemical releases) data with links to other TOXNET resources
http://sis.nlm.nih.gov/enviro/toxweblinks.html	Toxicology Web Links – evaluated sources of data	

Fee based sources



Sources of Health and Environmental Hazard Information

Databases	Available from	File Type	Subjects Covered	Years Included
Agricola	Commercial database vendors	Bibliographic, indexed	Agriculture, pesticides, human and environmental health	1970 - present
AMA Journals	Commercial database vendors	Full text	Medicine, occupational medicine	1982 - present
Encompass Literature (previously APILIT – American Petroleum Institute)	Subscribers only, Commercial database vendors, web version	Bibliographic, extensive indexing, CAS RNs	Toxicology, environmental health, risk assessment	1963 - present
Aquaculture	Commercial database vendors	Bibliographic, indexed	Environmental, aquatic toxicology	1970 - present
Aquatic Sciences & Fisheries Abstract	Commercial database vendors	Bibliographic, indexed	Environmental, aquatic toxicology	1978 - present
Biological Abstracts – BIOSIS	Commercial database vendors	Bibliographic, extensive indexing, CAS RNs	All aspects of biology including mammalian, human and environmental toxicology	1969 - present
CAB Abstracts	Commercial database vendors	Bibliographic, indexed	Agriculture, pesticides, human and environmental health	1972 - present
Cancerlit	Commercial database vendors	Bibliographic, extensive indexing, CAS RNs	Primarily human and animal chronic toxicology	1975 - 2002
Chemical Abstracts	Commercial database vendors	Bibliographic, extensive indexing, CAS RNs	Mammalian, human and environmental toxicology, risk assessment	1967 - present
Chemical Abstracts Registry File	Commercial database vendors	Extensive indexing, original source of CAS RNs	Index of all chemical compounds appearing in the published literature, includes physical/ chemical properties and indicators of amount of literature available	1967 - present

Databases	Available from	File Type	Subjects Covered	Years Included
Chemical Carcinogenesis Research Info. Service – CCRIS	Commercial database vendors	Data Tables/ Summaries	Cancer and chronic toxicity studies summarized	
Chemical Exposure	Commercial database vendors	Bibliographic, indexed	Human exposures to chemicals and their health effects summarized, small database	1974 - present
Chemical Information System (CIS) Databases: AQUIRE - Aquatic Information Retrieval CASR - Chemical Activity Status Report CESARS - Chemical Evaluation Search & Retrieval System ENVIROFATE - Environmental Fate GENETOX - Genetic Toxicity GIABS - Gastrointestinal Absorption ISHOW - Info. System for Hazardous Organics in Water OHM/TADS - Oil and Hazardous Materials/ Technical Assistance Data System PHYTOTOX - Terrestrial Plant Tox SANSS - Structure & Nomenclature Search System SUSPECT - Suspect Chemicals Source Book TSCATS - TSCA Submissions - Unpublished Data	Commercial database vendors	Data Tables/ Summaries	Summarized results searchable by endpoint, species, and route of administration. Some very unique databases, such as PHYTOTOX which only covers effects on plants (primarily agriculture related)	Varies
Chemlist. Australian Inventory, status through June 1996 EINECS , DSL, NDSL status through June 15, 1990 EINECS PMNs (European List of Notified Chemical Substances -	Commercial database vendors	Indexed	Indication of hazard based on regulatory lists upon which the material appears, and provides a measure of how much published hazard information is likely to be found.	Varies

Databases	Available from	File Type	Subjects Covered	Years Included
ELINCS) through March 2005 Japanese Existing and New Chemical Substances List (ENCS), status through Sept. 2004 Korean Existing Chemicals List (ECL) Inventory through December 2005 TSCA Actions, Inventory Status, and PMN's, coverage through January 6, 2006 Philippines Inventory of Chemicals and Chemical Substances status through 2004 Swiss Inventory of Notified New Substances status through 2004				
Dissertation Abstracts	Commercial database vendors	Bibliographic, indexed	All areas of health	1861 - present
EMBASE/Excerpta Medica	Commercial database vendors	Bibliographic, extensive indexing, CAS RNs	Health and environmental related areas	1974 - present
Energy Science & Technology	Commercial database vendors	Bibliographic, indexed	Primarily environmental effects	1974 – present
Engineering Index - Compendex	Commercial database vendors	Bibliographic, extensive indexing, CAS RNs	Environmental engineering (air, water, pollution, solid waste)	1970 – present
Enviroline	Commercial database vendors		Environmental effects (air, water, solid waste)	1970 – present
Environmental Bibliography	Commercial database vendors		Environmental effects (air, water, solid waste)	1974 – present
EPA's Integrated Risk Information Service – IRIS	Commercial database vendors	Data Tables/ Summaries	Summary of data used and cancer risk assessment done by the US-EPA	
ECB's ESIS – European Chemical	http://ecb.jrc.it/esis-	Data Tables/	Summaries of data submitted to the	

Databases	Available from	File Type	Subjects Covered	Years Included
Substances Information System	pgm/esis_reponse_self.php?	Summaries	EU (IUCLID, HPV data)	
GEOBASE	Commercial database vendors	Bibliographic, indexed	Environmental effects (air, water, solid waste)	1980 – present
Hazardous Substances Data Bank – HSDB	Commercial database vendors	Data Tables/ Summaries	Summaries of all health aspects including end use exposures/ measured levels in the ambient environment. Excellent database, peer reviewed but only covers a small number of chemicals.	
Life Sciences Collection	Commercial database vendors	Bibliographic, indexed	All aspects of health/ hazard information.	1978 – present
JICST - EPlus (Japanese Science & Technology)	Commercial database vendors	Bibliographic, indexed	Some coverage of health/hazard topics	1985 – present
Medline	Commercial database vendors	Bibliographic, extensive indexing, CAS RNs	All aspects of health/ hazard information.	1960 – present
National Technical Information Service – NTIS	Commercial database vendors	Bibliographic, indexed	All aspects of health/ hazard information published by US government.	1964 –present
NIOSH	Commercial database vendors	Bibliographic, indexed	Occupational surveys and other related health information	1973 – 1998
Oceanic Abstracts	Commercial database vendors	Bibliographic, indexed	Environmental effects	1964 – present
PASCAL	Commercial database vendors	Bibliographic, indexed	All aspects of health/ hazard information focused on European publications	1973 – present
Pollution Abstracts	Commercial database vendors	Bibliographic, indexed	Primarily environmental effects	1970 – present
Registry of Toxic Effects of Chemical Substances – RTECS	Commercial database vendors	Data Tables/ Summaries	Toxicity, environmental data, lowest published toxicity values for each chemical listed	
Royal Society of Chemistry Databases:	Commercial database vendors	Bibliographic, indexed	Toxicity, occupational hazards, exposures	1984 - present

Databases	Available from	File Type	Subjects Covered	Years Included
Chemical Hazards in Industry - CHI				1981 - present
Laboratory Hazards Bulletin - LHB				1981 – present
Chemical Safety NewsBase				
Science Citation Index	Commercial database vendors	Bibliographic, indexed	Toxicology, environmental, risk assessments	1978 – present
TRACE	BIBRA Information Services Ltd	Bibliographic, indexed	Toxicology and Health effects of chemicals	1963 – present

2.2 A database of information on the kinetic properties of pollutants

The use of dynamic speciation sensors for *in-situ* monitoring of the release is described in Section 3. These sensors can also be used to build a database of information on the kinetic properties of pollutants. It is proposed herein that the flux and reactivity of compounds governs their environmental impact. ECODIS has made substantive advances in determination of factors that govern the speciation dynamics of metal and organic pollutants. For example, for metal ion complexes, the degree of protonation of the involved species (metal and ligand) has a dramatic impact on the association/dissociation kinetics (van Leeuwen et al. 2007, Town and van Leeuwen 2008, van Leeuwen and Town 2009). Furthermore, fluxes in mixtures can be significantly different from the sum of the individual fluxes for isolated compounds (Salvador et al. 2007, Zhang et al. 2009). Speciation dynamics are also influenced by the nature of the complexing entity, e.g. dissolved versus colloidal ligands, or gel-like phases such as biofilms. Overall, a generic theoretical framework was developed for the association/dissociation dynamics of metal species in aquatic systems that describes complexes with a wide range of ligand entities. The fundamental concepts involve computation of an effective dissociation rate constant which accounts for the relevant ligand characteristics, e.g. surface potential, particle number concentration, Donnan potential, etc. A critical review article on this work has been published (van Leeuwen and Buffle 2009) and the main concepts are outlined in Table 4.

Table 4 Dynamics of metal ion species in aquatic systems

Type of inner-sphere complex	Characteristics	Dissociation kinetics
Dissolved	Small inorganic/organic species Macromolecular species (humic acids, polysaccharides, etc.)	Eigen (k_{w}, K^{os}) $k_{\mathrm{d}} = k_{\mathrm{w}} K^{\mathrm{os}} / K$
Hard colloid / surface bound	Colloidal/surface species Confined ligand distribution	surface Eigen (k_{w}, $K_{\mathrm{s}}^{\mathrm{os}}$, ψ^{s}) $k_{\mathrm{d}}^{*} = k_{\mathrm{d}} \exp(\psi^{\mathrm{s}}) \left\{ 1 + \frac{k_{\mathrm{a}} \overline{c_{\mathrm{s}}}}{4\pi a D_{\mathrm{M}} \rho_{\mathrm{p}}} \right\}^{-1}$ (sphere, low M/L)
Soft colloid bound	Confined ligand distribution Donnan potential	Donnan-Eigen (k_{w}, K^{os}, ψ^{D}) $k_{\mathrm{d}}^{*} = k_{\mathrm{d}} \exp(\psi^{\mathrm{D}}) \left\{ 1 + \frac{k_{\mathrm{a}} \overline{c_{\mathrm{s}}}}{4\pi a D_{\mathrm{M}} \rho_{\mathrm{p}}} \right\}^{-1}$ (sphere, low M/L)
Biofilm bound	Diffusive exchange with medium Efflux, lysis	$\left. \begin{matrix} k_{\mathrm{d}}, k_{\mathrm{d}}^{*} \\ k_{\mathrm{eff}} \end{matrix} \right\}$ coupled with k_{diff} $\mathrm{O}(D/d^{2})$

3 Prediction of the time course of the pollutant concentration in water and biota

The next important step of disaster management, following the identification of involved substances (chapter 1 of this report) and the collection of information on potential substance specific risks (see chapter 2) is to assess the concentration of the respective compounds to be expected at any location downstream of the release. The predicted concentration in water, sediment and biota is the basic input for the evaluation of the risk for organisms (chapter 4) living in the respective ecosystem compartment and/or feeding on such organisms and potentially accumulating toxic substances.

Detailed guidance exists on the derivation of the so called predicted environmental concentration (PEC) within the framework of REACH: Part R.16 of the ECHA guidance (ECHA 2008) describes the methodology used to predict the substance's fate and distribution characteristics on the basis of the assumption of equilibrium conditions. REACH aims at assessing the effect of the annual emission of a chemical due to production and normal use of the substance on the environment at the regional scale. Disasters are highly dynamic and predicting effects of accidental releases of hazardous substances requires considering the variation of the concentration in water and biota with time, as it is known that toxic effects induced by concentration peaks differ from those assignable to constant exposures with the same total dose. Chapter 4 of this guidance will deal with the dynamics of effects on organisms, whereas chapter 3 is focusing on the implications of the results of the ECODIS project relevant for the prediction of the time course of substance concentrations as a component of disaster management.

The first section of chapter 3 will summarize the ECODIS recommendations regarding speciation, partitioning and degradation processes, the so called fate processes, gives a simple method for the calculation of the spread of a pollutant plume and a short description of the respective model developed within ECODIS. Section 3.2 deals with the prediction of bioconcentration and biomagnification dynamics. Both sections, 3.1.and 3.2, focus on predicting environmental concentrations in water and biota which are the basis for immediate and short term decisions on actions to be taken in disaster management. On the long term, measured data can complement predictions. Section 3.3 summarizes monitoring techniques giving better insight into the long term dynamics of the chemical status of aquatic ecosystems.

3.1 Fate processes: speciation, partitioning, degradation, immobilisation, remobilisation

3.1.1 Speciation and partitioning

To predict the concentration of a pollutant in water and biota for a certain release of hazardous substances requires considering a large variety of fate processes playing a role for ecosystem budgets and internal transport processes (Figure 3). Pollutants can be present in different forms, or species. For example, several metal fractions, such as free metal ions, inorganic compounds, and metals bound to soluble, colloidal or particulate organic or inorganic matter contribute to the total amount of metal in the water. (section 3.3.2.1). For some pollutants partitioning between water and suspended particulate matter plays an important role (see footnotes of Table 2 of the Annex), some are subjected to degradation processes, immobilisation in the sediment and remobilisation processes.

Models used in disaster management calculating the concentration of a pollutant in water for a given location downstream the discharge consider these fate processes to a different extent. They are developed by experts adjusting the set of tools to the characteristics of the stream or river in terms of considered processes and flow characteristics. To give a comprehensive list of such models is outside the scope of this report[7]. The aim of this section is to highlight the results of the ECODIS project on fate processes, but, it should be noted that not all important results obtained were available when this report was prepared so that this section can not give a comprehensive overview and might be incomplete in some parts.

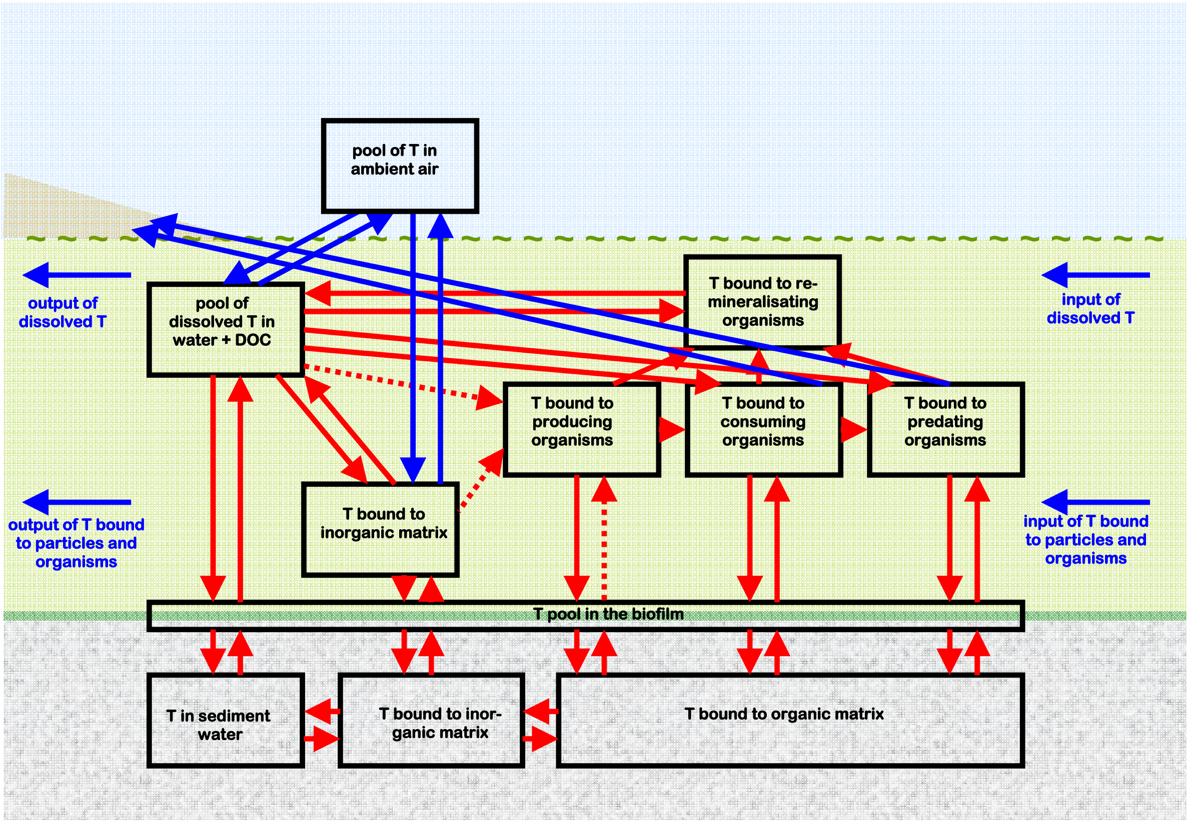


Figure 3 Pools of toxic substances (T) in aquatic ecosystems and fluxes connecting these pools. They are responsible for transport processes between the compartments air (blue), terrestrial soils (brown), water (yellow-green), biofilm (green) and sediment (grey). Blue arrows represent pathways relevant for the ecosystem budget, red arrows indicate transport processes within the system, dotted arrows represent potential modulating effects and influences. Ecosystems are sinks for toxic substances if the total input via particle bound and dissolved fluxes exceeds the total output, and a source if the amount of substance leaving the system is higher than the total amount transported into the system.

ECODIS research on the basic principles of metal speciation contributes to better knowledge of ecosystem internal exchange processes between the pools of toxics, especially the pool of free substance in aqueous solution and the pool of pollutants somehow bound to particles or complexed by dissolved organic matter. The stability of the binding has been extensively investigated and can now be well described in many

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[7] Models combining all fate processes relevant for a river or stream have not been applied within ECODIS. But, specific models accounting for certain subsets of processes have been used by several groups. According to Beck et al. (2009) the pH dependence of the speciation of cadmium containing minerals was calculated using PhreeqcI http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci/

cases. That certain aspects of current risk assessment procedures have to be put in question is one important implication of this research.

The concentration of a pollutant in water is generally used as input value for risk assessment procedures, which are generally based on the comparison of the predicted environmental concentration in the water with a known level of no concern. For pollutants with a high affinity to suspended particulate matter the concentration in the filtrate after exclusion of particles > 0.45 µm is used as assessment criterion, under the assumption that the fraction bound to particles is not bioavailable and therefore irrelevant for assessing the risk to organisms. ECODIS research has shown that only a part of the metal in the filtrate belongs to the free metal ion fraction assumed to be toxicologically relevant. A considerable part is complexed or bound or adsorbed to small "entities".

But, the assumption that bound or complexed toxics are irrelevant for toxic effects on organisms has to be revised as well. Within the ECODIS project the stability of the binding has been extensively investigated. That a fraction of colloidal bound metal contaminants was labile and/or mobile (dynamic) suggests that bound pollutant species might be bio-available as well.

A preliminary draft evaluation of the data collected during joint ECODIS measurement campaigns showed that the amount of metal in the "dynamic" fraction measured *in-situ* in unfiltered water of a river in South France was lower than the metal concentration of a filtered water sample in most cases. Thus, using the filtrate metal concentration (the total dissolved metal fraction) as criterium for risk assessment would rather over than underprotect aquatic ecosystems – under the assumption the dynamic metal fraction is the fraction relevant for bioavailability (see Tercier-Waeber and Taillefert, 2008). More research and evaluation work might elucidate these relationships in future.

3.1.2 Immobilisation and remobilisation

Important results have been obtained within the ECODIS project on pollutant exchange processes between water and sediment which are shown schematically in Figure 3. The in many cases large pools of contaminants in sediments and biofilms are not considered when WFD criteria are used to assign a "good" or "bad" chemical status to aquatic ecosystems. Thresholds defining the ecosystem status are set for concentrations in water and for some pollutants in suspended particulate matter, although it is known that immobilized organic and inorganic particles and detritus can be remobilized from the sediment due to changes in flow characteristics, temperature and water chemistry.

ECODIS results regarding the influence of sediment characteristics on the immobilization of metals reported in detail in deliverable 20[8] indicate that the rate of metal transfer from the water column to permeable sediments depends substantially on the particle affinity of the different metals studied (Figure 4). For instance, the metal with the highest particle affinity, Pb, was removed from the water column most rapidly. The four metals studied were removed in this order, from fastest to slowest: Pb > Cd > Cu ~ Ni, with Pb showing a factor of two faster removal than Cu (Figure 5). A comparison between sediments of two different permeabilities ($3.6x10^{11}$ m^2 – "fine," and $3.4x10^{10}$ m^2 – "coarse") was carried out to assess how sediment permeability affects metal uptake. Metals in the coarse sand chambers were removed from the water column at a rate almost twice that in the fine-grained sediments. Sediments amended with particulate organic matter removed metals less rapidly than did sediments without added organics, although this effect was quite small. In additional chamber experiments with metal-contaminated

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[8] D20: Exchange rates of pollutants at sediment/water interface as a function of hydraulic regime and permeability

sediments from the main project target site (Riou Mort, France) it could further be shown that, once captured, heavy metals are hardly released from the sands, even if sediments fall anoxic.

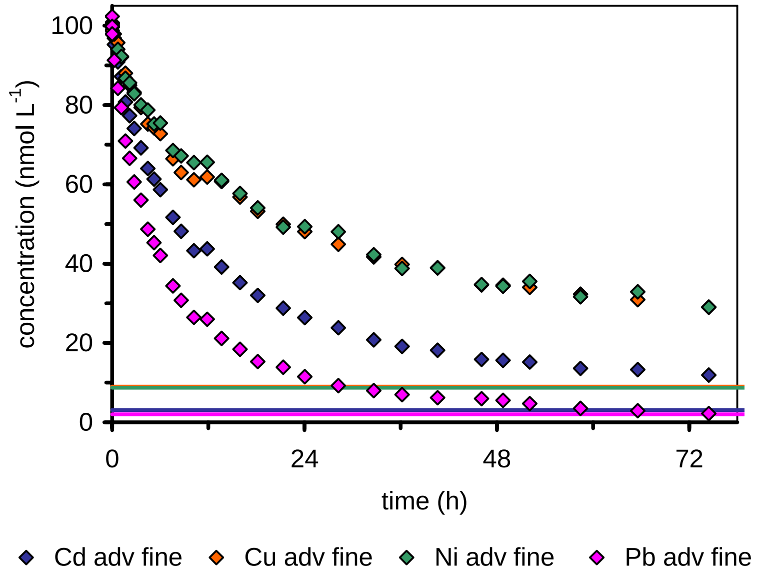

Figure 4 Chamber experiment. Decreasing heavy metal concentrations in the overlying water of the chambers reveals transfer of metals from the water column to sediments (F. Janssen, MPIMM, unpublished results).

In general, these results show that the transport of a metal pollutant plume in water overlying permeable sands will depend on the flushing of contaminated water through the sands, as well as the individual particle-reactivity of the metals. Especially in shallow waters with coarse grained sandy beds, advective pore water exchange may provide an efficient mechanism for transferring contaminant metal from the water column to the sediments.

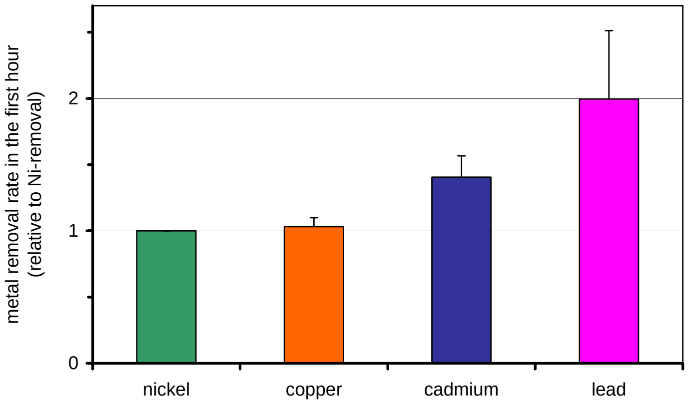

Figure 5 Chamber experiment. Rates of removal of the different metals from the water column correspond to the respective particle affinities (F. Janssen, MPIMM, unpublished results).

3.1.3 Methods for the prediction of the time course of the contaminant concentration in water at a given location downstream of the discharge

This part of the guidance describes how pollutant concentrations can be calculated for a given location downstream the release point at a given time after the accident. The simple spread calculation described in 3.1.2.1 provides a rough estimation of the concentration time course due to the transport of contaminated water body. It accounts for some fate processes by assuming that per unit of time a certain percentage of substance in the water is lost due to degradation and/or sedimentation, as the half time of the compound is used as an input parameter. It does not consider speciation, partitioning and resuspension. Section 3.1.2.2 deals with a transport model developed within the ECODIS project which will allow to perform predictions at both the local scale and lower spatial resolution. For important European streams like the Elbe, Rhine and Danube the authorities responsible for the management of disasters initiated the development and use of models to be used in case of chemical disasters. To describe these currently used transport models, the fate processes they consider and the set of input data they require is outside the scope of the present report which is more focused on the implications of ECODIS research.

3.1.3.1 Calculation of the spread of contaminated water in rivers and streams

In the following guidance is given on the method[9] suitable to assess the concentration of a substance in water (C_{wat} in mg l^{-1}) to be expected at a distance x (km) from the point of release under the assumption of a certain duration of the release (t_{input}) and a given mass flow (m_{input} in kg s^{-1}). The potential concentration at the point of release, C_{wat0} at x=0, can be assessed as

$$C_{wat0} = 1000 \cdot \frac{m_{input}}{F_{wat}} \quad , \qquad \text{mg l}^{-1} \qquad (1)$$

where F_{wat} is the water flow rate at the point of release in m^3 s^{-1}. Immediate total mixing is assumed here, but does not occur in nature so that C_{wat0} has to be regarded as a potential concentration. In reality water volumes with high and low concentrations occur in parallel. The distance from the release at which total mixing can be expected (x_{mix}) depends on eddies, the river ground structure, the flow rate and other factors.

Assuming the average flow velocity u_F (in m s^{-1}) the distance x_{wat} (in km) is covered in

$$t_x = \frac{x_{wat}}{3.6 \cdot u_F} \qquad \text{h.} \qquad (2)$$

The concentration within a moving volume of water is assumed to decrease exponentially with time due to degradation, sedimentation and other elimination processes. This decrease can be described as

$$C(t) = C_{wat0} \cdot e^{-\ln 2 \cdot \frac{t}{t_H}} , \qquad (3)$$

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[9] translated from Kaiser et al. (2000), Ermittlung und Berechnung von Störfallablaufszenarien nach Maßgabe der 3. Störfallverwaltungsvorschrift, Volume 1, Annex 2, chapter 2.2.2.

where the slope of this decrease is expressed as the hydrolytic half time t_H in h. Assuming that $x_{wat} \geq x_{mix}$ and taking into account that the flow rate at the location x_{wat} is by a factor of D higher or lower than the flow rate at the discharge position (x=0) the combination of (1) and (3) yields the following equation which can be used to calculate substance concentrations at the distance x_{wat} in mg m^{-3} or µg l^{-1} from discharge mass flows, dilution factors, water flow rates and half times (t_x is calculated using equation 2).

$$C_{xwat} = 1000 \cdot \frac{m_{input}}{D \cdot F_{wat}} \cdot e^{-\ln 2 \cdot \frac{t_x}{t_H}}, \qquad \mu g\ l^{-1} \text{ or } mg\ m^{-3} \qquad (4)$$

Figure 6 gives an example for such calculations showing the main characteristics of the spread of contaminated water in a river or stream. Anyway, some important transport characteristics in aquatic systems are not sufficiently described by the given set of equations. In nature, contaminants released into the water would be subjected to a variety of fate processes. Equation 4 accounts for processes leading to a decrease in the concentration with time, such as sedimentation, degradation, but, whether all these processes taken together yield in an exponential decrease is questionable. The second point is that resuspension and resolubilisation processes are not considered. The concentration time course calculated for a location downstream of the release shows an increase in concentration which is as fast as the decrease. But, resuspension and resolubilisation of a part of the eliminated fraction would lead to a delayed decrease in concentration, i.e. to a slower return to the background flux when the contaminated water body has passed.

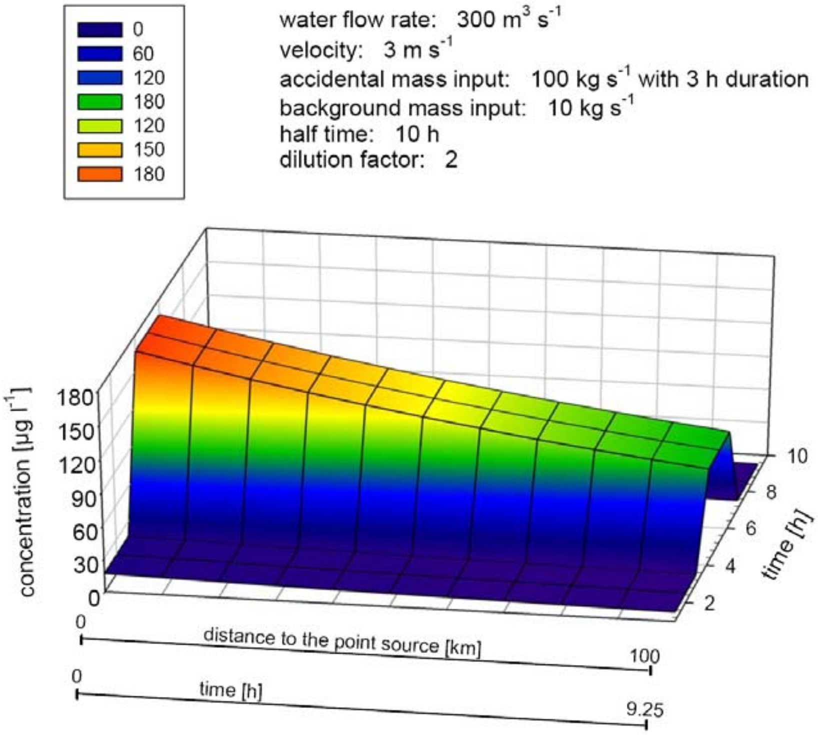

Figure 6 Results of a spread calculation using the equations given in section 3.1.2 and the indicated input values.

3.1.3.2 A software program for the prediction of local and large distance transport of contaminants in rivers and streams

Hydrodynamic, transport and chemical models which couple 3-dimensionel flow with transport of sediments and a broad scale of chemical processes to model the spread of a pollutant over a certain part of a stream have the advantage that they are able to model the spread of a pollutant in extremely high spatio-temporal resolution. But, large sets of input data are necessary to calibrate the model and extended computational and financial resources are needed. Since it is almost impossible to predict the spread of a pollutant in a whole catchment in case of a disaster and considering all relevant processes, within ECODIS another approach was followed. The flow characteristics are modelled for catchments consisting of sub-catchments (Figure 7), each with specific properties such as area and precipitation. The advantage is that the hydrology of a catchment at local scale with small rivers of first, second and higher orders can be described, in principle, with the same methodology as large catchments or river basins.

Coupling the catchment flow model to a simple chemical transport model allowed to predict chloride and nitrate discharge for the Hupsel catchment considering, among other inputs, the local variation of precipitation patterns with time. The key processes within the applied modelling approach[10] are now identified. The next step is the upscaling of the model to larger scale. For this purpose, it is applied to data from the Rhine catchment to investigate whether the model is indeed independent of scale. When this is the case, the modelling approach developed within ECODIS will provide a powerful tool to link water quantity to water quality and facilitate the comparison of responses of catchments independent of scale.

This outcome of ECODIS is promising as it might be possible to consider a wide variety of sub-catchment properties, such as storage pools of contaminants, soil characteristics, land use and socio-economic factors. Related information is provided by the "Catchment based Information System" of the JRC in Ispra (EUR 20703 EN). The publication also describes the LISFLOOD model simulating the hydrology and the river discharge in catchments for the prediction and simulation of floods in large European drainage basins like Rhine, Danube, Elbe and others.

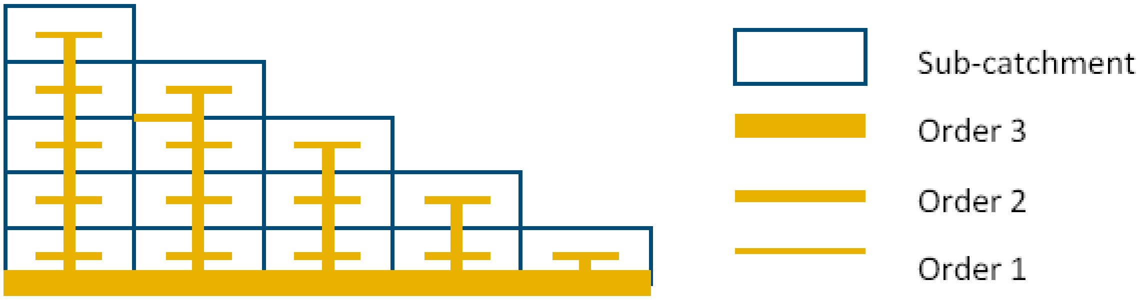

Figure 7 Example of a conceptualized catchment. Only the first 3 orders are considered in this example. Each sub-catchment has its own properties such as area, precipitation etc. The streams are divided into links, each with their own length, discharge and velocity.

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[10] The model describes transport by means of the convection-dispersion equation where the velocity and dispersion coefficient may vary over the length of the stream and at the moment chemistry is limited to Langmuir sorption. Input parameters are initial concentration profile, convective velocity (heterogeneous), dispersion coefficient (heterogeneous) and Langmuir constants. Waterflow is assumed to be steady state. The model is still being tested and needs further improvement to obtain better numerical stability and less numerical dispersion. More chemistry will be added in the future.

In the following paragraphs, a brief account of state-of-the-art 2D models for non-linear biodegradation in a spatially variable groundwater system is given. Several programs and models are available to compute non-linear biodegradation in the subsoil, namely (i) randomfield.m, (ii) GRASPER, and (iii) CONTRACT. Their features are outlined below:

Randomfield.m

Randomfield.m is a Matlab script which generates autocorrelated random conductivity fields, used in Monte-Carlo simulations to determine the ensemble macrodispersion.

GRASPER

This program is written in FORTRAN and converts the generated conductivity fields into steady flow fields. It uses a square FEV based grid, and remaps the original rigid grid to a grid which coincides with intersects of calculated flow and isopotential-lines. The remapping is performed to minimize the effects of numerical dispersion in the transverse direction, which is the direction that has the biggest impact on macrodispersion.

CONTRACT

This program is also written in FORTRAN and calculates the transport and biodegradation of various solutes based on an Eulerian approach. The biodegradation is non-linear and follows Monod-kinetics in combination with linear microbial decay. The user can customize parameters for the electron acceptor, contaminant and for microbial growth and decay. Adaptations have been made so the user can vary the length of the source. The model operates in 2D.

3.2 Prediction of the time course of the contaminants concentration in biota

Chapter R.16.4.3.5 of the ECHA guidance (ECHA 2008) describes the prediction of bioconcentration and biomagnification. Substance properties, such as partitioning characteristics between organic material and water determined in the laboratory or derived from field measurements are used to predict to which extent a substance can be assumed to accumulate in biota (for details see Table 4 of the Annex). Predicted bioconcentration factors may be, of course, compared to real bioconcentration factors calculated as the concentration in the organism divided by the concentration in water, or as the ratio of the uptake rate constant and the depuration rate constant[11].

The use of a simple factor to predict the concentrations of toxic substance in an organism is appropriate for the purpose for which the methodology was developed – the prediction of the concentration in biota of a pollutant emitted at a constant rate, but not if the concentration varies due to an accidental release of contaminants. To improve the prediction of biouptake and bioaccumulation under dynamic conditions was one of the major aims of research activities performed within ECODIS.

The outcomes regarding the question, which fraction or species of a contaminant should be used as the bioavailable concentration in natural water have been mentioned above (sections 3.1.1. and 3.1.2). Several sensor techniques were developed within the project with the aim to determine biouptake and bioaccumulation under natural conditions (Figure 8) by adjusting the sensor characteristics to the respective organism (See section 3.3 for further details). Methods suitable for the prediction of the time course of the contaminants concentration in biota are described together with the following step, the assessment of potential risk, in the report on dynamic risk assessment (chapter 4).

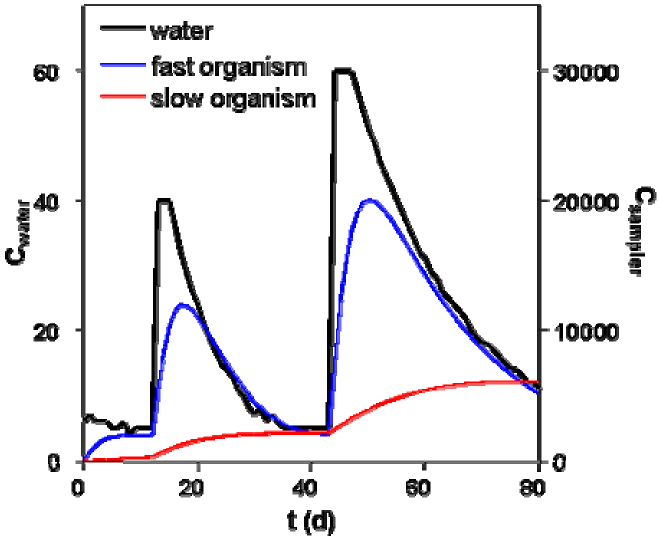

Figure 8 Exposure to a varying external pollutants concentration C_{water} leads to time courses of the concentration within the organisms which are dependent on species specific uptake and depuration rates. Passive samplers exhibiting similar characteristics allow assessing the concentration within biota by determining the concentration in the sampler $C_{sampler}$.

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[11] ECHA 2008, Part R.16, chapter R16.4.3.5 and Part R.7, chapter R.7.10, see also Table 4 in Annex I.

3.3 Long term monitoring of effects of disasters on aquatic ecosystems

Sections 3.1 and 3.2 dealt with the prediction of environmental concentrations based on knowledge of the composition of the release (concentration, reactivity, etc.), coupled with mass transport due to flow in the receiving water body. Predicted concentrations in water and biota are the basis for decisions on immediate and short term actions to be taken in disaster management. That is, they provide a basis for first-response actions that are undertaken before any direct information on the impacted system is available. In the intermediate and long term, direct monitoring is essential to characterise the dynamics of the disaster event, i.e. the evolution of pollutant speciation in the water body and the environmental reservoirs (soil, sediment, biota) as a function of time and space. The monitoring data serves to (i) characterise the *in-situ* reactivity of the pollutants, as determined by the nature of the receiving system (pH, ionic strength, particle loading, organic matter content etc.), and accordingly (ii) to refine the initial predictions based on the ecosystem specific information. Section 3.3.1 summarises available guidance on monitoring techniques developed for the implementation of the Water Framework Directive. New sensor and monitoring techniques developed and tested within the ECODIS project are detailed in section 3.3.2.

3.3.1 Available guidance on monitoring techniques developed for the implementation of the Water Framework Directive

A guidance on surface water chemical monitoring under the Water Framework Directive (WFD Guidance 2007) provides recommendations regarding monitoring strategies, techniques for sampling and analysis, data evaluation and other related information. Table 5 lists further sources of information on standardized monitoring methods (published in WFD Guidance 2007). Comprehensive information on monitoring and screening methods for the implementation of the Water Framework Directive is available in Quevauviller et al. (2008). Further guidance documents have been prepared within the SWIFT-WFD project[12]. The Chemical Monitoring Activity (CMA) under the Common Implementation Strategy of the WFD (Quevauviller 2006) aims at (i) the exchange of information about the best practice in chemical monitoring[13], (ii) quality assurance and quality control of chemical monitoring in the Member States and (iii) contributes to the definition of standard methods. Methods proposed to date focus on sampling and determination of total concentrations of substances. To date, speciation analysis and *in-situ* monitoring are not routinely applied.

3.3.2 Sensors for dynamic pollutant speciation, dedicated for disaster monitoring within the ECODIS project

ECODIS adopted a novel dynamic approach to monitoring and assessment of pollution disasters. Notably, the flux of a pollutant, i.e. the *rate* of accumulation, is recognised as a key parameter for determining risk. Correct interpretation of the fate and environmental impact of pollutants must consider the importance of the reactivity and fluxes of compounds, their exchange between compartments and biota via interfacial processes, and the relative time scales of processes. ECODIS dedicated a suite of dynamic sensors that

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[12] http://www.swift-wfd.com., download of "Guidelines for Laboratories carrying out measurements outside the laboratory where the results will be used to implement the Water Framework Directive" (2000/60/EC), "Guidelines for screening methods and emerging tools validation where the results will be used to implement the Water Framework Directive" (2000/60/EC), "A toolbox of existing and emerging methods for water monitoring under the WFD" and other documents.

[13] Results of a collaboration aiming at the comparison of sampling and analytical methodologies applied by laboratories from seven EU Member States is desribed in EUR 22922 EN 2007.

dynamically probe concentrations via fluxes at different effective timescales for monitoring of pollution disasters, involving both metals (section 3.3.2.1) and organics (section 3.3.2.2). The sensors can be deployed *in-situ*, thus allowing measurements in real-time. The general concepts involved in the ECODIS approach are detailed below, followed by specific descriptions of the individual techniques.

Table 5 List of html- links regarding standard monitoring methods (WFD Guidance 2007)

http://www.cenorm.be/catweb/cwen.htm	On-line Catalogue of European Standards
http://www.iso.org/iso/en/CatalogueListPage.CatalogueList/	ISO standards
http://standards.mackido.com/	This is a comprehensive catalogue of international standards, their nomenclature, and their reference details. • ISO Standards • EN Standards • British Standards • IEC Standards
http://standardmethods.org/	Since 1905, Standard Methods for the Examination of Water and Wastewater has represented "the best current practice of American water analysts." This comprehensive reference covers all aspects of water and wastewater analysis techniques. Standard Methods is a joint publication of the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF).
http://infotrek.er.usgs.gov/pls/htmldb/f?p=nemi:browse_methods:1914904511783287467	List of all methods in the National Environmental Methods Index (NEMI)
http://www.epa.gov/epahome/standards.html	EPA methods and guidelines

For a given pollutant and a given organism: (i) bioavailability is a measure of the fraction of total pollutant concentration that contributes to uptake, either directly, by direct passage through the membrane, or indirectly, e.g. after chemical conversion into bioactive species, and (ii) biouptake is the accumulation of pollutant by an organism, i.e. the integral of the flux or rate over a certain period of time. This is directly related to the length of time the organism spends in contact with the pollutant-containing medium, pollutant speciation, and organism metabolism. Similarly, a dynamic analytical sensor is characterized by its (i) response time, which is analogous to the effective time scale for *bioavailability*, and (ii) accumulation time, t_{acc}, i.e. the length of time over which pollutant species are accumulated in (loaded onto) the sensor prior to quantification. The signal resulting from the accumulation step represents an integration over all exposure variations in the test medium during this time period, t_{acc}, analogous to the concept of *bioaccumulation*. A comparison of relative timescales and spatial dimensions for selected environmental processes and analytical sensors is shown schematically in Figure 9.

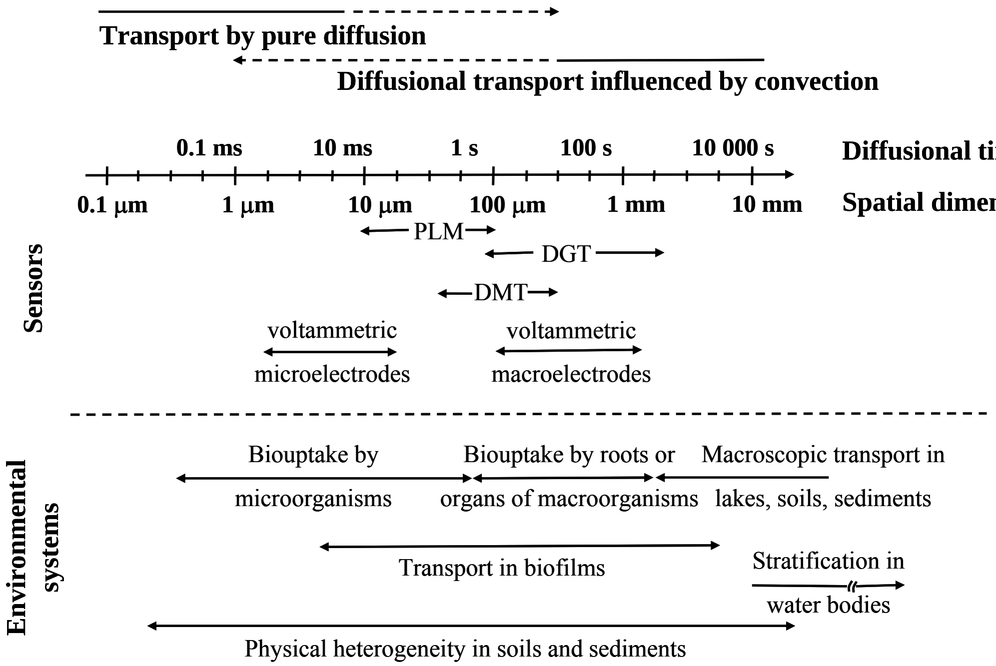

Figure 9 Schematic representation of diffusional timescales and spatial dimensions for a range of environmental processes and analytical sensors. PLM = permeation liquid membrane, DGT = diffusive gradients in thin film, DMT = Donnan membrane technique (from van Leeuwen *et al.* 2005).

Figure 9 shows that a given dynamic sensor will determine a certain proportion of the total pollutant concentration, the amount of which depends on the reactivity of the pollutant species and the kinetic window of the analytical technique. Similarly, the impact of the pollutant on a given environmental compartment is determined by the timescale of the process of interest, e.g. biouptake by a certain organism. ECODIS recommends monitoring with a suite of dynamic sensors. The resulting kinetic spectrum of pollutant properties allows interpolation of the flux relevant for the ecosystem process of interest. This information, coupled with, e.g. organism physiology, is input to dynamic risk assessment models (chapter 4).

In dynamic analytical sensors, the *diffusion time* is related to the diffusion of pollutant species in solution (for all techniques) and through a gel (DGT) and/or across a membrane (PLM, DMT). The *accumulation time* is the length of time over which the pollutant is accumulated in the electrode (GIME), the resin (DGT), or the receiving/strip solutions (DMT, PLM). The signal resulting from the accumulation step represents an integration of all fluctuations in the test medium and thus provides an average value for this time period. The effective response time (kinetic window) and accumulation time for the various sensors is summarised for metal species in Table 6. The lability index, $\mathcal{L}$, describes the ability of complexes to maintain equilibrium with the free species, X, within the context of an ongoing interfacial process in which a particular species, usually the free one, is consumed by an organism or at a sensor (Figure 9).

The principles of a dynamic sensor as compared to the process of biouptake are shown schematically in Figure 10

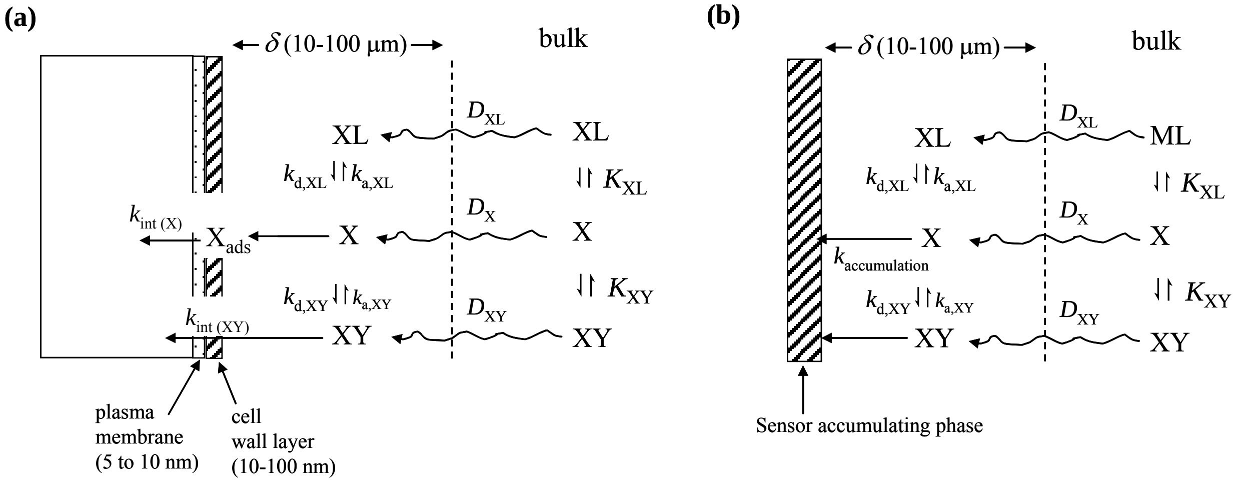

Figure 10 Schematic diagram of accumulation of a pollutant, X, at (a) a microorganism as compared to (b) a generic dynamic sensor. X denotes a metal species or an organic compound, and L and Y denote associated entities, e.g. complexants, particles etc. XY represents a lipophilic entity which may be transported intact through microorganism membranes. XL represents species that can only contribute to accumulation in a sensor or biouptake via prior dissociation into X. Symbols: k_a, association rate constant ($dm^3\ mol^{-1}\ s^{-1}$); k_d, dissociation rate constant (s^{-1}); K, equilibrium constant ($dm^3\ mol^{-1}$); δ, diffusion layer thickness (m); D, diffusion coefficient ($m^2\ s^{-1}$); k_{int}, internalization rate constant (s^{-1}).

ECODIS deployed a suite of dynamic sensors for metals and organics in-situ during several field campaigns (see ECODIS deliverable D29 “Protocol and tools for monitoring of chemical, biological and physical parameters on the site of a pollution). The principles of the various techniques are outlined below (see van Leeuwen *et al.* 2005 for further details), together with the additional features characterised in ECODIS. These sensors provide a measure of the speciation dynamics which result from the concentrations and properties of the target compounds within the impacted water body (sections 1 and 2).

3.3.2.1 Metal speciation techniques

Voltammetric sensors

The timescale of voltammetric techniques spans the second (macroelectrode) to millisecond (microelectrode) range (Figure 9). The technique involves (i) a deposition step, in which metal ions are reduced and accumulated in the electrode volume, followed by (ii) a quantitation step in which the accumulated metal is quantified by a reoxidation potential scan. Combination of measurements at a gel-integrated microelectrode (GIME) with one incorporating a complexing resin (CGIME) has been used to discriminate the voltammetrically labile species and free metal ions (Tercier-Waeber and Taillefert 2008, Noël et al. 2006). Further coupling with a flow injection system for sample pretreatment enables the total metal concentration to be determined in-situ (Tercier-Waeber et al. 2005). The voltammetric accumulation time is typically some 10 min, thus this technique can monitor metal species at relatively frequent intervals.

Table 6 Features of dynamic metal speciation techniques, and comparison with equilibrium-based sensors.

Method	Physicochemical basis	Characteristic diffusion length	Species measured	Lability criterion, $\mathcal{L}$ [a]	Typical analysis time/s
Dynamic techniques					
Voltammetries [b]	Diffusion in test medium	Macroelectrode, δ_s	Free metal plus dynamic complexes	$\Lambda\delta_s$	10^2-10^3
		Microelectrode, r_0		Λr_0	
GIME	Radial diffusion in gel	Microelectrode radius, r_0	Free metal plus dynamic penetrating complexes	Λr_0	10^2 -10^3 [c]
DGT	Planar diffusion in gel	Gel layer thickness, δ_g	Free metal plus dynamic penetrating complexes [d]	$\Lambda\delta_g$	10^3-10^5
PLM	Planar diffusion in sample and membrane	Diffusion layer thickness, δ_s (solution diffusion control)	Free metal plus dynamic complexes	$\Lambda\delta_s$	10^2 - 10^3
		Membrane thickness, δ_m (membrane diffusion control)	Free metal ion	na [e]	
Equilibrium techniques					
ISE	Equilibrium or steady-state membrane potential	na	Free metal ion	na	1 to 10
DET	Equilibrium gel / sample	na	All penetrating species	na	10^5
PLM	Equilibrium source / acceptor solutions	na	Free metal ion	na	10^4
DMT	Equilibrium sample / acceptor	na	Free metal plus part of cationic penetrating complexes	na	10^5
CLE-AdSV	Equilibrium with ML_{ad} in sample	na	Free metal plus complexes weaker than ML_{ad}	na	10^2 - 10^3

[a] $\mathcal{L} >> 1$ for the labile case, $\Lambda = \dfrac{k_d D_M^{1/2}}{k_a'^{1/2} D_{ML}}$ $(D_{ML} K' / D_M >> 1)$; [b] traditional techniques, including stripping ones; [c] equilibration in gel; [d] for $\delta_g >> \delta_s$; [e] na = not applicable

GIME = gel integrated microelectrode; DGT = diffusive gradients in thin films; PLM = permeation liquid membrane; ISE = ion-selective electrode; DET = diffusive equilibration in thin films; DMT = Donnan membrane technique; CLE-AdSV = competitive ligand exchange – adsorptive stripping voltammetry.

Permeation Liquid Membrane (PLM)

PLM involves a water-immiscible organic solvent, containing a carrier ligand, selective for the target metal, imbedded in a porous hydrophobic membrane sandwiched between two aqueous phases: the sample source solution on one side, and the receiving (strip) solution on the other. A metal flux occurs when the complexation strength increases from the test solution to the hydrophobic membrane and to the strip solution; it depends on diffusive transport in the hydrophobic membrane, the aqueous source, and the strip solutions. The flux, and thus the nature of the test species measured, can be varied by manipulation of these diffusion-controlling steps (Table 6). PLM was shown to provide a reasonable estimate of biouptake fluxes at microorganisms under certain conditions (Bayen *et al.*, 2006, 2007) and is utility for *in-situ* monitoring has been elaborated (Gunkel-Grillon and Buffle, 2008; Parthasarathy *et al.*, 2008; Zhang *et al.*, 2006, 2007).

Diffusive Gradients in Thin film (DGT) and Diffusive Equilibration in Thin film (DET)

A DGT sensor consists of a layer of hydrogel (0.4-2mm thick) overlying a layer of Chelex resin beads. Concentration gradients are established in the gel layer as species diffuse through it (planar diffusion) and accumulate in the resin. The lability and diffusion coefficients of penetrating complexes determine the amount of metal collected in the resin. The thickness of the gel strongly impacts on the metal flux and thus on the required deployment time, as well as the operational lability of the measured species (Table 6). For straightforward application, the time required to attain steady-state diffusion in the gel (typically of the order of 100 s) should be negligible relative to the deployment (accumulation) time (typically hours to days). It is generally assumed that the gel matrix is effectively uncharged and chemically inert with respect to the species of interest. However, nonideal behavior is observed at low ionic strength, as a consequence of a finite structural charge within the gel matrix. The ramifications of this charge for metal speciation analysis was characterised (Yezek *et al.*, 2008). Furthermore, it was demonstrated that particles up to radius of 130 nm can permeate the gel to a significant degree, and their contribution to the overall flux must be taken into account in the data interpretation (van der Veeken et al., 2008). The kinetic features of DGT have been evaluated and the range of attainable measurement time scales was found to be rather limited (Town et al., 2009).It is recommended that DGT is complemented by DET measurements; the latter is subject only to a size window.

Donnan Membrane Technique (DMT)

In DMT a charged porous membrane is placed between the sample solution (donor) and a receiving solution (acceptor). Discrimination between species is primarily based on their charge. The measurement is typically made after equilibrium has been attained (currently of the order of days). In ECODIS, DMT was employed to provide a measure of the free metal ion concentration that is complementary to PLM.

Field studies have been performed with several sensors in order to compare the analytical techniques for the detection of dynamic metal speciation in natural freshwaters (Sigg et al. 2006). As a result of the differences in the dynamic features of the techniques the measured trace metal concentration differed between the sensor techniques applied, showing that the combined application of a suite of sensors is, as mentined above, the appropriate methodology for metal speciation analysis in the field. The authors further emphasise that *in-situ* measurements (GIME) and *in-situ* exposure techniques (DGT, DMT, PLM) have the advantage that artifacts due to sampling, sample transport and handling are avoided.

3.3.2.2 Organic pollutant speciation techniques

ECODIS developed concepts for dynamic speciation analysis of organic pollutants that has up to now received scant attention. The approach adopted is analogous to that described above for metal species. For organics so-called passive samplers are used in which the accumulating phase is a solvent (PLM; Bayen and Buffle, 2009), a solid polymer (solid-phase microextraction, SPME; ter Laak *et al.,* 2008, 2009, Benhabib *et al*., 2009), or a rubber sheet (Rusina *et al*., 2007), each with its own kinetic window. The flux of organic pollutant towards the sensor was found to be enhanced in the presence of sorbents such as natural organic matter (ter Laak *et al.,* 2008, 2009) and nanoparticles (Benhabib *et al*., 2009). This observation indicates that the accumulation process is governed by the coupled diffusion of free and sorbed organic entities towards the sensor /sample solution interface. A lability criterion was derived to describe this process (Benhabib *et al*., 2009). The polarity of the accumulating phase can be varied to scan a range of polarity of target organics (Rusina *et al*.. 2007). Biouptake fluxes at organisms are expected to follow analogous concepts; again, the information from the sensors can be used to predict biouptake on a comparable timescale. A review of literature data on the biouptake of organic pollutants and measurements with passive samplers was prepared (Bayen *et al*., 2009).

3.3.2.3 A bioindicator system for the *in-situ* assessment of biouptake and bioaccumulation

It is generally agreed that there is an urgent need to link the gap between toxicity tests in the lab and ecotoxic effects in natural water. One important question is, whether effects of contaminants found in the laboratory can be extrapolated to natural conditions, where organisms are exposed to the toxic substance and other natural or anthropogenic stressors. The second question is, how can we assure that ecotoxocological evidence for toxicity obtained with samples from ecosystems affected by pollution - for example effects of contaminated sediment on a test organism[14] – is specific to an extent that allows to attribute the found effect[15] to a certain pollutant or pollutant group[16]. Organisms are exposed to increasingly complex mixtures of organic[17] and inorganic pollutants.

A bioindicator system for the *in-situ* assessment of biouptake and bioaccumulation developed within ECODIS has the potential to be an important step forward for the solution of the above mentioned problems. The SUBS (Stirred Underwater Biouptake System) method for monitoring of biouptake and bioaccumulation of Cd has been successfully applied within the ECODIS project (Davis et al. 2009). It is based on the exposure of suspensions of *Chlamydomonas reinhardtii* to natural water (Figure 11). The suspensions are kept in bags permeable for water and pollutants but impermeable for *Chlamydomonas* cells. The advantage of such systems is that they collect information on biouptake under natural conditions

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[14] Within ECODIS a bacterial bioluminescence toxicity assay with *Vibrio fisheri* was applied to detect effects of contaminated water and sediment suspensions on the indicator organisms. The assay was also used to assess the toxicity of polluted sediments of the Zlin area, Czech Republic (Bláha et al. 2009). Hilscherová et al. (2009) investigated the indication potential of bioassays in contaminated river sediments.

[15] For example, effects on the reproduction in crustaceans by pollutants affecting endocrine homeostasis reviewed by Mazurová et al. (2008a), Mazurová et al. (2008b), and Mazurová et al. (2009).

[16] A review focusing on the second topic has been published by Brack et al. (2007). The paper attempts to link chemical pollution to ecotoxic effects in European surface waters.

[17] An EU-wide survey of polar organic persistent pollutants in European river waters has been published recently by Loos et al. (2009). Benzotriazole, tolytriazole (which are anti-rust substances), caffeine, carbamazepine (a drug used for the treatment of epilepsy) and nonylphenoxy-acetic acid, a degradation product of industrial surfactants used in cleaning products were the most frequently detected compounds at noteworthy concentrations. These agents are known as so-called 'endocrine disrupting compounds'.

in terms of speciation, water chemistry and temperature and the exposed organisms are subjected to the natural variability in these factors.

Figure 11 SUBS system during the ECODIS field trip 2007. *Chlamydomonas reinhardtii* suspensions are exposed to natural water.

Within the ECODIS project the system was successfully applied to detect the cadmium biouptake rate of the exposed algae suspensions in the Riou Mort exhibiting relatively high Cd concentrations. Under these conditions exposure times as short as 2 hours were sufficient. In the Riou Mort river Cd speciation shows a typical diurnal variation (sections 1.3.2 and Annex I, 3.3) under certain conditions. Thus, the SUBS system would be suitable to detect fast changes in biouptake due to fast changes in metal speciation.

3.3.2.4 Sensor systems for the detection of changes in the species composition of biofilms

A further important achievement of the ECODIS project is the setup of a system suitable for the detection of changes in the algae species composition of biofilms. The WFD considers both the chemical and the ecological status of aquatic ecosystems. If changes in the species composition of biofilms can be used as indicators for general changes in the phytoplankton composition due to changes in water chemistry, the system can be used to monitor the ecological status of aquatic ecosystems.

Within ECODIS the growth of biofilms was followed in real-time using a non-invasive optical method. The Modular spectral imaging system (MOSI) described in detail in Polerecky et al. (2009) was applied to detect the reflectance characteristics of algal cells. Reflectance spectra of cyanobacteria differ from those of diatoms due to the group specific pigment composition of the cells. The advantage of the imaging system is that it allows detecting spectral characteristics of small biofilm spots (mm scale). In biofilms, consisting of both colour groups, patches of diatoms within homogenously distributed cyanobacteria were identified, and the growth of diatoms at the expense of cyanobacteria was followed (Figure 12). From the obtained reflectance spectra the relative contribution of both colour groups to the total biomass was assessed. Using not only reflectance but also fluorescence signals increased the specificity of the obtained data for algae colour groups.

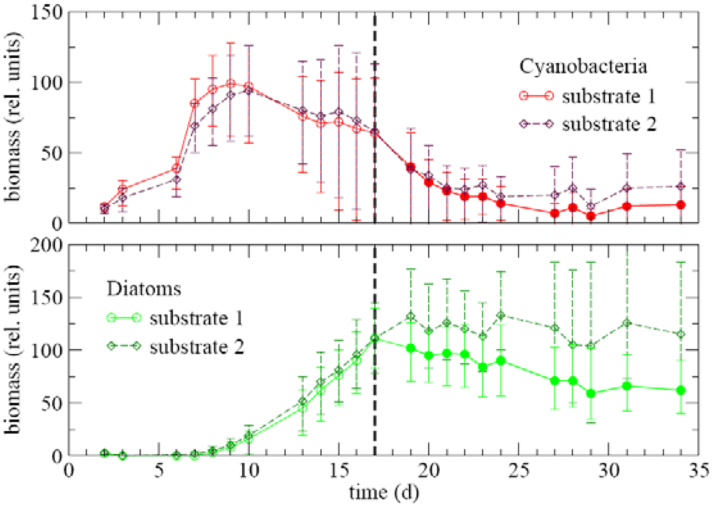

Figure 12 Shift in the relative contribution of cyanobacteria and diatoms to a biofilm investigated using a spectral imaging system expressed as relative biomass. Error bars correspond to the standard deviations due to the coverage patchiness of the biofilm. Substrate 1 refers to a shaded biofilm, substrate 2 to full illumination.

Use of reflectance based methods Polerecky et al. 2009, Bachar et al. 2008) bears the important advantage that low-cost reflectometers equipped with fiber optics might be suitable to detect reflectance spectra of biofilms. If the spectral signatures of the species constituting the biofilm are known through spectral imaging in the laboratory, these less sophisticated reflectometers might be applicable after some modifications in the field for the detection of biofilm colour changes. It should be noted, however, that these systems can be applied only under the precondition that the change in reflectance is very specific for changes in species composition.

4 Dynamic risk assessment

A substantial task in disaster management is to estimate whether the calculated[18] or measured[19] concentration of a hazardous substance in a given environmental compartment has to be regarded as a risk. This is done by comparing the derived concentrations to known levels of no concern[20], a term used for the concentration level above which adverse effects on organisms and/or the ecosystem have to be expected. The current risk assessment procedures are described in detail in numerous documents, for example in Part E "risk characterisation" of the "guidance for the implementation of REACH" (ECHA 2008). The document presented here aims at giving recommendations how the dynamics of relevant processes can be considered to a higher extent within the eco-toxicological risk assessment procedure.

This chapter on dynamic risk assessment does not include the assessment of the physic-chemical risk to aquatic ecosystems based on specific properties of the released substances, such as explosivity, flammability, oxidising potential and effects on pH and water temperature. The relevant physic-chemical properties of potentially hazardous compounds are listed in chapter 1.2. Although the physic-chemical risk can be assumed to be highly dynamic at both the local and regional scale, the document presented here will focus on the topics tackled within the ECODIS project and will not give details on physic-chemical risk assessment.

4.1 Prediction of the time course of threshold exceedances, of short- and long term deviations from the good chemical and ecological status of the ecosystem

According to the currently used risk assessment procedure predicted environmental concentrations are compared to predicted no effect concentrations or quality standards representing annual mean concentrations of no concern. Maximum concentration thresholds that should never be exceeded (Water Framework Directive) account somehow for dynamics, but evaluations based on the concentration versus time curve for water, sediment and biota with a higher time resolution than one sample per month would be more reliable. Once the pollutant concentration in water is known, the current ecotoxicological risk assessment paradigm has been up to now based on the examination of the PEC/PNEC ratio (PEC: predicted environmental concentration; PNEC: predicted no effect concentration). If PEC/PNEC > 1 then the risk is considered unacceptable for the ecosystem; conversely, if PEC/PNEC < 1 then the risk is considered acceptable and the environmental contamination of no concern. Thus, risk estimation following the current paradigm is reduced to estimation and tracking of the spatial and temporal variation of the concentration of the pollutant in the relevant environmental medium. The reader is referred to chapter 3 of this guidance document for information on available methods for prediction of the time course of environmental contamination and, consequently, of the exceedance or not of the PNEC values. The following table elucidates how to define PNEC for different species on the basis of accepted metrics of effect coupled to uncertainty factors to allow for lack of information on intra-species variability and inherent uncertainty in the physiological response of different aquatic organisms.

Table 7 Assessment factors for derivation of PNEC values.

Data available	PNEC
NOECs for three species (fish-Daphnia-algae)	lowest NOEC/10
LC50s for three species (fish-Daphnia-algae)	lowest LC50/100
LC50 for one or two species	lowest LC50/1000

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[18] For the prediction of pollutant concentrations in water, sediment and biota see chapter 3.1 and 3.2.

[19] For the monitoring of pollutant concentrations in water, sediment and biota see chapters 1.3 and 3.3.

[20] Sources of information on such levels of no concern are listed in chapter 2 of this report.

One of the drawbacks of this approach is that it assumes non-dynamic exposure to the toxicant species. PNEC is derived for chronic exposure to the substances of concern. PEC is usually derived for steady-state concentrations of pollutants in the environmental media examined. Furthermore, this approach does not take into consideration the capacity of the organism's physiology to handle the internalised concentration within a given timeframe.

For chemicals that act via an irreversible mechanism of action, the occupation of the target has been proposed as a suitable parameter for modelling time dependent toxicity (Legierse et al. 1999, Verhaar et al. 1999). More recently, damage and hazard assessment models have been developed to describe and predict the influence of exposure time on effect concentrations (Ashauer et al. 2007, Lee and Landrum 2006, Lee et al. 2002, Jager and Kooijman 2005). These more dynamic approaches do not only take into account the kinetics of exchange between external and internal concentrations, but also include the kinetic aspects of interaction with a target inside the organism. Although these new approaches (the critical target, hazard and damage models) offer sophisticated modelling tools, the available experimental data and input parameters are still too limited to allow a wide application in ecological risk assessment. The main lesson from these studies is that the internal effect concentration is not always constant in time and that the effects are not related to a peak concentration within the organism, but more to a time integrated dose (the area under the curve). Although most of the examples for irreversible mechanisms in the literature analyse the effect of exposure time on effect concentrations at a constant external exposure concentration, the model developed by Ashauer has also been applied to fluctuating and sequential pulses of pesticides (Ashauer et al. 2007)

The procedure for applying the PEC/PNEC ratio for ecological risk assessment is therefore strictly related to the kind of exposure, which will depend on the type of disaster. Disasters may be divided in three types:

(1) chemical accident disaster
(2) continuous chemical disaster
(3) a nature disaster

After a chemical accident disaster, for example an accident with a truck or accidental spills from factories, the concentrations will be highly dynamic. Concentrations will often reach a peak and then slowly decrease. During a more continuous chemical disaster, for example a continuous (or regular) release of contaminants from industrial or agricultural activities, concentrations fluctuate less. This may also be the case during what we call a nature disaster. The release of contaminants from sediments and soil after a flooding is an example of such a disaster.

These disasters may thus lead to very different exposure profiles in the environment. In disaster type 3, and in some cases during a type 2 disaster, the concentrations in the environment are relatively constant and do not show large variations over a period of days, week or even months. After an accident (disaster type 1), the concentrations will show a highly dynamic profile and will fluctuate during periods of hours and days. These two scenarios (constant and fluctuating exposure) will need a different risk assessment approach.

The ecological risk assessment at constant exposure concentrations does not differ from the standard risk assessment process using a PEC/PNEC ratio. Because concentrations do not fluctuate, experimental data for concentrations from a grab sample can be taken as the PEC. As an alternative, fate modelling can be applied to estimate the PEC.

4.2 Prediction of the dynamics of effects on organisms of different trophic levels and fish populations combined with the development of rules to assess which effects are acceptable

4.2.1 Methods to predict the dynamics of effects on algae, invertebrates, vertebrates, predators and fish populations

Total body burden estimates

For systems where the organisms are in equilibrium with the surrounding environment, it makes sense to use the external exposure concentration as effect parameter (LC50, NOECs and PNEC), also because the overwhelming majority of toxicity data is generated based on the external (aqueous) concentrations. The main difference between dynamic and the more classical risk assessment for constant exposure concentration is the fact that a single concentration measurement in the environment does not give sufficient information about the potential hazard and risk. Because the internal concentration within an organism is the driving force for toxicological effects, it makes more sense to use the internal concentration or body residue as dose or exposure parameter, in particular because in a highly dynamic system the internal concentrations do not immediately follow the time trends of the external exposure concentrations. For a larger organism, for example, the exchange kinetics are slow and internal concentrations will slowly respond to fluctuations in environmental concentrations. On the other hand, smaller organisms, such as algae, will respond much faster to these fluctuations. Therefore, the internal body residue is a much more powerful tool in a dynamic risk assessment process. As mentioned above, critical body residues (CBR) may also be time dependent. For the time being, however, and also because information about these kinetic aspects related to the toxicological damage inside the organism is still very limited, the CBR approach is the only realistic option at this moment.

The first step is the estimation of the internal concentration from the external concentration using a simple one compartment model with a first order kinetic process. This model leads to the following equations:

$$\frac{C_O}{C_a(t)} = \frac{k_w}{k_e} \cdot (1 - \exp^{-k_e \cdot t}) \qquad (1)$$

$$\frac{C_O}{C_a(t)} = BCF \cdot (1 - \exp^{-k_e \cdot t}) \qquad (2)$$

C_o	concentration in organisms
C_a	concentration in aqueous phase
k_w	uptake rate constant
k_e	elimination rate constant
BCF	$= C_o / C_a$ (at steady state)

In equation 1 and 2, the aqueous concentrations are constant, but these types of models can simply be translated to predict the body residues (BR) during fluctuating external (aqueous) concentrations. The kinetics of exchange between the organisms and the aqueous phase are faster, and this means that k_w and k_e are higher for smaller organisms than for larger organisms. Absolute values for these rate constants for different organisms and chemicals are related to the organisms' surface-volume (S/V) ratio and the chemicals' hydrophobicity (Hendriks et al., 2005, Bayen et. al, 2009a, Sijm and van der Linde, 1995). A very extensive overview of kinetics for a large set of organisms was recently prepared by Bayen and ter Laak (Bayen et al. 2009a). The models presented in this overview can be applied to predict the kinetic rate constants k_w and k_e for different organisms and chemicals. One should realize, however, that these models will likely result in worst case estimates of body residues because the one compartment model does not include biotransformation inside the organism as an additional elimination process.

When internal concentrations have been calculated, the second step in the risk assessment process is the comparison of estimated body residues at fluctuating exposure concentrations with the so called critical body residues (CBR) for each particular chemical and organism. Although this information is not available for each combination of organic chemical and organism, the U.S. Army Corps of Engineers and U.S. Environmental Protection Agency have collected critical body residues for a large number of chemicals and organisms. This information is available as a database: the "Environmental Residue-Effects Data Base" (http://el.erdc.usace.army.mil/ered/). Because the availability of experimental data for CBRs is still limited, an alternative approach is to use estimated CBRs based on information on the mode of action. This is in line with research into quantitative structure-activity relationships (QSARs), where information about the mode of action also plays a crucial role (Escher and Hermens 2002, Bradbury 1995, Verhaar et al. 1992, Verhaar et al. 2000). Traas et al. (2004) derived ranges of CBRs for chemicals with a certain mode of action. When experimental data are lacking, these estimated CBRs can be used in a risk assessment. The only drawback is that the estimated CBRs are not available for specific organisms. In the publication of Traas et al. (2004) a range of internal effect concentrations and their confidence limits are given and one could take the lowest value as a worst case estimate.

The profile of the internal concentration versus time generates a whole range of internal concentrations. Although theoretically it may be relevant to include a time aspect in the evaluation of the toxicological effects or hazard (Legierse et al. 1999, Verhaar et al. 1999, Ashauer et al. 2007, Lee and Landrum 2006, Lee et al. 2002a, Jager and Kooijman 2005, Lee et al. 2002b), the present state of our knowledge only allows an estimation of hazard related to a maximum internal concentration (the peak concentration in the profile).

A second choice that has to be made is the selection of organisms that are included in the risk assessment. In line with the classical risk assessment process, we propose to take three "representative" organisms, an algae, a crustacean (e.g. *Daphnia magna*) and a small fish (e.g. guppy), to generate the internal concentration profiles and to search for critical body residues for each of these three organisms. The final step, the assessment of the risk can be performed in a similar PEC/PNEC ratio calculation as used in the classical risk assessment process. The only difference is that, instead of taking external (aqueous) concentrations, the dynamic approach is using internal concentrations. Also the assessment factors as presented in Table 7 (above) can be applied to this dynamic risk assessment process.

Estimation of biologically effective dose

In the previous paragraph it has been said that under conditions of dynamic exposure a more thorough approach takes into account kinetics of pollutant exchange between external and internal compartments and amongst different organs. This allows relating the risk not only to a peak concentration within the organism, but more to a time integrated dose (the area under the curve) to take into consideration also later effects. Once the area-under-the-curve is known, toxicity modelling allows linking this value to specific pathology indices.

Field observations of aquatic biological species have shown that when an organism comes into contact with a contaminant, both through food ingestion or dermal contact or inhalation, the contaminant accumulates selectively in specific organs, and even shows a different behaviour during the uptake and depuration phase. Some contaminants can persist in some organs also after the end of exposure and in some compartments the contaminant accumulation can continue even after the end of the uptake phase. Accumulation results in elevated concentrations in specific organs responsible for the toxicity to the animals (Labrot et al. 1999, McGeer et al. 2003).

Physiology-based pharmacokinetic (PBPK) models help understanding the exchange processes and the selective accumulation of the contaminant in target tissues. PBPK models combined with dose-response models allow to estimate organ-specific morbidity indices. In this calculation a distinction should be made between internal dose and biologically effective dose. Internal dose is the amount of a substance taken up by an organism or into organs or tissues of interest. The biologically effective dose is, however, the amount of the toxic form of the substance that reaches the critical cellular target. For exposure monitoring, internal dose metrics could be sufficient biomarkers. For effect and (finally) risk assessment, biomarkers of the biologically effective dose are needed since they are related to the mechanism of toxic action of the substance in question.

In physiology-based pharmacokinetic modeling it is important to identify which are the compartments that play a fundamental role in the uptake, accumulation and transformation of the contaminant. These differ amongst species and contaminants. The assumption is that the contaminant distribution within the body is controlled by the blood flow rate. In other words, tissue blood concentrations are in equilibrium with tissue concentrations. Dynamic conditions of pollutants in internal organs are described at each time step through contaminant diffusion and flows at the interface organism-water and within the organism.

In the general compartment, controlled by the blood flow rate, the concentration of a chemical in a compartment is given by ordinary differential equations of the following general type:

$$\frac{dV_{tb} \cdot C_{tb}}{dt} + \frac{dV \cdot C}{dt} = Q \cdot (C_a - \frac{C}{P}) - rex \qquad (3)$$

And for the equilibrium between tissue blood concentration and tissue concentration,

$$C_{tb} = \frac{C}{P}$$

where:

C_{tb} = concentration of a chemical in tissue blood leaving the compartment (mass/volume)

C = tissue concentration (mass/volume)

P = tissue/blood equilibrium distribution ratio (Partition Coefficient)

V_{tb} = tissue blood volume (volume)

V = tissue volume (volume)

Q = blood flow rate through the tissue (volume/time)

C_a = concentration of the chemical in arterial blood entering the compartment (mass/volume)

rex = elimination rate

Additional terms may be present in specific compartments, as for example the contaminant exchange between water and gill, and the food assimilation in the alimentary canal.

Once the PBPK model has been developed, its calibration and validation are of fundamental importance. Several physiological, biochemical and physicochemical parameters have to be calibrated against existing data. Sensitivity analysis techniques can help to identify those exerting the strongest influence on the system under different initial and boundary conditions. Generally, attention has to be posed on attributing values to the partition coefficients and to the exchange rates. Literature data are rare for those parameters, and when available, they sometimes show wide ranges of variability.

Uncertainty and variability analysis

Uncertainty and variability are significant aspects in PBPK models, which should be separately analysed.

Variability typically refers to differences in the values of model parameters among individuals (inter-individual variability) or across time within a given individual (intra-individual variability). Variability may stem from genetic differences, physiological status, age, etc. (Krewski et al. 1995). Variability is inherent in animal and human populations and cannot be reduced and it is necessary to take variability explicitly into account within the calibration process.

Uncertainty, on the other hand, essentially is a result of lack of knowledge (Rowe 1994) and may have various sources. Toxicokinetic parameters are known only with finite precision and the use of standard values tends to give a false impression of precision for physiological parameter values (and thus for model predictions). At best, such standard or default values are approximate values for the average of a population. There always will be uncertainty about their true value for a particular group of animals or humans, and even more for a particular individual exposed. In addition, most chemical-specific parameters tend to be imprecise; i.e., they may have been measured *in-vitro* rather than *in-vivo* or they may be accessible only after fitting a model to toxico-kinetic data.

A good way to take into account the propagation of variability and uncertainty of input parameters to model predictions makes use of the Monte Carlo approach (Cronin et al. 1995, Gearhart et al. 1993, Thomas et al. 1996, Spear et al. 1991). This method is based on multiple repetition of model running using instead of fixed values of the model parameters a probability distribution for each of them and selecting randomly from its specified distribution. In this way a large number of different values for the model predictions is calculated. Those values can be used to create histograms approximating the probability distribution of any model prediction.

Monte Carlo methods also permit to distinguish between variability and uncertainty in model predictions when it is possible to separate the two for each model parameter as well as to carry out global sensitivity analysis.

One practical limitation of such approach, however, is that most of the simulations conducted using Monte Carlo methods are based on the assumption that all model parameters are independent from each other. This leads to very large confidence intervals in model predictions overestimating their actual spread (Portier et al. 1989).

A new comprehensive method was developed to avoid these limitations. It is still based on general Monte Carlo approach but the selection of all the models parameters is taken from their joint probability distribution (Gelman et al 1996).

The Bayesian statistical analysis can yield naturally such a joint distribution (called joint posterior distribution). Such an analysis leads to more relevant and useful classical Monte Carlo simulations, taking into account dependencies among all toxicokinetic parameters when computing model predictions (Bernillon et al. 2000).

Once the PBPK model has been calibrated and validated, this will enable the calculation of internal burdens for the target tissues. These will serve as internal dose exposure for the calculation of the toxicity model.

Integrated dose-response-time relationships

The straightforward and most common way for calculating fish mortality (or any other toxic effect) through a dose-effect relationship, is to relate mortality to the pollutant concentration in water. This can be done through Hill equations (4) with the maximum mortality (M_{max}) set to 100.

$$M(t) = \frac{M_{\max} \times C_w^n}{LC_{50}^n(t) + C_w^n} \qquad (4)$$

Where:

LC_{50} is the concentration of contaminant in water which causes the mortality of 50% of the exposed population.

C_w is the waterborne concentration and

n is the Hill coefficient

However, this equation provides a time-dependent mortality value as a function of the external concentration Cw and therefore,as mentioned above, a less reliable risk indicator as compared to those calculated as a function of internal doses.

The second approach consists of linking the internal concentrations of contaminants obtained for each organ through the PBPK model (both during the exposure and after the end of the exposure) to the related health end-point through biokinetic and toxicological parameters.

In this way it will be also possible to compare the mortality obtained as a function of pollutant concentration in water with that obtained as a function of the internal concentration, and to assess whether residual contaminant concentrations in the body can still represent a risk even when the external concentration of the medium is returned to control values.

For this approach, Liao et al. (2005) present two ways for calculating the mortality as function of internal organ concentration:

$$M_i = \frac{M_{\max} \times C_{f,i}^n}{(BCF_i \times LC_{50}(\infty))^n + C_{f,i}^n} \qquad (5)$$

$$M(t) = \frac{M_{\max} \times C_f^n(t)}{C_{L,50}^n(t) + C_f^n(t)} \qquad (6)$$

Where

M_i = mortality in target organ *i* for time of exposure approaching to infinite

M(t) = time-dependant mortality in target organ *i*

BCF_i = the Bioconcentration Factor for target organ *i*

C_f = Contaminant concentration in target organ *i*

$C_{L,50}(t)$ = organ-specific internal concentration which causes mortality of 50% of the population

n = the Hill coefficient

The two mortalities are related with each other by the $C_{L,50}(t)$, which can be expressed as in equation (7) (Liao et al. 2005):

$$C_{L,50}(t) = AUC_f \left(\frac{(k_2 + k_G)(1 - e^{-(k_2+k_G)t}}{(k_2 + k_G)t + e^{-(k_2+k_G)t} - 1} \right) + BCF(1 - e^{-(k_2+k_G)t})LC_{50}(\infty) \qquad (7)$$

and when the exposure approaches to infinity

$$C_{L,50}(\infty) = BCF \times LC_{50}(\infty) \qquad (8)$$

The mortality calculated with equation 5 represents the maximum mortality for that organ exposed to the specific concentration, and being the most conservative is that most used.

The calculation of the $C_{L,50}(t)$ implies an AUC-based toxicity model (AUC= Area Under the Curve), which relates the internal lethal body burden to biokinetic and toxicological parameters, such as the bioconcentration factor, the depuration rate constant (k_2), the uptake rate constant (k_1), the growth rate constant (k_G) and the $LC_{50.}$

The quoted biokinetic and toxicological parameters vary according to the kind of exposition and to the exposed species, as discussed above for the physiological parameters needed for the PBPK models. Values of those parameters can be found in literature or can be calculated using known formulas.

The integrated PBPK-Dose-Response modelling approach estimates target organ concentrations and dynamic responses from fluctuating concentrations of chemical contaminants of the aquatic environment. It couples a mathematical description of the pollutant kinetics in the body of the species based on physiological considerations with a pathology model which considers health risk metrics as a function of the biologically effective dose of the pollutant in different target organs.

This formulation relates ecotoxicological risk to the time course of the concentration of the pollutant in the water medium, allowing the identification of key dose metrics in specific target organs as early biomarkers of effects. By dynamically coupling the PBPK and the pathology models the complete dose–response profiles can be predicted for aquatic biota exposed to any dynamic concentration profile of waterborne pollutants.

Both the PBPK and the pathology (toxicity + pharmacodynamic) models are expressed as a system of coupled ordinary differential equations (ODEs). The use of the integrated PBPK-Dose-Response model also permits a better interpretation of the hazard associated with complex exposure. However, attention has to be given in the choice of the organs to analyse to assess the risk to the fish.

If now the results are drawn in a three-dimensional phase space (pollutant concentration in organs vs. time vs. mortality), it is possible to calculate a time-integrated biologically effective dose of the toxicant, which considers not simply the area under the dose-response curve, but rather the complex volume delimited under the three-dimensional dose-response-time surface.

4.2.2 Toxicological testing allowing to assess whether a predicted effect on organisms or populations has to be classified as a risk

To assess toxic and ecotoxic effects of chemicals during and/or following pollution disasters, numerous factors should be carefully considered to derive robust and quality information about adverse effects of the disaster situation on health of both humans and ecosystems. Thus, it is widely accepted that characterization of toxicity cannot rely on results of the single test but a set (battery) of rationally selected bioassays should be used for actual exposure scenarios. Following are the major points integrating the results derived during the ECODIS with the current state of knowledge:

- Exposure situation/scenario: Impacts of the pollution disasters are determined by the (i) chemical characteristics of the released contaminants (metals vs. organic compounds etc.; important environmental parameters such as chemical persistence, bioaccumulation, transport in water, soil, air, etc.), and (ii) parameters of the actual affected locality, ecosystem or region (geology and hydrology, climate, geomorphology, living biota including humans etc.). Prior to any toxicity testing, these conditions should be first evaluated by toxicologist experts and appropriate biotests selected (considering also economy of the testing). There is no single biotest that might be applicable for all disaster situations.

- Temporality of effects (acute/chronic): Bioassays should definitely provide information about risks of acute toxicity to biota (often lethality) that occurs as an immediate effect of the disaster. However risks of chronic sublethal effects (such as reproduction toxicity, chemical-induced cancerogenicity etc.) should also be assessed and appropriate bioassays developed and used.

- Natural mixtures and bioavailability: In spite of extensive experimental and modelling efforts, current knowledge does not allow certain predictions of environmental toxicity from the toxicity data of individual chemicals. Toxicity of environmental samples is a result of the interactions among complex mixtures of (i) inorganic and (ii) organic contaminants (iii) at variable concentrations (iv) within a complex of inherent environmental factors affecting bioavailability (pH, organic material content, suspended particles etc.). Therefore, robust bioassays for direct testing of complex mixtures should be developed and used.

- Fast response tests should be preferred (especially for the first tier testing during pollution disaster) as rapid information on toxicity is necessary to make appropriate decisions on protective measures.

- Toxicity and ecotoxicity. The first and immediate efforts during the chemical disaster are to save and/or protect health of human population, and information about **toxic risks to humans** must be derived. However, risks to other biota must be estimated in parallel and **ecotoxicity to major ecosystem functional groups** should be assessed (trophic levels - producers - plants/algae; consumers - invertebrates/vertebrates; destruents - microorganisms).

- Toxicological extrapolations. It was shown that effects of some chemicals (especially rapid and acute toxicity) might be extrapolated from one organism to others. Therefore (under specific and rather rare scenarios), experts may decide to use a single biotest and extrapolate the derived data.

- Standardization. Many bioassays have been studied and used for years, and they have also been standardized by international institutions, e.g. ISO, OECD, US EPA. These assays should be preferentially selected but they have many limitations regarded the other above mentioned criteria.

With the support of the ECODIS project, a comprehensive interactive **internet portal of toxicological bioassays DATEST 2.0** have been developed (http://projects.cba.muni.cz/datest/, Appendix 1). The portal integrates information on a wide range of ecotoxicological methods for the environmental risk assessment (standardized and validated as well as experimental). It has a search capabilities based on a comprehensive set of biotest parameters, and it should serve to toxicological experts both to select appropriate biotests and interpret the assay data.

A complex protocol for rapid and/or *in situ* assessment of toxic effects in all major trophic levels of biota including producers, consumers and decomposers is suggested. Previous research resulted in the set of validated toxicological assays, and their advantages and limitations as well as direct applications for the ecological risk assessment are available online in the form of the interactive web portal DATEST 2.0 (http://projects.cba.muni.cz/datest/). In addition to the standardized bioassays, which form the traditional core of the routine risk assessment, research in this frame of ECODIS aimed to integrate novel ecotoxicological tools suitable for complex environmental toxicity testing. The developed procedure involves both rapid acute bioassays such as kinetic bioluminescence inhibition test as well as more complex tools evaluating chronic toxicity (including endocrine disruptive effects or reproduction toxicity). Bioavailability was confirmed to play a key role in ecotoxicity, and understanding of its relationship to the toxic effects of chemical species (both metals and organic contaminants) will require further research attention.

1) Photosynthetic micro-algae and cyanobacteria (**trophic level - producers**) form dense biofilms on illuminated surfaces in streams, shallow lakes and seas, and they constitute an important component in the ecosystem. We used oxygen and pH microsensors to characterize the activity and micro-environmental conditions in the photosynthetic biofilms (both natural and artificial) exposed to toxic metals Cu and Cd. Our results showed that, over a period of several days, photosynthetic biofilms are resistant to high concentrations of Cu and Cd that are typically considered highly toxic and correspond to disaster conditions. The ECODIS results highlight the role of light and mass transfer limitation in the response of phototrophic biofilms to environmental pollutants. Furthermore, they identify a number of factors that need to be controlled or at least additionally monitored when conducting ecotoxicological tests. For example, light intensity (and spectral quality) and water flow-rate above the biofilm surface will strongly influence the effect of a pollutant, by influencing the pH and the cell growth rate. Intrinsic efficiency of cells to form a biofilm, as well as the overall density of cells and the amount and quality of excreted EPS in the biofilm, will also play an important role.

2) Bacterial bioassays (**trophic level - decomposers**) based on the inhibition of bioluminescence were used for ecotoxicological investigations for decades. However, their direct application to environmental samples (which are often turbid or coloured) was limited. In its studies ECODIS focused on contaminated sediments, and a novel bioassay, which allows extremely rapid 30 second assessment of toxicity of various types of samples (including turbid waters, sediment suspensions etc.) was validated. Kinetics of the bioluminescence naturally produced by marine bacteria *Vibrio fisheri* is continuously monitored after addition of the tested sample, and the change (decline) in emitted light is proportional to the toxic effect. The assay allows parallel testing of series of samples in the microplate format. Although the assay seems to be less sensitive than standardized long-term toxicity assays (also with respect to very short 30s exposure time), it provides good responses to the peaks of contamination during environmental disastrous situations. High natural variation in the toxicity of contaminated sediments (IC50 0.8 to >80 mg sediment dry wt/mL) was found, although sediments are considered less variable than flowing water. Interestingly, only minor correlations of toxicity with contaminant levels were found. Exchangeable protons (H+), content of organic carbon and two parameters from the silicate analysis were found to determine toxic responses

3) *In-ivo* bioassays for chronic toxicity with invertebrates (**trophic level - consumers**) represent ecologically relevant models for ecotoxicological studies. One of the major environmental problems, which affect natural aquatic communities, is endocrine disruption caused by contaminants able to interfere with hormone-regulated processes. The presence of specific chemicals affects endocrine balance in

invertebrates. ECODIS work emphasizes the need for integrated approaches combining *in-vitro* and *in-vivo* bioassays with identification of chemicals to elucidate ecotoxicological impacts of contaminated samples (Mazurová et al. 2008a,b).

4) *In-vitro* assays for rapid screening of specific types of toxicity (**trophic level - consumers, vertebrates**) are valuable tools in complex assessment of toxic chemical species and contaminated environmental matrices. Genotoxicity can be assessed by SOS-chromotest and GFP-yeast test, the presence of compounds with specific-mode of action by *in vitro* bioassays for dioxin-like activity, anti/androgenicity and anti/estrogenicity, toxicity can be tested by Microtox. Associations can be found with concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) as master variables. There were significant interrelations among dioxin-like activity, antiandrogenicity and content of organic carbon, clay and concentration of PAHs and PCBs, which documents significance of abiotic factors in accumulation of pollutants (Zounková et al. 2007). The ECODIS work demonstrated the strength of the specific bioassays in indication of the changes in contamination and emphasizes the crucial role of well designed sampling plan, where both spatial and temporal dynamics should be taken into account, for the correct interpretations of information in risk assessments.

5 Measures to minimize risk

Within the first hours after the occurrence of an emergency case a group of experts on civil protection should come together in order to draw decisions necessary for the protection of human health and the environment, e.g. experts on drinking water extraction, soil and groundwater protection. Depending on the type of disaster, specific techniques should be applied to reduce the short term risk. For example, oil spills or airborne hazardous compounds deposited on the water surface would require barriers on the water surface preventing the spread. Transport models are applied to calculate the spread of the pollutant plume. Such technical measures to minimize risk at the short term time scale are not the focus of the ECODIS project and will not be described in detail in the guidance presented here, as respective rules are provided by civil protection services and environmental authorities at the member state, regional or local level.

Decisions on long term measures to minimize the risk attributable to an accidental release of hazardous chemicals, i.e. decisions on measures supporting the recovery of impaired ecosystems, should be seen as one component of an integrated management of the water/sediment/soil/groundwater system. Such integrative approaches for the understanding and managing of multi-component systems have been developed at the river basin scale (for details on river basin management see Annex II, Part 4). Recently, a decision support system consisting of simulation models, databases and management options has been developed for the Elbe river basin (Lautenbach et al. 2009). Anyway, how to *manage* freshwater ecosystems impaired by a disaster is not a research topic of the ECODIS project and therefore the report presented here can not provide recommendations regarding the remediation technologies to be used and management tools to be applied. The extended review of the currently available information on remediation and river basin management given in Part B of this document accounts for the importance of effective measures reducing the negative impacts of disasters on freshwater ecosystems.

The ECODIS research fosued on monitoring techniques and their application for the investigation of the chemical status of ecosystems impaired by chemical disasters. Deep insight into the fate of contaminants in the system, the processes interconnecting relevant pools and especially the fraction of pollutant which is potentially mobile or bioavailable, is an important precondition for the management of ecosystems affected by chemical disasters. The obtained results will improve the methods suitable to collect the information necessary to draw decisions on remediation measures.

ANNEX to Part A: Supporting information: Cadmium related ECODIS results and thresholds set for the protection of the environment and human health

Table of Contents

1 Accidental releases of cadmium into aquatic ecosystems

Cd metal is used for NiCd batteries (portable batteries contain 11-15g Cd per 100g battery), alloys (e.g. Cu-Cd-alloys) and plating (resistant and highly ductile coatings of metals and alloys). Cd oxide is the starting material for a variety of compounds such as pigments (e.g yellow Cd sulfide) or heat stabilizers in rubbers and plastic[21]. Total Cd emissions to water in the EU-16 countries[22] are dominated by releases due to the production of iron, steel and other metals and the procession of phosphates for fertilizer production. Cadmium is one of the priority substances listed in the Water Framework Directive since it is present in the environment at annual mean concentrations which, in some areas in Europe, are above the thresholds of no concern. Information on physicochemical properties[23] and risk classification for Cd and CdO is given in Table 1 of this Annex.

For Cadmium diffuse inputs into aquatic ecosystems seem to play a more important role than accidents. In the MARS database[24] collecting data on major industrial accidents in Member States of the European Union (mandatory) and from other OECD countries (on a voluntary basis) only one accident[25] is reported for the combination water contamination and Cd as one of the substances involved. Two other accidents[26] are reported for heavy metals (see Part C for detailed information about MARS). Diffuse cadmium inputs

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[21] EUR 22919 EN, Chapter 2.2.

[22] Table 3.1.5.5 in EUR 22919 EN, Chapter 3.1.3.4

[23] see section 1.2 of the chapter 1 “Characterization of the release” of the guidance on pollution disaster monitoring and ecological impact prediction.

[24] http://mahbsrv.jrc.it

[25] A fire in a laboratory affected NiCd accumulators

[26] Contamination with heavy metals was due to an accident in a zinc and lead production plant and a fire in a chemical waste deposit.

into rivers and streams can be due, for example, to surface-water runoff in contaminated areas and leaching of cadmium containing waste. Within the ECODIS project joint *in-situ* measurements were carried out in rivers of the Lot-Garonne fluvial system in France which have been characterised with respect to metal pollution due to mining and industrial activities in previous studies (Blanc et al. 1999, Grousset et al., 1999 and Coynel et al. 2007). One of the two rivers exhibits relatively high and variable cadmium concentrations due to previous mining and industrial activities and present run off from mining waste during rain events.

2 Monitored Cd concentrations in water

Table 2 of this Annex provides information on both, monitored Cd concentrations for several types of aquatic ecosystems and threshold values set for their protection. In the stream Elbe annual mean concentrations of cadmium were found which were distinctly below the Predicted No Effect Concentration ($PNEC_{water}$) defined within REACH and Environmental Quality Standards for annual average levels and maximum concentrations set within the WFD (for details see footnotes of Table 2). Higher concentrations and threshold exceedances were monitored in water of smaller rivers such as the Mulde river, a tributary to the Elbe, and in Riou Mort, both affected by anthropogenic Cd pollution. In streams, a lower proportion of the total Cd is found in the filtrate, the < 45 µm fraction, than in small rivers, and the variability of concentrations seems to be distinctly lower.

Selected results of the joint Cd monitoring activities carried out within the ECODIS project are shown in Figure 1. Water of the Lot river was less contaminated with cadmium than water of Riou Mort (Figure 1, B). Upstream of the Riou Mort mouth the assessment of the chemical status of the Lot river resulted in Cd concentrations (Figure 1, B) below the threshold set in the Water Framework Directive for the maximum allowable concentration (Figure 1, C: table 2). The concentration in the contaminated water of Riou Mort made up the twelve fold of the MAC-EQS in 2007 and the 5.7 fold in 2008. Although the concentration was lower in the second year, the amount of metal passing the sampling site per second was much higher (Figure 2, C) as a result of the higher water flow rate (Figure 2, A) due to strong precipitation during the measurement period.

3 Selected ECODIS results on fate processes

3.1 Flow rate and Cd speciation

Metal speciation was investigated under conditions of high (Riou Mort) and low (Lot river) water hardness and high (2008) and low (2007) flow rates. At increased flow rates a higher proportion of the total metal in the water is bound to particles > 0.45 µm, due probably to a significant re-suspension of particles from the sediment under high water flow velocity. Combining *in-situ* data obtained with the GIME sensor and the total dissolved Cd fraction determined in the filtrate shows that the Riou Mort water shows characteristics in speciation which are present as well, but to a lower extent, in water of the Lot river at the first station downstream of the confluence. In the Riou Mort water a higher proportion of the total dissolved Cd was dynamic (free metal ions + dynamic (labile and mobile) complexes with a size of a few nm) as compared to the reference station at the river Lot (B in Figure 1).

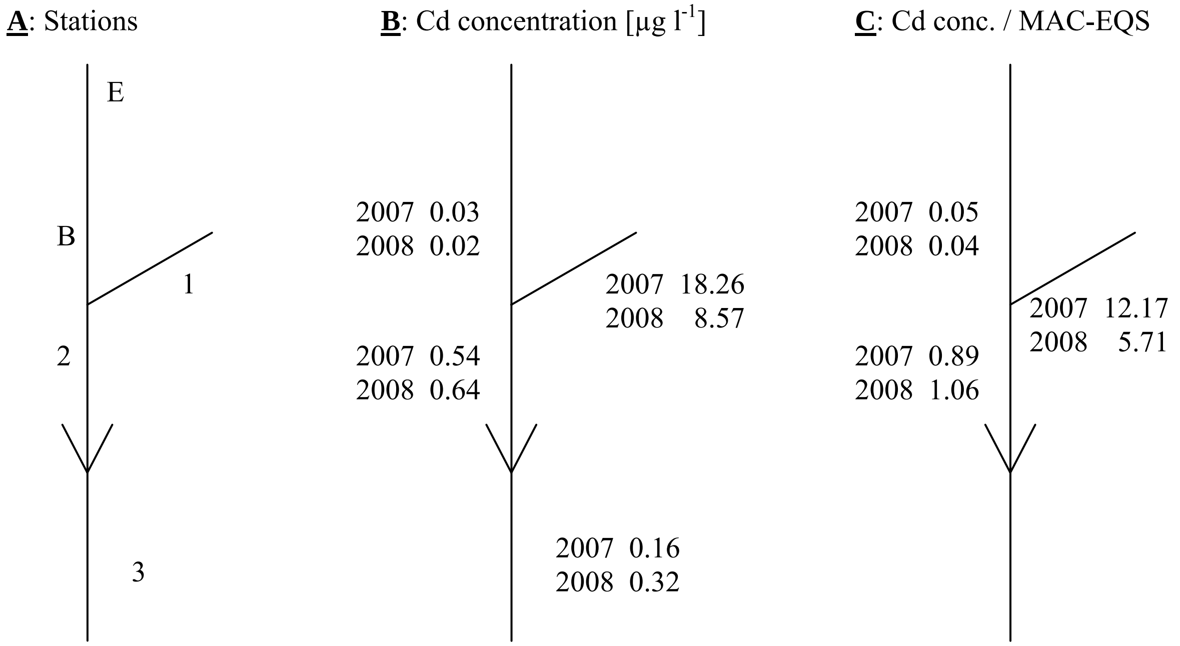

Figure 1 Example for monitoring activities carried out within the ECODOIS project at the Lot river (vertical line) in France and the Riou Mort, a river contaminated with metals due to mining and industrial activities. The Riou Mort is a tributary of the river Lot. The confluence is located 3.3 km upstream of Bouillac. **A**: The sampling/measuring sites were: Boisse-Penchot[27] (B) located 2,6 km upstream of the Riou Mort mouth, Joanis bridge (1) at Riou Mort, 2 km upstream of the confluence, Bouillac (2) is located 3.3 km downstream of this point, and Capdenac (3) 10 km downstream the Riou Mort discharge. The flow data for river Lot are available for a station in Entraygues (E), about 40 km upstream of Bouillac. **B**: Cadmium concentration in filtered water samples taken on 30.4.2007 and 25.4.2008 determined using ICP-MS[28]. **C**: ratio of the detected Cd concentration to the MAC-EQS[29] of the WFD, i.e. the concentration set by legislation as the level of no concern for the respective hardness class of the water[30] (class 3 for river Lot and class 5 for Riou Mort).

3.2 Cd sink or source function of the ecosystems investigated within ECODIS

Sink-source relationships of the ecosystems and the dynamics of immobilisation and remobilisation processes are reflected by the data shown in Figure 2. In 2007 the amount of Cd passing station 2 located 3.3 km downstream of the confluence of the rivers was lower than the sum of the fluxes calculated for stations 1 and B and thus clearly reflecting the immobilisation of the metal immediately downstream the

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[27] 44°35', 2°12'

[28] Inductively coupled plasma mass spectroscopy.

[29] Maximum allowable concentration. For river Lot and Riou Mort the hardness classes of 3 and 5 correspond to MAC-EQS values of 0.6 and 1.5 µg l^{-1} and AA-EQS of 0.09 and 0.25 µg l^{-1}, respectively (see also Table 2.) AA-EQS is the threshold set for the annual mean concentration (12 samples taken over the year)

[30] The hardness was calculated from the reported Ca and Mg concentrations, for more information on the hardness classes see footnote "d" of Table 2.

Riou Mort mouth. Contrasting results were obtained in 2008. The amount of cadmium passing station 2 was much higher than the sum of the Cd fluxes calculated for stations 1 and B (Figure 2, C). Probably Cd was remobilised with resuspended sediment due to differing flow characteristics and especially to the high flow rate present in 2008.

The cadmium immobilisation found for the first kilometers downstream of the RiouMort – Lot river confluence is in agreement with results reported by Blanc et al. (1999). The authors investigated the cadmium budget for the Lot-Garonne fluvial system. Modelling results suggest that 95 % of the dissolved cadmium input into the Lot river is taken up by the particulate phase over 0.5 km downstream the Riou Mort mouth. The Cd contribution of the Lot to the Garonne was 90 % particulate, whereas the Cd input into river Lot is 75% dissolved. 87 % of the latter was attributed to the Riou Mort tributary.

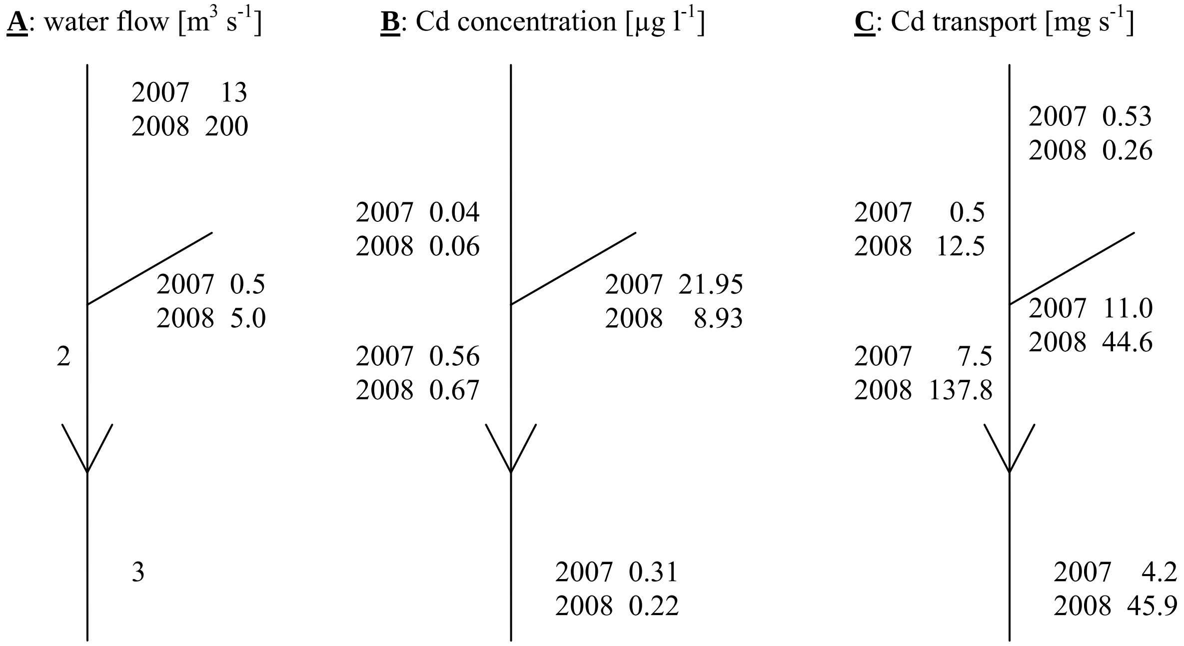

Figure 2 Example for *in-situ* data reflecting the Cd sink function of the part of the river lot downstream of the Riou Mort discharge observed in 2007 at low water flow rate and the source function for Cd of the same part reflected by the data sampled in 2008 at more than tenfold higher water flow and thus re-mobilisation of immobilised metal. For information on the sampling/measuring sites see the legend of Figure 1. **A**: average water flow rate for the rivers Riou Mort and Lot[31] and total Cd concentrations (**B**) for the 29.4.2007 and the 28.April 2008. **C**: Calculated amount of total Cd passing the measuring site per second.

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[31] The river Lot water flow rates were detected more than 30 km upstream, so that the real flow rates might have been higher due to discharges of other rivers. The flow data were taken from graphs and have to be regarded as approximate values.

3.3 Monitoring of diurnal variations in total dissolved Cd

A diurnal variation in dissolved Cd determined with ICP-MS was observed in water of Riou Mort during an ECODIS measurement campaign performed in June 2008[32]. Concentrations were low during the day, and high at night (Figure 3) as described in detail in Beck et al. (2009). These cycles were apparently driven by variations in water pH, as photosynthesis in the benthic biofilms caused pH to increase during the day. During the night respiration lead to a decrease in pH. These pH changes then affected Cd sorption to surfaces in the river such as colloids, particles, and the benthic biofilms[33]. At high pH the Cd concentration in filtered water was relatively low showing that the fraction bound to particles (> 0.45 µm) was relatively high (Figure 4). The assumption that photosynthetic activity was responsible for diurnal pH and Cd variation in the water are supported by laboratory experiments with biofilms showing that diel metal cycles could be replicated, and were indeed stopped when photosynthesis was inhibited.

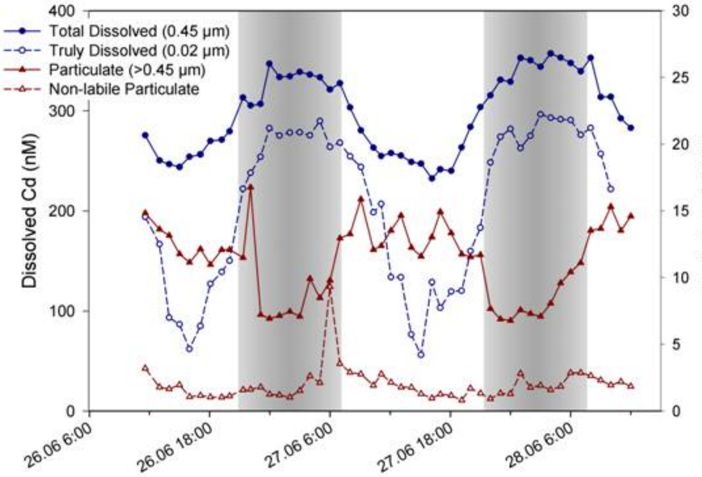

Figure 3 Time course of dissolved and particulate Cd in the Riou-Mort detected using ICP-MS with samples taken during a joint ECODIS measuring activity in June 2008 (Beck et al. 2009). For more details see ECODIS deliverable D26: "Influence of microbial processes on pollutant exchange".

Continuously working voltammetric sensors were also applied to detect metal cycling. Continuous in-situ measurements of the dynamic metal fraction using GIME sensors (section 1.3.1) revealed clear diurnal cycles for Cu, Pb and Cd (Tercier-Waeber et al. 2009). In April 2007, the minimum Cd concentration occurred in the late afternoon, a pattern which is in coincidence with the above mentioned variation in total dissolved cadmium concentration detected in June 2008. In contrast, the data recorded in April 2008 show a lower amplitude and highest Cd concentrations in the afternoon. This observation, coupled with other monitored data, strongly suggested that, in the Riou-Mort River, the diurnal cycling of Cd_{dyn} is controlled by the balance between two distinct, competitive processes: biofilm-induced sorption processes and photo-reduction of small colloidal Mn oxides. In the presence of optimum conditions for biofilm photosynthesis, sorption processes prevail, whereas in the absence of significant biofilm activity, photoreduction seems to control Cd_{dyn} (see Tercier-Waeber et al 2009 for details). In summary, the results clearly show that benthic biofilms and other processes can have a profound impact on heavy metal cycling in natural waters. The

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[32] The water column of the Cd-contaminated French river, Riou Mort, was sampled hourly to investigate how diel cycles in water parameters (e.g., temperature, pH, oxygenation) influence metal concentrations and partitioning between different pools of metal species.

[33] The data suggests that early in the morning, the pH at the biofilm surface decreases in the light, and metal transfer is from the water to the benthic substrate. Later in the day, as the bulk water pH changes, dissolved Cd transfers from the truly dissolved pool onto colloids and particles. After photosynthesis stops late in the day, the metal ions desorb from surfaces and return to the dissolved pool. Interestingly, the "truly dissolved" (< 0.02 µm) Cd pool showed the most substantial variation; this operationally-defined fraction may be representative of the bioavailable metal concentrations, and indicates that these diel cycles could be ecologically relevant.

implication of these findings routine monitoring of contaminants in the environment has been mentioned in section 1.3.2 of the guidance.

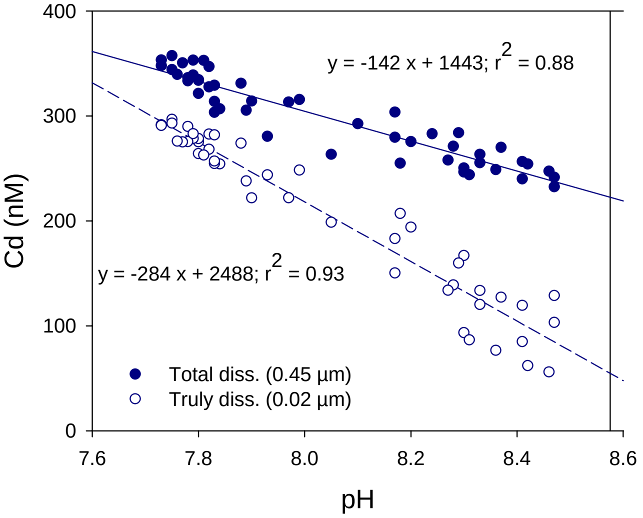

Figure 4 Co-variation of dissolved Cd and pH in the Riou Mort (June 2008). The Cd concentration was determined using ICP-MS in the filtrate obtained using 0.45 µm and 0.02 µm pore size filter (Beck et al. 2009).

4 Bioconcentration and bioaccumulation factors for cadmium

Table 4 reflects the high variation in bioconcentration and bioaccumulation factors between and within trophic groups (algae, invertebrates and vertebrates). These factors have been determined in numerous studies evaluated for the European Union Risk Assessment Report[34] "Cadmium oxide and Cadmium metal". Differences in experimental conditions lead, among other factors, to this variability. Table 4 gives, in addition, bioaccumulation factors calculated for three fish species of the Riou Mort from data reported in a study on cadmium contamination in the organs of fish collected in the Riou Mort. The risk assessment report assumes a (median) bioconcentration factor of 15 $l\ kg^{-1}_{ww}$ for vertebrates and the whole body content, whereas different organs exhibit bioconcentration factors varying over a wide range (from 2.9 to 2596 $l\ kg^{-1}_{ww}$). The data for chubs (*Leuciscus cephalus, Cyprinidae*) revealed highest bioconcentration factors for kidneys and lowest for muscle meat.

5 Cadmium risk to fish eating birds and human health

Both the REACH risk assessment report and the WFD related Cd EQS Data Sheet define a concentration of 0.16 mg $kg^{-1}_{\text{wet weight}}$ as the level of no concern. Concentrations in prey or food above this threshold are regarded as a risk to mammals and fish eating birds. Concentrations in muscle meat of fish collected in Riou Mort were distinctly lower than this threshold, whereas oncentrations in some organs exceeded the threshold value. The lower thresholds set for edible parts of fish aiming at the protection of human health were only slightly exceeded in fish sampled in the cadmium contaminated Riou Mort. Whether fish collected in the Mulde, a river with Cd concentrations exceeding $PNEC_{water}$ (Table 1) showed cadmium concentrations in muscle meat which were above the threshold set for the protection of human health, was dependent on the species and the age of the individuum. The eel (*Anguilla anguilla*) with a higher fat content did not meet the threshold, whereas breams (*Abramis brama, Cyprinidae*) showed Cd concentrations below the threshold level.

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[34] EUR 22919 EN

Table 1 Cadmium – General substance information, physicochemical properties and risk classification[a]

	Cd metal	Cd oxide
CAS number	7440 – 43 – 9	1306 – 19 – 0
atomic/molecular weight	112.41 g	128.41 g
physical state	Solid	Solid
relative density	8.64 g cm^{-3}	8.15 g cm^{-3}
solubility in water	quoted as insoluble[b]	quoted as insoluble[c]
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 chield	
	T; R48/23/25 toxic, danger of serious damage to health by proplonged 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	

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[a] EUR 22919 EN, Chapter 1.1 and 1.3.

[b] The dissolved Cd concentration in water with 100 mg l^{-1} substance at pH 8 measured after 7 days was about 135 µg l^{-1} for cadmium metal powder and 227 µg l^{-1} for Cd oxide powder (EUR 22919 EN, Table 1.1).

Table 2 Cadmium in water, concentrations in μg l^{-1}.

Mandatory A level, defining quality of surface water intended for the abstraction of drinking water		5	Council Directive 75/440/EEC, OJ No L194, 1975
Drinking water standard never to be exceeded at the tap		5	Council Directive 98/83/EC, OJ No 330/32, 1998
Standard for drinking water quality		3	Guidelines for drinking-water quality (WHO 2008)
Environmental Quality Standard AA-EQS[c] (Annual Average) for the protection of pelagic communities of inland surface waters, i.e. rivers and lakes (depending on water hardness class[d])		≤ 0.08 (Class 1)	Water Framework Directive (WFD 2008), Annex I
		0.08 (Class 2)	
		0.09 (Class 3)	
		0.15 (Class 4)	
		0.25 (Class 5)	
Environmental Quality Standard MAC-EQS[d] (Maximum Allowable Concentration) for the protection of pelagic communities of inland surface waters, i.e rivers and lakes (depending on water hardness class[e])		≤ 0.45 (Class 1)	
		0.45 (Class 2)	
		0.6 (Class 3)	
		0.9 (Class 4)	
		1.5 (Class 5)	
Environmental Quality Standard AA-EQS[d] (Annual Average) for other surface waters, i.e. transitional, coastal and territorial waters		0.2	
NOEC (chronic tests only) min / median / max / n	Fish and amphibians	0.47 / 4.2 / 62 / 19	EUR 22919 EN, Chapter 3.2.2.5
	Aquatic invertebrates	0.16 / 2.0 / 11 / 22	
	Primary producers	0.85 / 6.9 / 31 / 8	
Predicted No Effect Concentration PNEC$_{water}$ [e]		0.19	EUR 22919 EN, Chapter 3.2.2.6.3

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[c] For Cd, Pb, Hg and Ni the EQS refers to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 μm filter or any equivalent pre-treatment. For other substances the EQS is expressed as total concentration in the whole water sample (see also Lepper 2005). If natural background concentrations for metals are higher than the EQS value Member States may take this into account when assessing the monitoring results against the EQS (WFD 2008). The natural background concentration of cadmium in the Rhine is 0.003 μg l^{-1} "dissolved" Cd and 0.3 mg kg^{-1} suspended particulate matter (Cd-EQS-Data-Sheet 2005). This publication further gives AA-EQS values for suspended particulate matter calculated as AA-EQS$_{SPM}$ = AA-EQS$_{filtrate}$ * K$_{p}$, where K$_{P}$ is the substance specific partition coefficient defined as the concentration of Cd in SPM (mg kg^{-1}) divided by the concentration in the filtrate (mg l^{-1}). The applied K$_{p}$ for Cd of 130000 l kg^{-1} has been derived from a review of several studies (Cd-EQS-Data Sheet (2005), chapter 5). The AA-EQS$_{water}$ values of 0.08, 0.15 and 0.25 μg l^{-1} are thus corresponding to AA-EQS$_{SPM}$ values of 10, 20 and 30 mg kg^{-1}, respectively.

[d] Water hardness Class 1: < 40 mg CaCO$_3$ l^{-1}; Class 2: 40 to < 50 mg CaCO$_3$ l^{-1}; Class 3: 50 to < 100 mg CaCO$_3$ l^{-1}; Class 4: 100 to < 200 mg CaCO$_3$ l^{-1}; Class 5: ≥ 200 mg CaCO$_3$ l^{-1} (WFD 2008). Water hardness refers to compounds titrated with EDTA (Calcium and Magnesium Ions), expressed as mg CaCO$_3$ l^{-1} (European legislation) equivalent to ppm CaCO$_3$ according to the nomenclature used in the United States.

[e] For the dissolved phase of a water sample obtained by filtration through a 0.45 μm filter. The PNEC for water of 0.19 μg l^{-1} was derived using the sensitivity distribution method for extrapolation. Application of the assessment factor method yields a PNEC for water of 0.016 μg l^{-1} using the lowest assessment factor of 10. Both methods used for the calculation of PNECs from NOECs are desribed in ECHA 2008, Part R10, chapter R.10.3. Since the number of reliable toxicity studies on Cd effects is high, the sensitivity distribution method could be used. Applying the U.S. EPA algorithm describing the dependence of Cd toxicity on water hardness (EUR 22919 EN, chapter 3.2.2.6.4) yields in the equation PNEC$_{water,H}$ =0.09((H/50)^0.7409), where H is the hardness in mg CaCO$_3$

Cd concentration in water of the Mulde river, annual mean values 2006, monitoring station Dessau[f]				0.29 filtered 0.40 total	Gewässergütebericht der Elbe 2006 (ARGE-Elbe 2008)
Cd concentration in water of the Elbe river, annual mean values 2006, monitoring station with lowest concentrations (Seemannshöft)[g]				0.02 filtered 0.12 total	
Cd concentration in water of the Elbe river, annual mean values 2006, monitoring station with highest concentrations (Magdeburg)[g]				0.06 filtered 0.16 total	
Temporal trends in the measured Cd concentration in the Rhine, The Netherlands total Cd in the water [µg l^{-1}] and Cd in SPM [mg kg^{-1}]			1990	0.18 µg l^{-1} 5.3 mg kg^{-1}	EUR 22919 EN, Annex J
			1995	0.24 3.8	
			1998	0.15 3.5	
			1999	0.13 3.0	
			2000	0.09 7.5	
Cd concentration[g] in water revealed from ECODIS studies	Riou Mort	29. April 2007[h] (flow < 1 m^3 s^{-1})		19.9 filtered 21.9 total	Calculated from data determined within ECODIS provided by M. Tercier-Waeber, University of Geneva, Ch
		25. April 2008[i] (flow ca. 5 m^3 s^{-1})		8.6 filtered 11.9 total	
		27. June 2008 (flow < 1 m^3 s^{-1})	Night maximum	40.3 filtered 41.0 total	Calculated from data in Beck et al. (2009) and ECODIS D26: "Influence of microbial processes on pollutant exchange".
			Day minimum	25.8 filtered 27.3 total	
	Lot river[j]	2.6 km upstream of the Riou Mort mouth[k]	29. April 2007 (flow low)	0.03 filtered 0.04 total	Calculated from data determined within ECODIS provided by M. Tercier-Waeber, University of Geneva, Ch
			25. April 2008 (flow high)	0.02 filtered 0.11 total	
		10 km downstream of the Riou Mort mouth[l]	29. April 2007 (flow low)	0.23 filtered 0.31 total	
			25. April 2008 (flow high)	0.16 filtered 0.32 total	

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l^{-1}. and PNEC$_{water,H}$ is PNEC at the hardness H. The hardness correction is not recommended in the Cd risk assessment report with the argument that no NOEC data are available for low water hardness.

[f] No measured water hardness data available.

[g] Detected using ICP-MS

[h] Average over 3 samples taken during the day, standard deviation < 11 % of the average.

i Average over 3 samples taken during the day, standard deviation < 4 % of the average.

[j] Approximate flow rates for River Lot taken from graphs showing the data detected in Entraygues (about 40 km upstream of the Riou Mort discharge) were 13 m^3 s^{-1} on the 29th of April 2007 and about 200 m^3 s^{-1} on the 25th of April 2008.

k Station Boisse-Penchot, one sample per day.

[l] Station Capdenac, on 29. April 2007 mean of 2 samples differing < 0.3 µg l^{-1}; on 25. April 2008 average over 3 samples taken during the day, standard deviation < 10 % of the average.

Table 3 Cadmium in sediment, concentrations in mg $kg^{-1}_{dry\ weight}$

Specific Quality Standard for the protection of benthic communities in freshwater sediment[m]	2.3	Cd-EQS-Data Sheet 2005, chapter 6.1.2, refering to EUR 22919 EN, chapter 3.2.4.3.
Specific Quality Standard for the protection of benthic communities in marine sediment	- [n]	

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[m] The Quality Standard for sediment given Cd-EQS-Data Sheet 2005, chapter 6.1.2 equals the $PNEC_{sediment}$ of 2.3 mg Cd $kg^{-1}_{dry\ weight}$ reported in the Cd risk assessment report (EUR 22919 EN, chapter 3.2.4.3) and was calculated using the assessment factor method described in ECHA 2008, Part R10, chapter R10.5.2.2. The generic $PNEC_{sediment}$ derived with the equlibrium partioning method which can be used if no toxicoloy data are available was 2.5 mg Cd $kg^{-1}_{dry\ weight}$ (Cd-EQS-Data Sheet 2005, chapter 6.1.2.).

[n] The derivation of quality standards for marine sediments was not possible due to a lack of toxicity data of marine benthic organisms (Cd-EQS-Data Sheet 2005).

Table 4 Cadmium bioconcentration[o] and bioaccumulation[p] factors for freshwater organisms in l kg^{-1} and for benthic invertebrates and vertebrates in kg kg^{-1}.

bioconcentration factor (min / median / max)	algae[q]	wet weight	1636 / 7535 / 23143	EUR 22919 EN, chapter 3.2.7.2.1
		dry weight	2222 / 11512 / 310000	
	invertebrates	wet weight	396 / 994 / 17560	
		dry weight	546 / 5000 / 33333	
	vertebrates	wet weight	0.51 / 229 / 6484	
		dry weight	5 / 233 / 33333	
	vertebrates, total body content	wet weight	0.51 / 15 / 511	
		dry weight	5 / 80 / 1385	
bioaccumulation factor (min / median / max)	vertebrates, total body content	wet weight	1 / 42 / 623	EUR 22919 EN, chapter 3.2.7.2.2
		dry weight	4 / 167 / 2492	
bioaccumulation factor (min / median / max)	invertebrates [kg $_{\text{dry weight}}$ kg^{-1} $_{\text{wet weight}}$]		0.38 / 0.43 / 0.44	EUR 22919 EN, chapter 3.2.7.4.1
	invertebrates [kg $_{\text{dry weight}}$ kg^{-1} $_{\text{dry weight}}$]		0.01 / 0.28 / 1.15	
	vertebrates [kg $_{\text{dry weight}}$ kg^{-1} $_{\text{wet weight}}$]		0.006 / 0.07 / 0.18	
bioconcentration factors for organs of fish species collected in Riou Mort [l kg$^{-1}_{\text{ww}}$] (for conc. in fish see table 5, total Cd conc. in water 29 µg l^{-1})	roach (*Rutilus rutilus*)	muscle	2.14	Calculated from data given in Andres et al. (2000)
	carp bream (*Abramis brama*)		1.48	
	chub (*Leuciscus cephalus*)		2.93	
		kidney	2596	
		intestine	551	
		liver	269	
		gills	93	

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[o] Bioconcentration factors [l kg^{-1}] are calculated as the concentration in the organism [mg kg^{-1}, on a wet weight or dry weight basis] divided by the concentration in water [mg l^{-1}] or as the ratio of the uptake rate constant [l kg^{-1} d^{-1}] and the depuration rate constant [d^{-1}] as described in ECHA 2008, Part R.16, chapter R16.4.3.5 and Part R.7, chapter R.7.10. In this table "dry weight" means that all data reported on a dry weight basis were converted to wet weight data. For this conversion an average dry matter content of 10% was assumed. High water hardness and high contents of humic acids are associated with low BCF. At Cd concentrations > 10 µg l^{-1} in the water the concentration in fish tissue does not increase further so that the BCF decreases.

[p] Bioaccumulation factors account for all uptake routes, i.e. water and food for freshwater vertebrates (ECHA 2008, Part R.16, chapter R16.4.3.5 and Part R.7, chapter R.7.10). The "wet weight" data were calculated assuming a mean dry weight to wet weight ratio of 0.25 for the whole fish.

[q] BCFs for algae were obtained by measuring the Cd concentration in water and algae. High BCFs do not necessarily reflect high Cd intake in algae because a significant proportion of Cd is adsorbed to the cell wall.

Table 5 Cadmium in food of mammals and birds, in tissues of the prey of predators, and human health related concentrations in edible parts of fish in mg $kg^{-1}_{wet\ weight}$

Predicted No Effect Concentration $PNEC_{oral}$ [r] for the protection of mammals and birds (Cd content in food of mammals and birds)		0.16	EUR 22919 EN, chapter 3.2.7.5.1
Specific Quality Standard for the protection top predators (Cd content in prey)		0.16	Cd-EQS-Data Sheet 2005, chapter 6.1.3, refering to EUR 22919 EN, chapter 3.2.7.5.1
Maximum level for Cd	in muscle meat of fish	0.05	EC 1881/2006[s]
	in muscle meat of a selection of certain fish species[t]	0.1	
	in muscle meat of sword fish (*Xiphias gladius*)	0.3	
	in bivalve molluscs	1.0	
Cd in muscle meat of fish harvested in the Mulde river[u]	carp bream (*Abramis brama*) n=6	< 0.001 – 0.009	ARGE-Elbe (2003)
	eel (*Anguilla anguilla*) n=7	< 0.005 – 0.109	
Cd in muscle meat of fish[v] species sampled in Riou Mort	roach (*Rutilus rutilus*) n=8	0.062 ± 0.036	Andres et al. (2000)[w]
	carp bream (*Abramis brama*) n=3	0.043 ± 0.025	
	chub (*Leuciscus cephalus*) n=12	0.085 ± 0.013	
Cd in organs of chubs (*Leuciscus cephalus*) collected in Riou Mort	Kidney	75.3	
	Intestine	16.0	
	Liver	7.8	
	Gills	2.7	

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[r] Applying the assessment factor method (see footnote Table 2) revealed $PNEC_{oral}$ values of 0.3 and 0.16 mg kg^{-1} for mammals and birds, respectively. The overall $PNEC_{oral}$ value is based on the lowest NOEC. $PNEC_{oral}$ concentrations calculated using statistical extrapolation are 1.9 mg kg^{-1} for mammals and 0.75 mg kg^{-1} for birds. Guidance on the derivation of $PNEC_{oral}$ is given in ECHA 2008, Part R10, chapter R.10.8. The risk for fish eating predators (mammals or birds) can be calculated as the ratio between the predicted concentration in their food ($PEC_{oral\text{-}predator}$) and the $PNEC_{oral}$ value. Section R.16.5.7 of ECHA 2008 describes how $PEC_{oral\text{-}predator}$ should be calculated.

[s] Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

[t] Anchovy (*Engraulis spec.*), bonito (*Sarda sarda*), common two-banded seabream (*Diplodus vulgaris*), eel (*Anguilla anguilla),* grey mullet *(Mugil labrosous labrosus),* horse mackerel or scad *(Trachurus spec.),* louvar or luvar *(Luvarus imperialis),* sardine (*Sardina pilchardus*), sardinops (*Sardinops spec.*), tuna (*Thunnus spec., Euthynnus spec. Katsuwonus pelamis*), wedge sole (*Dicologoglossa cuneata*).

[u] Fish was harvested in May 2002. The corresponding Cd concentration in the water, averaged over the 12 months prior to harvesting, was 0.396 µg l^{-1} (minimum and maximum values 0.11 and 0.70 µg l^{-1}, respectively, n=13), the data are available via http://www.arge-elbe.de/wge/Download/DDaten.php.

[v] The three fish species belong to the cyprinidae, a group showing a wide tolerance to environmental factors, especially temperature and oxygen. Young chubs are omnivorous eating mostly small insects and detritus, while oldest individuals become carnivorous. Roaches are preferentially herbivorous, and breams consume invertebrates by sucking the sediments (Andres et al. 2000).

[w] The concentrations were taken from graphs published by Andres et al. (2000). They have to be considered as approximate values.

Part B: Related EU legislation, other research activities and River Basin Management

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1 Related EU legislation

The most important EU legislations which may to be taken into account in pollution disaster impact assessment and monitoring are:

- REACH (registration, evaluation and authorization chemicals produced and used as foreseen)
- SEVESO (industrial accidents, novel techniques and prevention)
- IPPC (emissions and prevention)
- WFD (monitoring, measures and ecology)
- UNECE (industrial accidents and transboundary effects)

Although all of these legislations include chemicals, currently no EU legislation exists which incorporates chemical disaster events and impact assessment/monitoring of aquatic ecosystems.

1.1 REACH - Registration, Evaluation, Authorisation and restriction of Chemicals Regulation

This EU regulation (http://echa.europa.eu/reach_en.asp) on Registration, Evaluation, Authorisation and restriction of Chemicals (REACH) requires demonstration of the safe manufacture of chemicals and other substances (including metals) and their safe use throughout the supply chain. REACH is based on the precautionary principle. The regulation was agreed by Council and European Parliament on 18 December 2006 and entered into force on the 1st of June 2007. It aims to have a good balance between improving the protection of human health and the environment, and maintaining industry competitiveness. The regulation rationalises the current EU regulatory system for chemicals and replaced over 40 pieces of previous legislation. It carries forward existing EU restrictions regime and safety data sheets systems. REACH introduced new registration requirements covering all substances supplied above 1 tonne per year, and new authorisation requirements covering substances of very high concern (e.g. carcinogens). Finally, REACH transfers responsibility for gathering data and carrying out initial risk assessments from the authorities to industry.

The key REACH elements are:

- Registration – a manufacturer or importer will need to register any substance supplied to the EU market above 1 tonne per year;
- Evaluation – the authorities will carry out annual in-depth evaluations (i.e. assessments) of substances flagged as being of potential high risk (e.g. on the basis of information provided at registration);

- Authorization – the uses of substances of very high concern, e.g. CMRs (Carcinogens, Mutagens, and toxic to Reproduction), PBTs (Persistent, Bioaccumulative, and Toxic), and vPvBs (very Persistent, very Bioaccumulative) will require authorisation;

REACH has published guidances which describe the information requirements under REACH with regard to substance properties, exposure, use and risk management measures, in the context of the chemical safety assessment (Figure 1). These guidance documents are aimed to help all stakeholders with their preparation for fulfilling their obligations under the REACH Regulation.

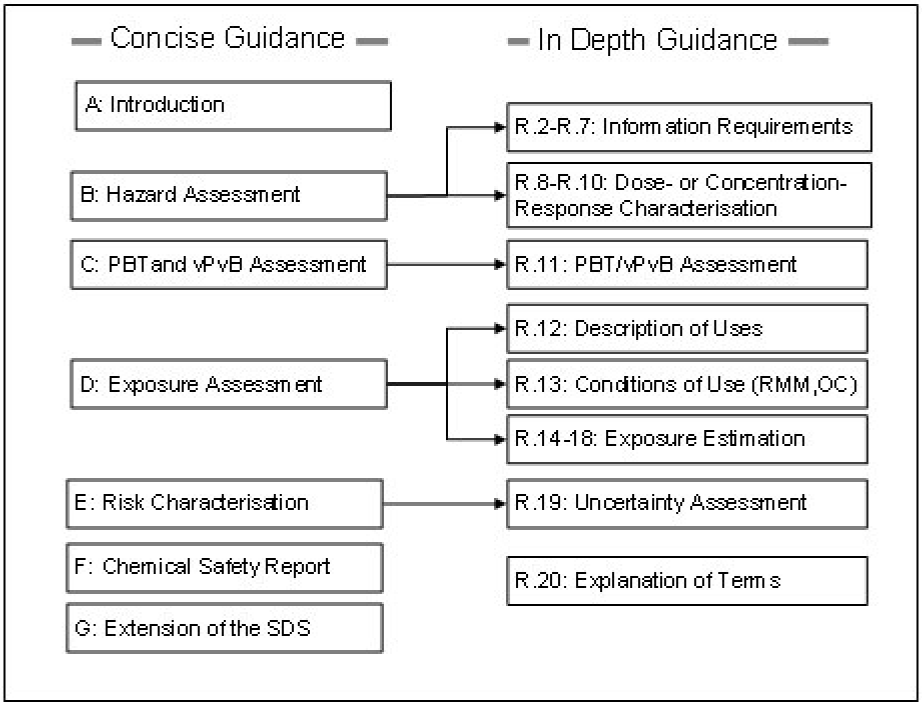

Figure 1 Guidelines of REACH (http://guidance.echa.europa.eu/docs/guidance_document/information_requirements_en.htm)

1.2 SEVESO Directive

The council directive on the major-accident hazards of certain industrial activities (Seveso I) defines a number of requirements for the operators of industrial sites where a certain amount of dangerous substances is present. In particular, operators of sites where the amount of dangerous substances exceeds the thresholds laid down in Annex 1 of the directive has to define a major accident prevention policy, and for the upper tiers to establish a safety report, implement a safety management system and define an internal emergency plan. These requirements aim at preventing major accidents and mitigating their consequences, in order to protect human health and the environment.

The Seveso I Directive has currently been replaced by the Seveso II Directive. The aim of the Seveso II Directive is to 1) prevent major-accident hazards involving dangerous substances, and to 2) limit, as accidents do continue to occur, the consequences of such accidents not only for man (safety and health aspects) but also for the environment (environmental aspect).

The scope of the Seveso II Directive has been broadened and simplified at the same time. It solely relates to the presence of dangerous substances in establishments. ‘Presence of dangerous substances’ is defined as the actual or anticipated presence of such substances or the presence of substances which may be generated during loss of control of an industrial- chemical process. Thus, the scope covers both, industrial “activities” as well as the storage of dangerous chemicals.

There are two major changes with regard to the Seveso I Directive:

- The old Directive contained a list of particular installations described by a number of activities. The Seveso II Directive no longer contains such a list. Therefore, the need to define the term industrial activity no longer exists. Moreover, the list of named substances has been reduced from 180 to around 50 substances.
- Whereas the old Directive applied to installations, the Seveso II Directive applies to establishments which are defined as “the whole area under the control of an operator where dangerous substances are present in one or more installations, including common or related infrastructures or activities”.

The Seveso II Directive follows a so-called two-tier approach which means that for each named substance and for each generic category of substances and preparations, two different qualifying quantities (threshold levels) are mentioned, a lower and an upper value.

1.3 IPPC - Integrated Pollution Prevention and Control Directive

The European Union defines the obligations with which highly polluting industrial and agricultural activities must comply. It establishes a procedure for authorising these activities and sets minimum requirements to be included in all permits, particularly in terms of pollutants released. The aim is to prevent or reduce pollution of the atmosphere, water and soil, as well as the quantities of waste arising from industrial and agricultural installations to ensure a high level of environmental protection.

The IPPC Directive (Council Directive 96/61/EC of 24 September 1996) imposes a requirement for industrial and agricultural activities with a high pollution potential to have a permit which can only be issued if certain conditions are met, so that the companies themselves bear responsibility for preventing and reducing any pollution they may cause.

Integrated pollution prevention and control concerns highly polluting new or existing industrial and agricultural activities, as defined in Annex I to the Directive (energy industries, production and processing of metals, mineral industry, chemical industry, waste management, livestock farming, etc.). In order to receive a permit an industrial or agricultural installation must comply with certain basic obligations in order to ensure mandatory environmental conditions. In particular, it must:

- use all appropriate pollution-prevention measures, namely the best available techniques (which produce the least waste, use less hazardous substances, enable the recovery and recycling of substances generated, etc.);
- prevent all large-scale pollution;
- prevent, recycle or dispose of waste in the least polluting way possible;
- use energy efficiently;
- ensure accident prevention and damage limitation;
- return sites to their original state when the activity is over.

In addition, the decision to issue a permit must be based on considering a number of specific requirements, in particular including:

- emission limit values for polluting substances should be met (greenhouse gases are not classified as polluting substances and thus the emissions trading scheme applies);
- any soil, water and air protection measures required;
- waste management measures;
- measures to be taken in exceptional circumstances (leaks, malfunctions, temporary or permanent stoppages, etc.);
- minimisation of long-distance or transboundary pollution;
- release monitoring;
- all other appropriate measures.

1.4 WFD - Water Framework Directive

The Water Framework Directive (WFD 2000) came into force in December 2000, with member states being required to transpose the Directive into domestic law. It is the most significant piece of European water legislation for over 20 years and brought about changes to the management of the water environment. It rationalised and updated previous water legislation and replaced a number of European Directives. By taking an integrated approach to managing water as it flows through catchments, its lakes, rivers and groundwater to estuaries and the sea, the Directive overall aims to:

- prevent further deterioration and protect and enhance the status of aquatic ecosystems and associated wetlands;
- promote sustainable water consumption;
- progressively reduce or phase out discharges, emissions and losses of priority substances and priority hazardous substances;
- progressively reduce the pollution of groundwater; and
- contribute to mitigating the effect of droughts and floods.

The Directive together with the recently adopted new version (WFD 2008) applies to all surface freshwater bodies, including lakes, streams and rivers, groundwaters, as well as estuaries and coastal waters to one mile from low-water. The concept of an integrated River Basin Management Plan (RBMP) is at the heart of Directive, and sets out environmental objectives for the water status. This is based on:

- ecological and chemical parameters;
- common monitoring and assessment strategies;
- arrangements for river basin administration and planning; and
- programmes of Measures (PoMs) in order to meet the RBMP’s objectives.

The first step has been to identify River Basin Districts, which are characterised by assessing the pressures and impacts on the water environment, such as overuse or pollution. The next step was to prepare the RBMP based on known data from the area which sets out how improvements of water quality will be made and how to reduce the risks.

The Directive’s objectives are to be achieved by 2015, and there are several key pieces of work to be carried out before this date. In 2007 the significant water management issues for the River Basin Districts had to be stated, and the full River Basin Management Plans were consulted on in 2008. Then from 2009 to 2012 the plans will be enacted, and reviewed between 2013 and 2015.

1.5 UNECE – United Nations Economic Commission for Europe

Water and industrial accidents

Major industrial accidents may cause far-reaching transboundary effects and may lead to accidental water pollution. Therefore, the Signatories to the Convention on the Transboundary Effects of Industrial Accidents and the Parties to the Convention on the protection and Use of Transboundary Watercourses and International lakes decided to cooperate on issues related to the prevention of accidental pollution of transboundary waters. Several workshops and seminars were held and a joint research group established. The conclusions and recommendations of these activities were then adopted at the second Meeting of the Parties to the Water Convention, held in The Hague (23-25 March 2000) and endorsed by the first meeting of the Conference of the Parties to the Industrial Accidents Convention, held in Brussels (22-24 November 2000).

In 2000, the Parties to both Conventions extended the mandate of the joint expert group to support and provide guidance in the implementation of the above recommendations and agreed on the groups future work plan as contained in decision 2000/5 on the prevention of accidental water pollution taken by the first meeting of the Conference of the Parties to the Industrial Accidents Convention (http://www.unece.org/env/teia/water.htm).

Major areas falling under the responsibility of the joint expert group

- inventory of existing safety guidelines and best practices for the prevention of accidental transboundary water pollution;
- assistance in adapting these guidelines to the specific needs and circumstances in river basins;
- drawing up safety guidelines and best practices for tailing dams, pipelines, and navigation of ships on rivers;
- alarm and notification systems;
- international response exercises;
- transboundary contingency planning; and
- methodologies to identify hazardous activities that handle smaller amounts of substances than those specified in Annex I to the Industrial Accidents Convention.

Following the second meeting of the Conference of the Parties to the Industrial Accidents Convention, the joint expert group received the following additional requests to:

- establish a common reporting scheme on the implementation of the conclusions and recommendations of the Hamburg seminar, adopted by the governing bodies of the Industrial Accidents and the Water Conventions;
- evaluate individual country responses and compile a first joint implementation report to be presented to both governing bodies, possibly at a joint meeting in 2006; and
- review and provide further guidance on the location criterion related to the water path contained in the "Guidelines to facilitate the identification and notification of hazardous activities for the purpose of the Convention" contained in the appendix to decision 2000/3 of the Conference of the Parties to the Industrial Accidents Convention.

2 Monitoring under the Water Framework Directive: conceptual framework

The text in this subsection on monitoring requirements of the WFD has been quoted from chapter 2 in "Guidance on Monitoring under the Water Framework Directive" (WFD Guidance 2007). Annex V of the WFD (WFD 2000) indicates that monitoring information from surface waters is required for:

- The classification of status. (*Note: Member States must provide a map for each river basin district in their territory illustrating the classification of the ecological and chemical status of each body of water using the colour-coding system specified by the Directive*);
- Supplementing and validating the Annex II risk assessment procedure;
- The efficient and effective design of future monitoring programmes;
- The assessment of long-term changes in natural conditions;
- The assessment of long-term changes resulting from widespread anthropogenic activity;
- Estimating pollutant loads transferred across international boundaries or discharging into seas;
- Assessing changes in status of those bodies identified as being at risk in response to the application of measures for improvement or prevention of deterioration;
- Ascertaining causes of water bodies failing to achieve environmental objectives where the reason for failure has not been identified;
- Ascertaining the magnitude and impacts of accidental pollution;
- Use in the inter-calibration exercise;
- Assessing compliance with the standards and objectives of Protected Areas; and,
- Quantifying reference conditions (where they exist) for surface water bodies should.

'Good status by the year 2015'

Basically, this is what the WFD is all about: "achieving good water status by the year 2015".[58]
The assessment of the **status** of waters is considered to be the key requirement of the monitoring under the WFD. Therefore, this issue has been elaborated in the sections below.

What is "good status"?

WFD article 2.18 (WFD 2000) gives the following definition: 'Good surface water status' means the status achieved by a surface water body when both its ecological status and its chemical status are at least 'good'. Figure 2, copied from a Guidance Document (REFCOND 2003), provide a convenient flow-chart for the status assessment in accordance with the WFD.

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[58] WFD Article 4 further mentions "good ecological potential" for the artificial and heavily modified bodies of water, and generally "to prevent further deterioration of the status of all bodies of water".

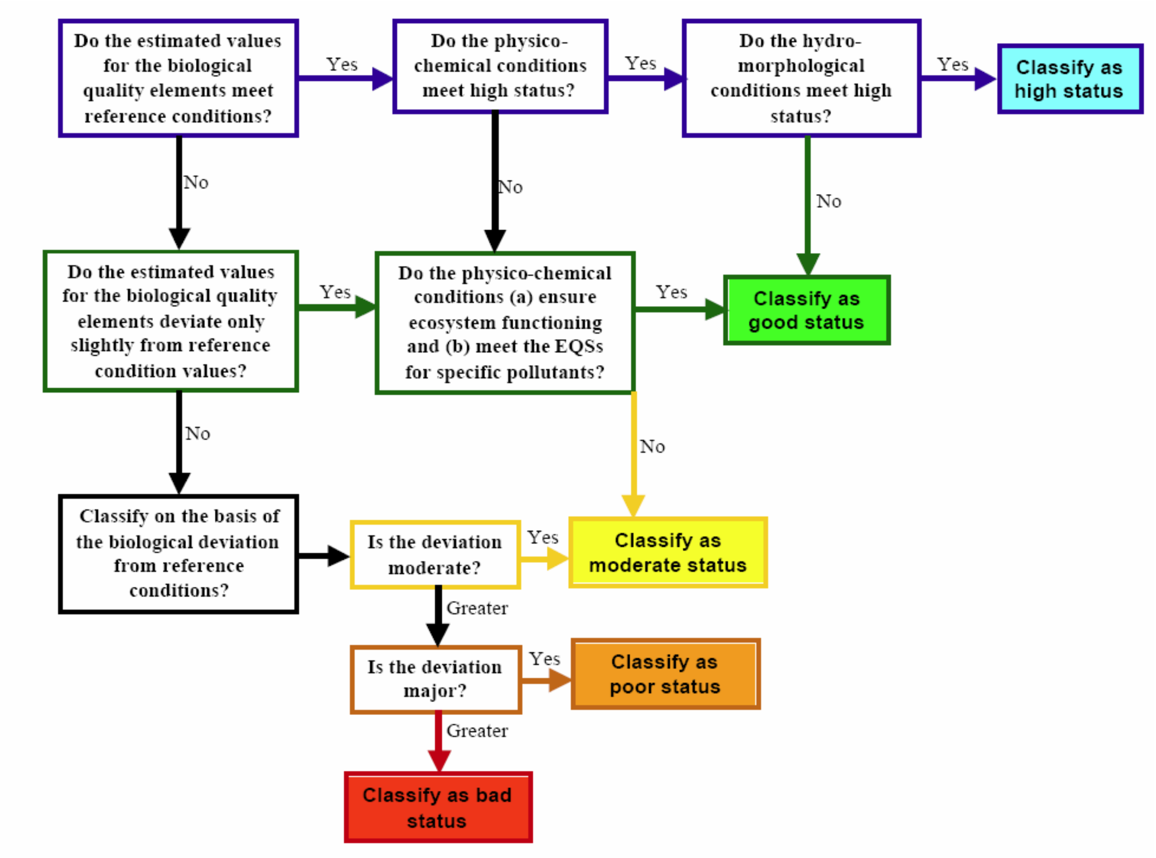

Figure 2 Indication of the relative roles of biological, hydromorphological and physico-chemical quality elements in ecological status classification (taken from REFCOND 2003).

The assessment scheme above requires the following major inputs:

- **measurement data** for the biological, physico-chemical and hydro-morphological conditions (quality elements);
- **assessment criteria** for comparing actual conditions to criteria like “reference conditions”, “high status”, “good ecosystem functioning”, “Environmental Quality Standards (EQS)”, etc.

Measurement data: quality elements for monitoring under the WFD

Table 1 summarises the quality elements as included in WFD Annex V (WFD 2000) completed with details in Chapter 3 in the “Guidance on Monitoring under the Water Framework Directive” (WFD Guidance 2007).

Table 1 Overview of quality elements for monitoring under the Water Framework Direc tive (WFD 2000).

Quality element	Rivers	Lakes	Transitional waters	Coastal waters	HMWB[59]
BIOLOGICAL					***(X)***
Phytoplankton	X(60)	X	X	X	
Phytobenthos	X	X			
Macrophytes	X	X			
Macroalgae			X	X	
Angiosperms			X	X	
Benthic invertebrate fauna	X	X	X	X	
Fish	X	X	X		
PHYSICO-CHEMICAL					***(X)***
General conditions*	X	X	X	X	
Priority Substances	X	X	X	X	
Other specific pollutants	X	X	X	X	
HYDROMORPHOLOGICAL					***(X)***
Hydrological					
Quantity and dynamics of water flow	X	X			
Connection to groundwater	X	X			
Residence time		X			
River continuity	X				

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[59] HMWB=Heavily Modified and artificial Water Bodies. According to Annex V.1.1.5 “The quality elements applicable to artificial and heavily modified surface water bodies shall be those applicable to whichever of the four natural surface water categories above most closely resembles the heavily modified or artificial water body concerned”.

[60] The information about monitoring phytoplankton in rivers seems not to be consistent. In Annex V.1.1.1, phytoplankton is not mentioned! Then again, in sections like V.1.2 (Normative definitions of ecological status classification) and V.3.1.4 (Frequency of monitoring) phytoplankton is mentioned also for rivers. In the Guidance document on monitoring [1], phytoplankton is indicated as “Mandatory QE specified in Annex V.1.2” in the legend of its figure 3.1. In the report prepared by the ECOSTAT Working Group [11], footnote 3 in chapter 3 mentions the following: “Phytoplankton is not explicitly included in the list of quality elements for rivers in Annex V, 1.1.1, but is included as a biological element in Annex V, 1.2.1. It should therefore be possible to use phytoplankton as a separate element, if needed and appropriate especially in low land large rivers where phytoplankton may be important.”

Freshwater flow/hydrological budget			X		
Freshwater flow				X	
Direction of dominant currents				X	
Morphological					
River depth & width variation	X				
Structure & substrate of river bed	X				
Structure of riparian zone	X				
Current velocity	X				
Channel patterns	X				
Lake depth variation		X			
Structure & substrate of lake bed		X			
Structure of lake shore		X			
Depth variation			X	X	
Quantity Structure & substrate of the bed			X	X	
Structure of the intertidal zone			X	X	
* thermal conditions, oxygenation conditions, nutrient conditions, transparency, salinity, acidification status (acidification status only for rivers and lakes)					

Which of the quality elements are to be included in the monitoring depends partially on the type of monitoring. It is agreed that the following criteria apply:

- The Directive specifies quality elements for the classification of ecological status that include hydromorphological, chemical and physico-chemical elements supporting the biological elements.
- For surveillance monitoring (see below) parameters indicative of all the biological, hydromorphological and all general and specific physico-chemical quality elements are required to be monitored.
- For operational monitoring, the parameters used should be those indicative of the biological and hydromorphological quality elements most sensitive to the pressures to which the body is subjected, and all priority substances discharged and other substances discharged in significant quantities.

Assessment criteria: surface water status

Article 2 of the WFD (WFD 2000) contains the following definitions:

17. ‘Surface water status’ is the general expression of the status of a body of surface water, determined by the poorer of its ecological status and its chemical status.
18. ‘Good surface water status’ means the status achieved by a surface water body when both its ecological status and its chemical status are at least ‘good’.

WFD Annex V.1.2 provides the normative descriptions of ecological status classifications in its section 1.2 (WFD 2000):

- For the biological quality elements different descriptions for ‘high’, ‘good’ and ‘moderate’ status are provided;
- For the hydromorphological quality elements only a specific description for ‘high’ status is given; ‘good’ or ‘moderate’ status it is described as “Conditions consistent with the achievement of the values specified above for the biological quality elements”;
- For the physico-chemical quality elements ‘high’ and ‘good’ status are detailed; ‘moderate’ status is (similar to the hydromorphological quality elements) described as “Conditions consistent with the achievement of the values specified above for the biological quality elements”.

Ecological status

The ecological status comprises two groups of quality elements:

- biological quality elements
- physico-chemical quality elements, supporting the biological elements

The latter group also is named ‘general conditions’ (compare WFD, Annex V, 1.2), and includes: thermal conditions, oxygenation conditions, nutrient conditions, transparency, salinity and the acidification status.

Biological status

For the biological quality elements, Member States are expected to establish the so-called Ecological Quality Ratios (EQR), as indicated in WFD Annex V.1.4.1.(ii): “In order to ensure comparability of such monitoring systems, the results of the systems operated by each Member State shall be expressed as ecological quality ratios for the purposes of classification of ecological status. These ratios shall represent the relationship between the values of the biological parameters observed for a given body of surface water and the values for these parameters in the reference conditions applicable to that body. The ratio shall be expressed as a numerical value between zero and one, with high ecological status represented by values close to one and bad ecological status by values close to zero.”

The basic WFD principles for classification of ecological (biological) status based on Ecological Quality Ratios are shown in Figure 3.

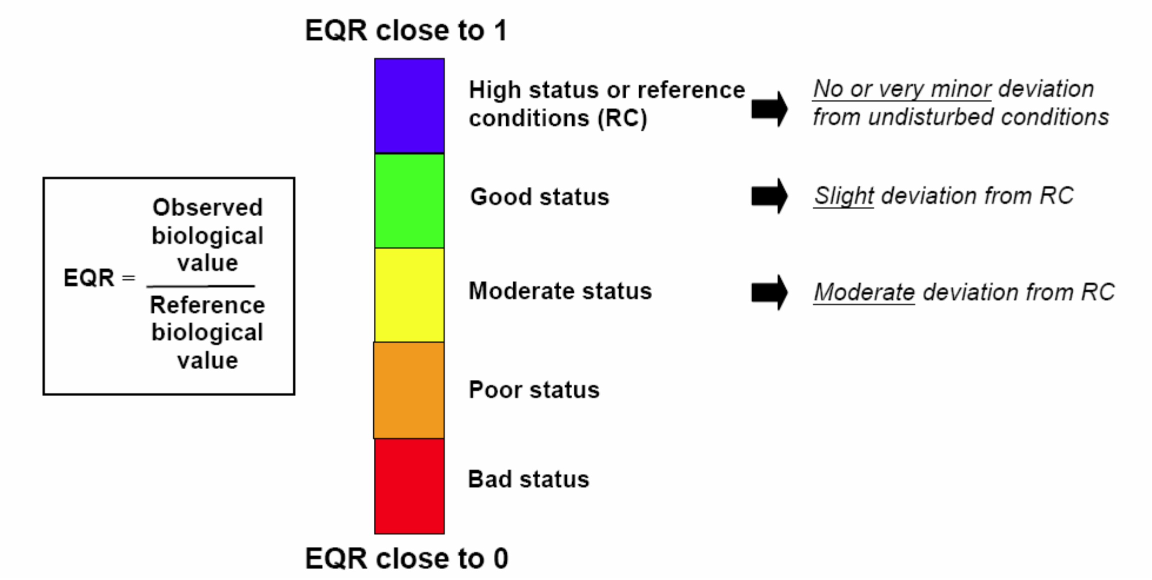

Figure 3 Basic principles for classification of ecological status based on Ecological Quality Ratios (REFCOND 2003).

Complications for application of the EQR concept include:

- The definition and specifications of *reference conditions*. Very few European countries can state that they still possess ‘undisturbed or nearly undisturbed aquatic ecosystems’. The problem arises that it is difficult to define references representing water bodies with ‘no or very minor deviation’ from undisturbed conditions. The issue gets even more complicated by the necessity to use *type-specific* references (reference conditions for lakes and rivers differ, as well as for marine waters and freshwaters, or between rivers and lakes – also within one country).
- The EQR may seem to be a concrete measure (a number between 0 and 1), but several yet insufficiently quantified factors apply, like “reference biological value” or “slight deviation from reference conditions”.
- Variability of biological systems (in time and in space). Water systems are dynamic; conditions change over time with (multi-)annual, seasonal and/or daily cycles, but are also driven by fluctuating conditions like weather and other random incidences. Therefore, it needs a careful approach and proper expert knowledge when collecting and interpreting biological data for a status assessment.

Physico-chemical parameters (supporting the biological elements)

Annex V.1.2 (WFD 2000) describes the ‘good’ status of the physico-chemical quality elements as follows:

General conditions

- Temperature, oxygenation conditions and transparency do not reach levels outside the ranges established so as to ensure the functioning of the ecosystem and the achievement of the values specified above for the biological quality elements.
- Nutrient concentrations do not exceed the levels established so as to ensure the functioning of the ecosystem and the achievement of the values specified above for the biological quality elements.

It is not fully clear to which extent Member States are expected to define the five quality classes for the physico-chemical ‘general conditions’ quality elements (and to establish type-specific ecological quality ratios here as well). WFD Annex V.1.4.2 seems to imply so. On the other hand, according to the scheme given in Figure 3 (copied from the REFCOND Guidance document) it would be sufficient to have defined the ‘high’ and ‘good’ status only.

Working Group 2 A Ecological Status (ECOSTAT) mentions in the Guidance Document No 13 (WFD 2005) of the common implementation strategy for the water framework directive (2000/60/EC) the following: (Chapter 2, 2.6) “The values of the physico-chemical quality elements must be taken into account when assigning water bodies to the high and good ecological status classes and to the maximum and good ecological potential classes (i.e. when downgrading from high status/maximum ecological potential to good ecological status/potential as well as from good to moderate ecological status/potential). This is discussed in detail in Section 4. For the other status/potential classes the physico-chemical elements are required to have “conditions consistent with the achievement of the values specified (in Tables 1.2.1 - 1.2.5) for the biological quality elements. Therefore, the assignment of water bodies to moderate, poor or bad ecological status/ecological potential may be made on the basis of the monitoring results for the biological quality elements. This is because if the biological quality element values relevant to moderate, poor or bad status/potential is achieved, then by definition the condition of the physico-chemical quality elements must be consistent with that achievement and would not affect the classification of ecological status/potential.”

In chapter 4 of the Guidance Document No 13 (WFD 2005) of the common implementation strategy for the water framework directive (2000/60/EC) furthermore it is mentioned “If the monitoring results for both the biological quality elements and the general and specific physico-chemical quality elements in a water body meet the conditions required for good ecological status/potential, the overall ecological status/potential of the water body will be good. However, if one or more of the general physico-chemical quality elements or specific pollutants do not meet the conditions required for good ecological status/potential but the biological quality elements do, the overall ecological status/potential will be moderate.”

A feature to be taken into account is: type-specific conditions. Annex V.1.3 requires the Member States to establish **type-specific** reference conditions (‘high’ status) for surface water bodies types, for hydromorphological, physicochemical and biological conditions. It is reasonable to assume that conditions “to ensure ecosystem functioning” therefore can vary between waters, implying a differentiated set of criteria for ‘good status’ for the various types of water bodies.

Chemical status

WFD Annex V Subsection 1.4.3 on the presentation of monitoring results and classification of chemical status only discriminates two classes, ‘good’ and ‘failing to achieve good’.
Annex V.1.2 describes the ‘good’ status of the remaining physico-chemical quality elements as follows:

Specific synthetic pollutants

- Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 without prejudice to Directive 91/414/EC and Directive 98/8/EC. (< EQS).

Specific non-synthetic pollutants

- Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6[61] without prejudice to Directive 91/414/EC and Directive 98/8/EC. (< EQS[62]).

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[61] Where it is added that “Application of the standards derived under this protocol shall not require reduction of pollutant concentrations below background levels: (EQS > bgl).”

Priority substances

The WFD explicitly distinguishes between the groups of so-called priority substances, comprising both synthetic and non-synthetic pollutants, and “other pollutants”.

In Article 16.7, the WFD (WFD 2000) mentions the following “The Commission shall submit proposals for quality standards applicable to the concentrations of the priority substances in surface water, sediments or biota”. Under the auspices of the Expert Advisory Forum on Priority substances (EAF-PS) and its expert group on Analysis and Monitoring of the Priority Substances (AMPS), these environmental quality standards have been developed and adopted (WFD 2008). For the heavy metals it is further relevant to notice that natural background concentrations can be taken into account by the member states when assessing the monitoring results against the EQSs if the natural background is higher than the EQS values or if water hardness or pH affects the bioavailability. The EQS for the heavy metals apply to *the dissolved concentration*.

Other specific synthetic and non-synthetic pollutants

For other specific synthetic and non-synthetic pollutants, the countries are expected to establish their own EQS. The general procedure for setting these EQS is described in WFD Annex V.1.2.6.

Hydromorphological status

WFD Annex V.1.2 (WFD 2000) provides specific normative descriptions of ‘high’ status for hydromorphological elements. For ‘good’ or ‘moderate’ status, the normative descriptions for hydromorphological quality elements are merely described as “Conditions consistent with the achievement of the values specified above for the biological quality elements”.

According to the ‘flow-chart’ included in the REFCOND Guidance Document (Figure 2 in this report) the assessment can result in a ‘good status’ without considering hydromorphological quality elements. Furthermore, Annex V.1.4 of the WFD 2000 on “Classification and presentation of ecological status” does not contain any explicit mentioning of hydromorphological quality elements. How to deal with hydromorphological quality elements seem not to be precisely defined within the WFD.

Typology; water bodies

In the previous subsection, the term water bodies was used, referring to yet another specific WFD feature (Figure 4).

Water bodies are an essential unit in the WFD. Checking whether or not the surface waters are of good status to a great extent depends on the assessment of the conditions of individual water bodies (therefore water bodies also sometimes called ‘compliance checking units’). Water bodies ‘at risk’ (assessed, either expected to be of less than good status) are to be monitored according to the criteria for ‘operational monitoring’.

Surveillance, operational and investigative monitoring

The WFD (WFD 2000) also introduced new terminology when dealing with monitoring, like surveillance, operational, or investigative monitoring (Figure 5). The interpretation of “where and what” to monitor under for instance surveillance- or operational monitoring has also introduced some more questions. In practise, the WFD descriptions (even in combination with the Guidance documents) still leave room for own interpretations.

It goes beyond the scope of the study presented here to go into detail on the complications and possible interpretations of the various WFD implied monitoring programmes. In the following, pragmatic ‘working definitions’ are given:

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[62] EQS = environmental quality standard

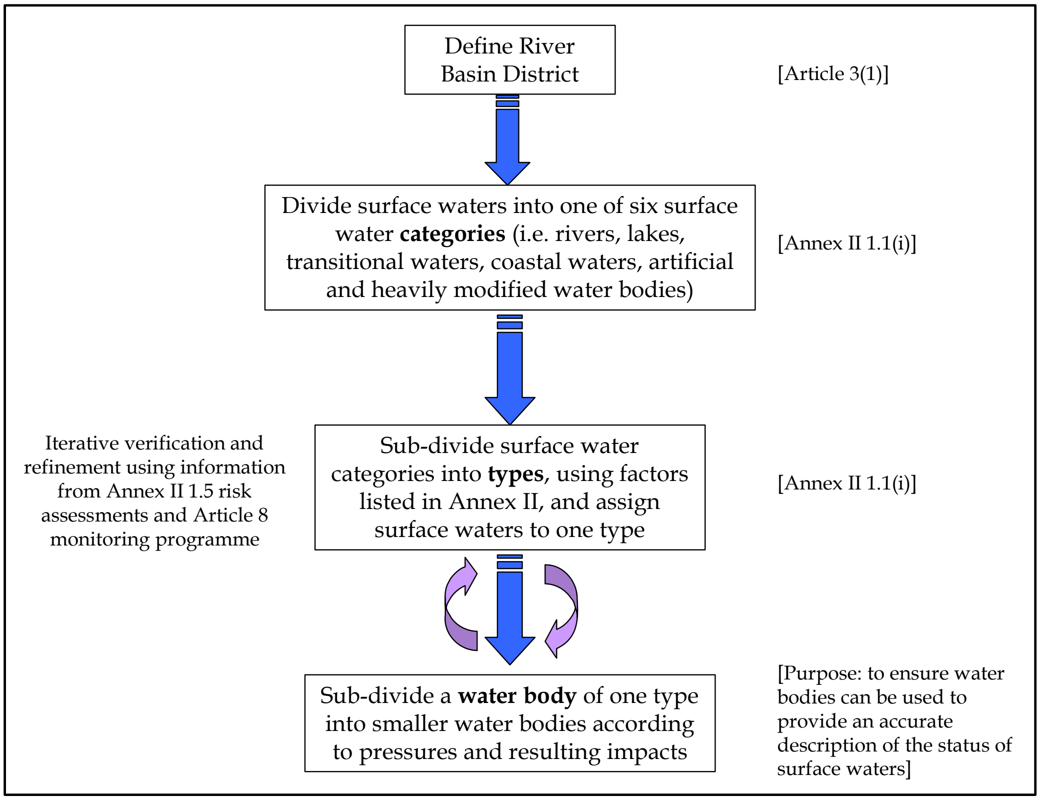

Figure 4 Summary of suggested hierarchical approach to the identification of surface water bodies (*in: COAST Guidance Document No 5, WFD 2005*).

Surveillance monitoring implies monitoring:

- parameters indicative of all biological quality elements,
- parameters indicative of all hydromorphological quality elements,
- parameters indicative of all general physico-chemical quality elements,
- priority list pollutants which are discharged into the river basin or sub-basin, and
- other pollutants discharged in significant quantities in the river basin or sub-basin,
- at a relatively limited number of locations;
- during one year in each six years planning period.

Operational monitoring implies monitoring of

- parameters indicative of the biological quality element, or elements, most sensitive to the pressures to which the water bodies are subject,
- all priority substances discharged, and other pollutants discharged in significant quantities,
- parameters indicative of the hydromorphological quality element most sensitive to the pressure identified.
- at (*a sufficient representative number of*) water bodies “at risk”;
- during all years of the six years planning period.

Investigative monitoring is not considered to be monitoring in the true sense[63]. It seems to resemble more of survey kind of activities. No official guidelines presently exist on investigative monitoring.

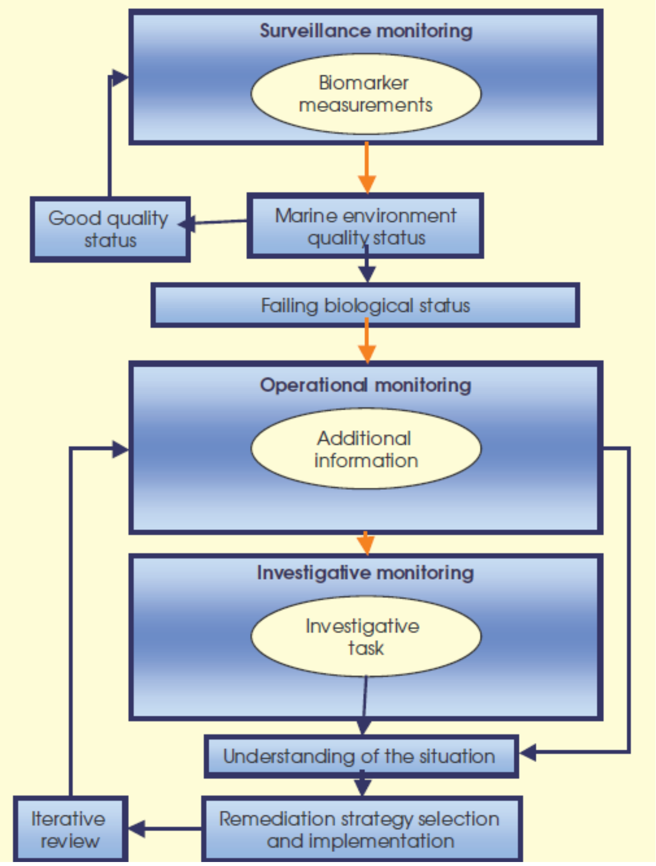

Figure 5 Monitoring scheme under the WFD (from PRAGMA Final Technical Report 2007).

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[63] The UN/ECE Guidelines on Monitoring and Assessment of Transboundary Rivers define monitoring as: "Monitoring is the process of repetitive observing, for defined purposes, of one or more elements of the environment according to pre-arranged schedules in space and time and using comparable methodologies for environmental sensing and data collection. It provides information concerning the present state and past trends in environmental behaviour."

Descriptions of surveillance and operational monitoring in WFD, Annex V.1.3

1.3.1. Design of surveillance monitoring

Objective
Member States shall establish surveillance monitoring programmes to provide information for:
- supplementing and validating the impact assessment procedure detailed in Annex II,
- the efficient and effective design of future monitoring programmes,
- the assessment of long-term changes in natural conditions, and
- the assessment of long-term changes resulting from widespread anthropogenic activity.

The results of such monitoring shall be reviewed and used, in combination with the impact assessment procedure described in Annex II, to determine requirements for monitoring programmes in the current and subsequent river basin management plans.

Selection of monitoring points
Surveillance monitoring shall be carried out of sufficient surface water bodies to provide an assessment of the overall surface water status within each catchment or subcatchments within the river basin district. In selecting these bodies Member States shall ensure that, where appropriate, monitoring is carried out at points where:
- the rate of water flow is significant within the river basin district as a whole; including points on large rivers where the catchment area is greater than 2 500 km^2,
- the volume of water present is significant within the river basin district, including large lakes and reservoirs,
- significant bodies of water cross a Member State boundary,
- sites are identified under the Information Exchange Decision 77/795/EEC, and at such other sites as are required to estimate the pollutant load which is transferred across Member State boundaries, and which is transferred into the marine environment.

Selection of quality elements
Surveillance monitoring shall be carried out for each monitoring site for a period of one year during the period covered by a river basin management plan for:
- parameters indicative of all biological quality elements,
- parameters indicative of all hydromorphological quality elements,
- parameters indicative of all general physico-chemical quality elements,
- priority list pollutants which are discharged into the river basin or sub-basin, and
- other pollutants discharged in significant quantities in the river basin or sub-basin, unless the previous surveillance monitoring exercise showed that the body concerned reached good status and there is no evidence from the review of impact of human activity in Annex II that the impacts on the body have changed. In these cases, surveillance monitoring shall be carried out once every three river basin management plans.

1.3.2. Design of operational monitoring

Operational monitoring shall be undertaken in order to:
- establish the status of those bodies identified as being at risk of failing to meet their environmental objectives, and
- assess any changes in the status of such bodies resulting from the programmes of measures.

The programme may be amended during the period of the river basin management plan in the light of information obtained as part of the requirements of Annex II or as part of this Annex, in particular to allow a reduction in frequency where an impact is found not to be significant or the relevant pressure is removed.

Selection of monitoring sites

Operational monitoring shall be carried out for all those bodies of water which on the basis of either the impact assessment carried out in accordance with Annex II or surveillance monitoring are identified as being at risk of failing to meet their environmental objectives under Article 4 and for those bodies of water into which priority list substances are discharged. Monitoring points shall be selected for priority list substances as specified in the legislation laying down the relevant environmental quality standard. In all other cases, including for priority list substances where no specific guidance is given in such legislation, monitoring points shall be selected as follows:

- for bodies at risk from significant point source pressures, sufficient monitoring points within each body in order to assess the magnitude and impact of the point source. Where a body is subject to a number of point source pressures monitoring points may be selected to assess the magnitude and impact of these pressures as a whole,
- for bodies at risk from significant diffuse source pressures, sufficient monitoring points within a selection of the bodies in order to assess the magnitude and impact of the diffuse source pressures. The selection of bodies shall be made such that they are representative of the relative risks of the occurrence of the diffuse source pressures, and of the relative risks of the failure to achieve good surface water status,
- for bodies at risk from significant hydromorphological pressure, sufficient monitoring points within a selection of the bodies in order to assess the magnitude and impact of the hydromorphological pressures. The selection of bodies shall be indicative of the overall impact of the hydromorphological pressure to which all the bodies are subject.

Selection of quality elements

In order to assess the magnitude of the pressure to which bodies of surface water are subject Member States shall monitor for those quality elements which are indicative of the pressures to which the body or bodies are subject. In order to assess the impact of these pressures, Member States shall monitor as relevant:

- parameters indicative of the biological quality element, or elements, most sensitive to the pressures to which the water bodies are subject,
- all priority substances discharged, and other pollutants discharged in significant quantities,
- parameters indicative of the hydromorphological quality element most sensitive to the pressure identified.

3 Relevant projects dealing with chemical (disaster) pollution & ecosystem impairment

3.1 MODELKEY

The MODELKEY project (Models for assessing and Forecasting the Impact of Environmental Key Pollutants on Marine and Freshwater Ecosystems and Biodiversity) was initiated in 2005 for the duration of 5 years (http://www.modelkey.org/).

MODELKEY comprises a multidisciplinary approach aiming at developing interlinked and verified predictive modelling tools as well as state-of-the-art effect-assessment and analytical methods generally applicable to European freshwater and marine ecosystems:

- to assess, forecast, and mitigate the risks of traditional and recently evolving pollutants on fresh water and marine ecosystems and their biodiversity at a river basin and adjacent marine environment scale,
- to provide early warning strategies on the basis of sub-lethal effects *in-vitro* and *in-vivo*,
- to provide a better understanding of cause-effect-relationships between changes in biodiversity and the ecological status, as addressed by the Water Framework Directive (WFD), and the impact of environmental pollution as causative factor,
- to provide methods for state-of-the-art risk assessment and decision support systems for the selection of the most efficient management options to prevent effects on biodiversity and to prioritise contamination sources and contaminated sites,
- to strengthen the scientific knowledge on an European level in the field of impact assessment of environmental pollution on aquatic ecosystems and their biodiversity by extensive training activities and knowledge dissemination to stakeholders and the scientific community.

Three key sub-projects can be distinguished which are relevant to ECODIS:

- **KEYTOX** aims at tool development and application for effect-directed identification of site- and basin-specific key toxicants (including state-of-the-art effect assessment and analytical methods) for the establishment of cause-effect relationships and improved risk assessment (Figure 6).

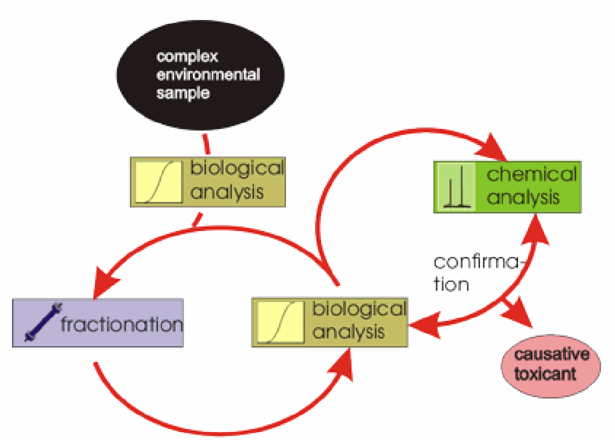


Figure 6 Schematic overview of KEYTOX (from http://www.modelkey.org/).

- **EXPO** will focus on the establishment of easy-to-use exposure models for the prediction of risks of toxic pollution in river basins and adjacent coastal areas including modules on most relevant processes including sediment erosion and sedimentation, transport and fate, and bioavailability and food web accumulation (Figure 7).

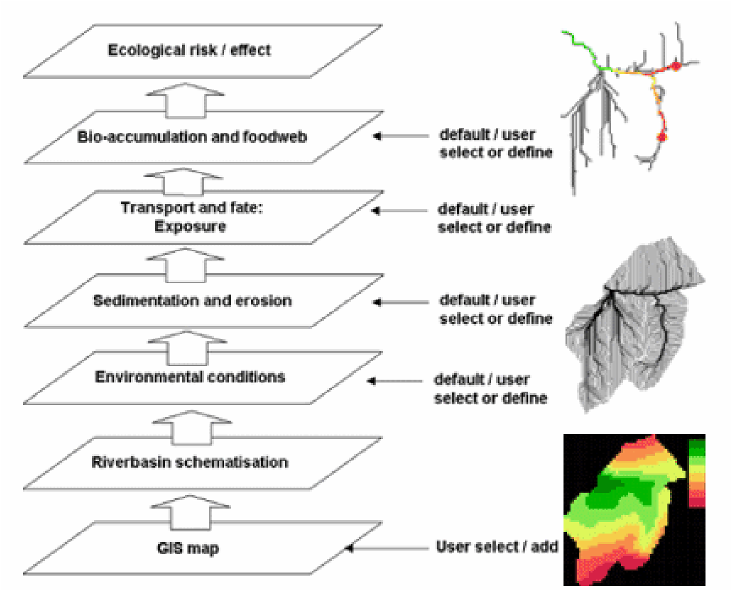


Figure 7 Schematic overview of EXPO (from http://www.modelkey.org/).

EFFECT deals with the development of probabilistic and deterministic models to diagnose, predict and mechanistically simulate the ecological effects of exposure to toxic substances on community composition and food chain propagation (Figure 8).

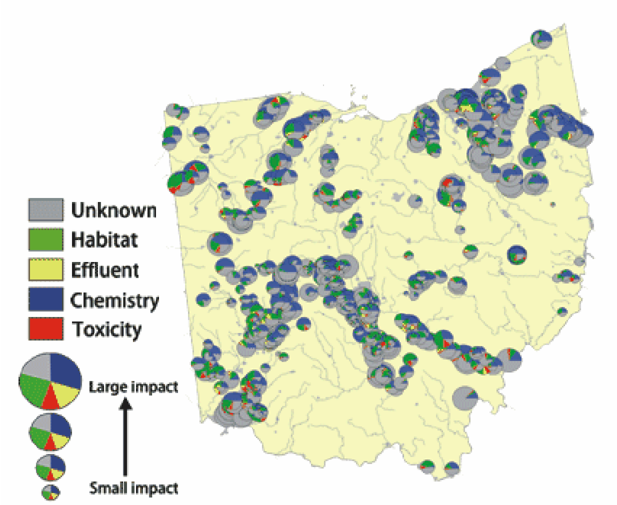


Figure 8 Schematic overview of EXPO (from http://www.modelkey.org/).

3.2 PRAGMA

The PRAGMA project (http://www.iris.no/Internet/pragma.nsf) is a pragmatic and integrated approach for the evaluation of environmental impact of oil and chemicals spilled at sea. The project was initiated in 2007 with the purpose of delivering input to European guidelines. A final technical report of the project has been published and can be downloaded at http://www.iris.no/Internet/pragma.nsf/wvDocId/D7C4469928525536C1257212002F82CC/$file/FINAL-TechRep.pdf. The IRIS (http://www.iris.no/internet/home2004.nsf) and Cedre (http://www.cedre.fr/) were the main partners.

The objectives of the PRAGMA project are:

- To evaluate existing methodologies based on biologically-important effect markers used in monitoring programmes and following some recent case studies with oil spill and chemical spill along the costal zone of the member states
- To propose the methodologies that can be used as a common platform in environmental monitoring of spills and contingency plans
- To incorporate simple, cost-efficient and manageable analytical tools in future pollution monitoring programmes within the member states.
- To promote the exchange of scientific and technical expertise in the field of environmental pollution monitoring
- To run pilot studies in laboratories
- To disseminate the protocols, research results at international/European level

PRAGMA addressed several issues among which the long term impact of oil spills was investigated more specifically. Beyond the immediate catastrophic effect of a spill causing death of thousands of marine organisms, a major environmental risk to consider is the long term impact of oil and chemical spills on the local ecosystem. Effects on the biodiversity of benthic organisms or/and the comparison between contaminant levels measured in water, sediment and biota to threshold levels established by international or national agencies are used as the main decision criterium (Figures 9 and 10).

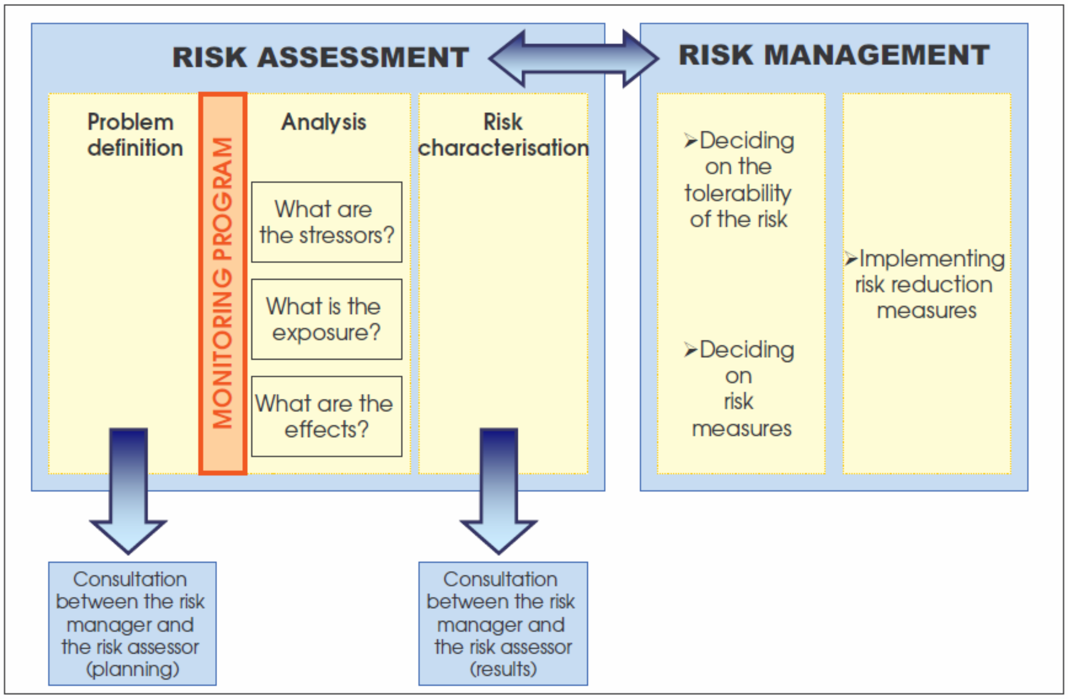


Figure 9 Steps in risk management process (from PRAGMA Final Technical Report 2007).

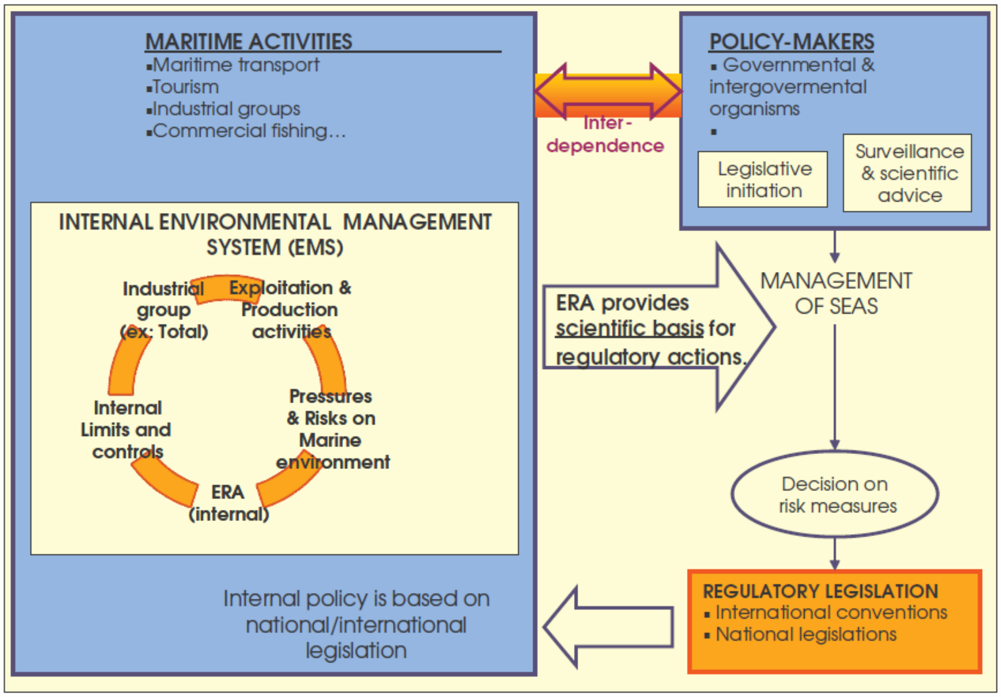


Figure 10 Importance of ecological risk assessment (ERA) as policy tool to assist regulators in decision-making (from PRAGMA Final Technical Report 2007).

Biodiversity is ecologically very relevant but requires years of observation because significant changes in populations might be visible only on a long temporal scale. Also, it is not easily applicable for organisms living in the water column. The chemical data resulting from sensitive and accurate measurements provide both qualitative and quantitative figures of the presence of toxic substances and hence reflect the hazard of exposure for the marine biota. Yet, the threshold levels which are defined according to the EU-Technical Guidance Document (ECHA 2008) allow defining the risk based on the PEC/PNEC ratio but are not an expression of the actual impacts. In recent years, new criteria based on the measurements of biological markers ("biomarkers") capable of identifying subtle changes with possible important consequences for the organisms sampled in polluted zone have been proposed (Figure 11).

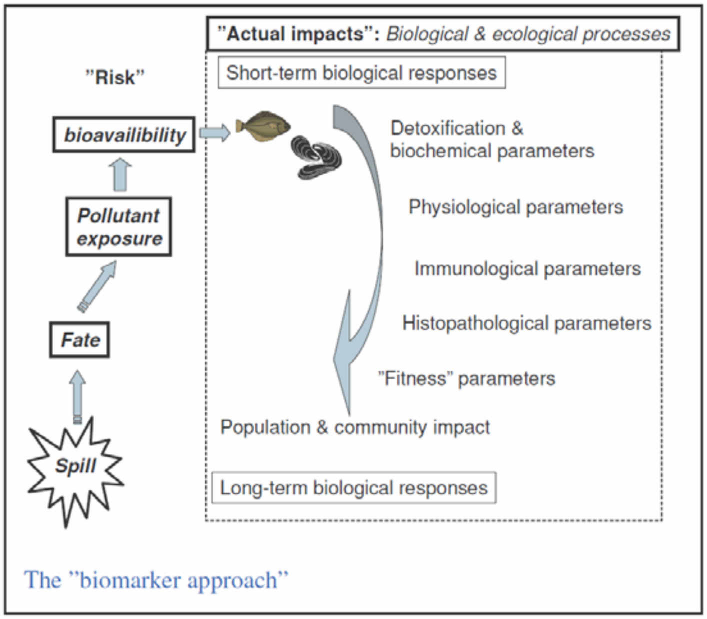
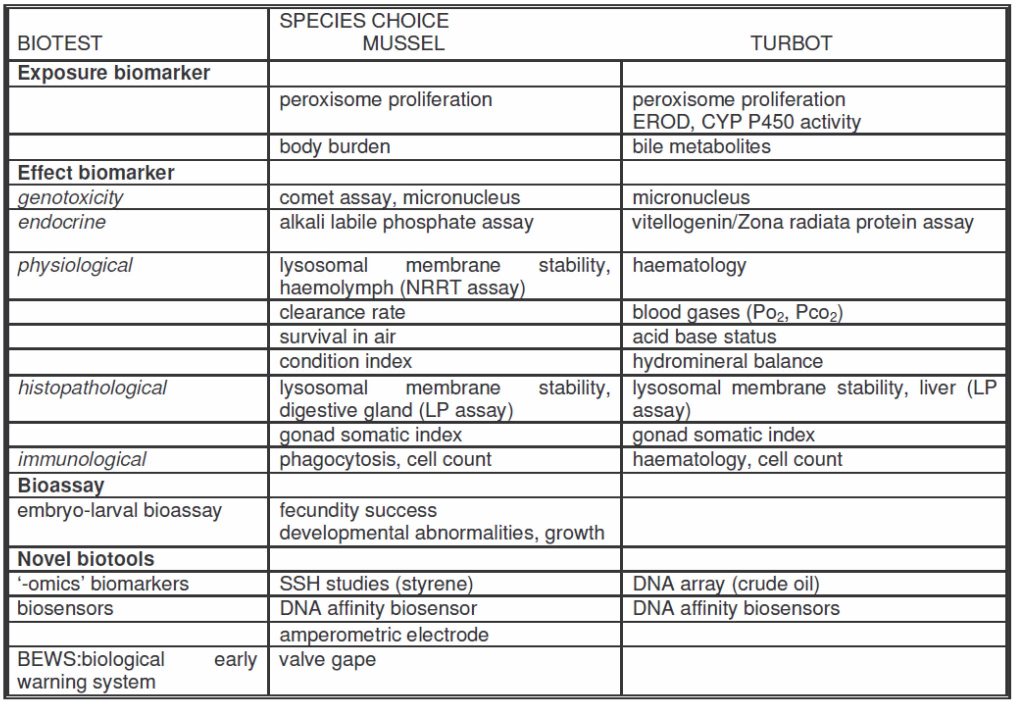


Figure 11 The "biomarker" approach proposed by PRAGMA as a way to assess actual impacts on marine ecosystems (from PRAGMA Final Technical Report 2007).

Chemical analysis reveals information on the presence of a hazardous substance, whereas a biomarker response indicates that the pollutant has induced a biological response. Eventually, that response may persist over long time even though the presence of the pollutant is no longer detectable. The ultimate goal with biomarkers is to evaluate the general health of individuals following exposure. Parameters related to growth and reproduction are particularly ecologically relevant since they can help to predict impairments beyond the individual level. Other analytical techniques related to developing cost-effective screening devices used at the desired temporal and spatial scale ought to be considered in the pragmatic assessment of environmental impact. Lately, arrays of sensors based on physical, chemical and biological signals have been proposed for the monitoring of the environment (Table 2).

Table 2 Biotests methodologies studied under PRAGMA (from PRAGMA Final Technical Report 2007).



	SPECIES CHOICE	
BIOTEST	MUSSEL	TURBOT
Exposure biomarker		
	peroxisome proliferation	peroxisome proliferation EROD, CYP P450 activity
	body burden	bile metabolites
Effect biomarker		
genotoxicity	comet assay, micronucleus	micronucleus
endocrine	alkali labile phosphate assay	vitellogenin/Zona radiata protein assay
physiological	lysosomal membrane stability, haemolymph (NRRT assay)	haematology
	clearance rate	blood gases (Po_2, Pco_2)
	survival in air	acid base status
	condition index	hydromineral balance
histopathological	lysosomal membrane stability, digestive gland (LP assay)	lysosomal membrane stability, liver (LP assay)
	gonad somatic index	gonad somatic index
immunological	phagocytosis, cell count	haematology, cell count
Bioassay		
embryo-larval bioassay	fecundity success developmental abnormalities, growth	
Novel biotools		
'-omics' biomarkers	SSH studies (styrene)	DNA array (crude oil)
biosensors	DNA affinity biosensor	DNA affinity biosensors
	amperometric electrode	
BEWS:biological early warning system	valve gape	

A combination of sensors as front line monitoring tools and both chemical and biological markers could be incorporated in future marine monitoring programmes (Figure 12). This approach ought to be harmonised at the EU level in order to implement these techniques in current assessment and monitoring guidelines. Based on this concept, the goal of PRAGMA will be to evaluate a battery of tools based on well known biological methodologies and other now available tools based on biosensors for their possible incorporation in current EU guidelines related to spill events and for the monitoring of the environmental effect of spills (Figure 13).

3.3 FACEiT

FACE-IT (Fast Advanced Cellular and Ecosystems Information Technologies) is a research project (2005-2009) supported by the Sixth EU Framework Programme. (http://www.unil.ch/Jahia/site/face-it/lang/en/pid/22703) and aims

- To develop adequate and effective biological methods to detect the presence, nature and magnitude of pollution disasters and their effects on aquatic living beings.
- To predict the medium and the long-term consequences for the aquatic ecosystem and the self-regeneration capacity after a disaster.
- To link different biological, physico-chemical and modelling approaches in order to achieve an integrated measurement and effect prediction.
- To disseminate the scientific and technical outcomes of the project to the different main actors of disaster management.

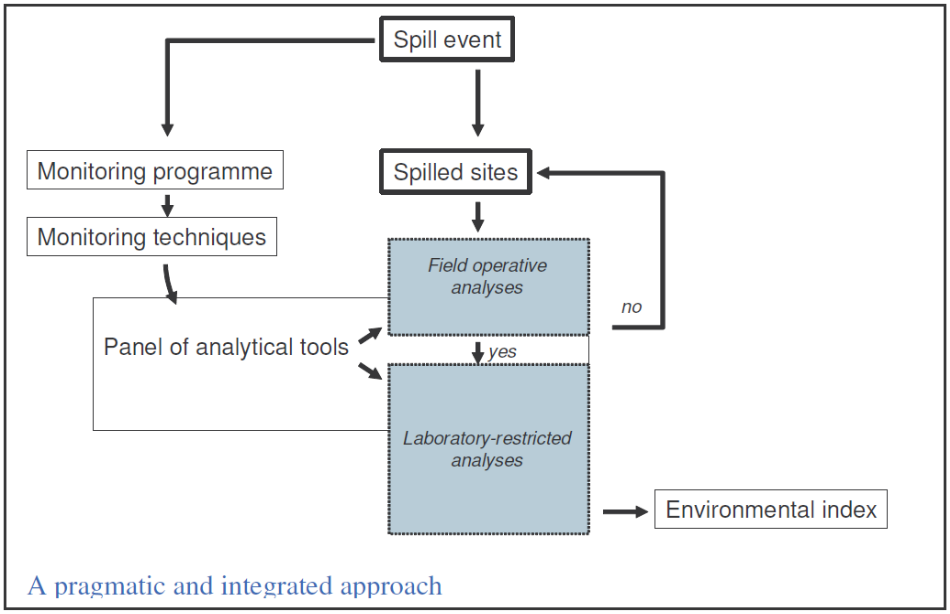


Figure 12 Possible way of conducting monitoring programmes following spill events (from PRAGMA Final Technical Report 2007).

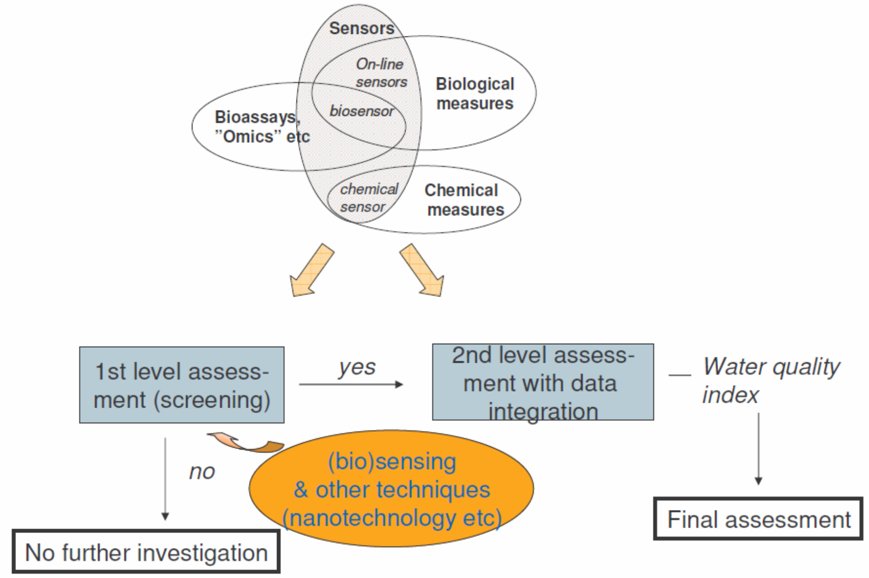


Figure 13 Recommended cost-effective approach for environmental monitoring and the decision making process in impacted marine areas according to PRAGMA (from PRAGMA Final Technical Report 2007).

Marine and freshwater ecosystems continue to be threatened by large scale pollution disasters. Such disasters are often caused by oil-related activities, but pollution nature, magnitude and site of occurrence all can be very different, with unpredictable impacts on the responses of individual organisms, the biodiversity and the functioning of the aquatic ecosystems. Proper disaster management requires a multifaceted approach, including pollution prevention, remediation technologies, biological effect prediction and ecosystems' restoration or natural attenuation.

The FACEiT project contributes to disaster management strategies by developing innovative biomonitoring technologies and biomodelling. The main disaster target of FACEiT is oil pollution. Biomonitoring development will concentrate on increasing the rapidity and reliability of cellular detection systems, on finding new cellular and ecosystem's markers to analyze and predict the potential effects of pollution disasters, and to assess and model the potential for self restoration of ecosystems.

In order to reach this purpose, FACEiT develops and tests biological pollutant monitoring technologies on different levels of biological complexity. The most simple of these consists of microbial reporter systems, which can detect either specific oil-related pollutants or are responsive to general toxic stress. At the *in-situ* level, FACEiT designs methods to detect pollutant compromised viability and cell integrity of unicellular planktonic and microbial communities. To target a higher cellular complexity, FACEiT develops tests based on mammalian cell lines and fish eggs.

The overall cellular response to pollution disasters will be analyzed from transcriptomic and proteomic changes. Multibiomarker test on pollutant-exposed marine organisms will serve to validate the responses of single cell and egg tests. FACEiT will also address pollutant disaster effects at the level of the ecosystem. Here, the consortium will develop methods to detect diversity changes, to understand the response of marine microbial communities to oil disasters and to predict the potential for natural attenuation. Finally, FACEiT will devote part of its efforts to design computer models which can predict the chemical and the biological fate in organisms, communities and the natural environment, where the disaster is potentially occurring.

In order to validate the newly developed biomonitoring technologies, the FACEiT project will compare the effectivity of the methods among each other and with existing physicochemical methods on highly polluted samples from contaminated sites, and on two occasions directly in the field. The consortium has chosen a chronic oil-pollution disaster site (Etang de Berry, France) and the North Sea shipping route to validate the biomonitoring tools for their merits in disaster management. FACEiT has a strong interest in developing prototypes up to market level implementation. Finally, two advanced courses will be organized and a final handbook will be prepared in order to introduce and transfer FACEiT results, technologies and concepts to different potential end-user communities, such as remediation companies, oil producers, public laboratories or policy makers.

On January 20-22, 2009, FACEiT will organize an international symposium: "Monitoring Effects of Aquatic Oil Pollution". Newly developed biomonitoring tools of the FACEiT project will be presented (http://www.unil.ch/webdav/site/face-it/shared/FACEiT2009.pdf)

3.4 FEAT tool

A Flash Environmental Assessment Tool, FEAT, (http://ochaonline.un.org/ochaunep) has been developed as a “first aid” tool to identify environmental impacts and support initial response actions in disaster contexts. It does not take the place of in-depth environmental assessments, which may be appropriate at later stages of the disaster response.

Natural disasters such as earthquakes, floods and hurricanes can damage infrastructure and result in secondary environmental impacts such as immediate or potential releases of hazardous materials. These can pose acute risks to human life and health, and adversely affect surrounding environments that are vital for livelihoods. Natural disasters may also trigger physical impacts such as salt water intrusion, mudslides, slope instability and flooding. Disaster response teams are faced with the difficult task of not only dealing with the disaster at hand, but also identifying and responding appropriately to these potential environmental impacts. However, thousands of toxic chemicals could be involved in any given disaster, each with its own toxicity profile, and with a multitude of exposure pathways (e.g. air, water and soil) and receptors (e.g. humans, livestock, fishing grounds). In such complex situations, it can be easy to overlook or misjudge important risks. At the same time, given the often overwhelming demands of disaster situations, complex and full-fledged environmental assessments would be inappropriate. Therefore, a practical, accurate, yet simple tool such as FEAT is required to assist initial response teams such as United Nations.

Modular approach

FEAT consists of three increasingly detailed assessment modules (Figure 14). This approach allows for maximum flexibility in differing and evolving disaster conditions. It also recognizes that users will have varying questions and needs, at different stages of the initial disaster response. The modules can be used independently, but taken together they represent the typical steps usually followed from the first notification of a disaster to the end of the initial response.

- The First Alert Module helps to scan for the presence of certain potentially high risk facilities in the affected area (FEAT Module 1/FM1)
- The Priorities Module helps users to determine objects of interest within an area and to, prioritize field visits (FEAT Module 2/FM2); and,
- The Facilities and Object Assessment Module helps users determine risks from individual facilities such as factories, or objects, such as storage tanks and trucks of chemicals (FEAT Module 3/FM3).

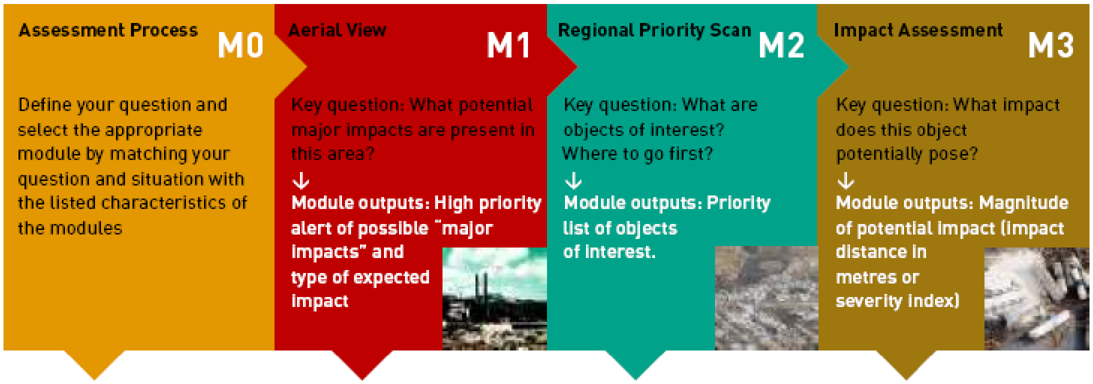


Figure 14 Three different steps can be distinguished within FEAT.

These modules provide pre-defined impact assessment information that helps the user to identify the potential magnitude of the impact of a given hazard and quantity. To determine whether the potential impact is actually relevant, it must also be determined whether exposure is likely. The FEAT Likely Scenarios Module (LSM) provides the most likely and important combinations of the type of hazard, the receptors, pathways and the type of impact to be expected, as described in more detail below.

Each FEAT module links to a table that provides the user with the information needed to use that particular module. The tables are numbered in accordance with the corresponding module. For example, the Module 1 (FM1) is the First Alert Module, and its corresponding table is Table FT1.

All modules follow the same basic steps.

Operational output: "metres of probable effect distance"
FEAT Module 2 and Module 3 combine all information on substance toxicity and chemical impacts into a single unit, called "metres of probable effect distance". This concept is easy to use anywhere. To express the severity of various long-term potential effects, such as carcinogenic hazards, a severity index is used.

One basic concept for the entire assessment tool
The core concept of FEAT can be expressed by the formula:

Impact = f (hazard, exposure, quantity).

Stated differently, all FEAT assessments are based on three impact-determining factors:

1. intrinsic hazard of the compound
2. possibility of exposure (if there is no receptor and/or no pathway, there is no exposure and thus no impact)
3. quantity (the larger the quantity, the more severe the impact).

A situation has a relevant impact only if the hazard, exposure and the quantity are all significant. The magnitude of the impact depends on the combined contribution of all three impact determining factors. For example: a highly toxic material in large quantities has a small impact if minimal exposure takes place. By contrast, small amounts of a substance with only medium toxicity will have a high impact if people or the environment is highly exposed.

FEAT provides the user either with predefined information or requests estimates for all three impact-determining factors. It then provides a predefined estimate of the impact in terms of metres of expected impact distance or severity indexes.

3.5 CALAMARIS: sensitivity/vulnerability mapping

In order to improve the efficacy of contingency planning and combat operations in case of chemical accidents it may be crucial to have maps that show areas vulnerable to certain pollutants. There is a need for maps distinguishing between areas with different ecological vulnerability. Although such maps do not exist yet for freshwater ecosystems (rivers), they do for marine ecosystems in case of oil spills at sea. Oil spills at sea occurring with calamities lead to serious ecological effects. In order to cope adequately with oil incidents the Dutch Rijkswaterstaat (RWS) is working on remediation strategies in the framework of the project 'crisismanagement' which are based on the consideration of potential ecological damage. RWS has developed for this purpose uniform ecological vulnerability maps for the Dutch North Sea, Wadden Sea and Delta area (Lahr et al., 2007), which will be made available in a geo-application for risk management called CALAMARIS. The application will be extended in the future to freshwater surface waters. The project CALAMARIS (calamity preparation repression and advice / clean-up) was initiated by the Dutch National Institute for Coastal and Marine Management (RIKZ) for the purpose of the development of knowledge and tools for chemical incidents at sea (RIKZ, 2003).

The RIKZ and RWS published in 2007 a report (Offringa and Lahr, 2007) http://login.safetyatsea.se/files/demoa/final_report.pdf., with the purpose of designing a flexible method for making maps for different seasons that could be regularly updated with new data and additional information on marine species and toxic chemicals (Figure 15). Currently a multitude of methods exist in Europe for ecological sensitivity/vulnerability mapping of marine waters (Table 3).

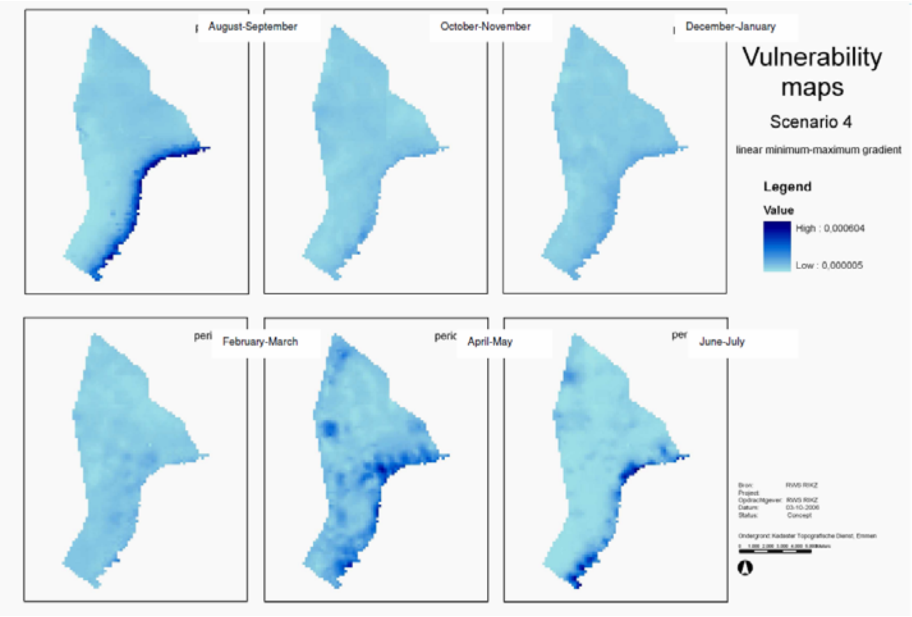
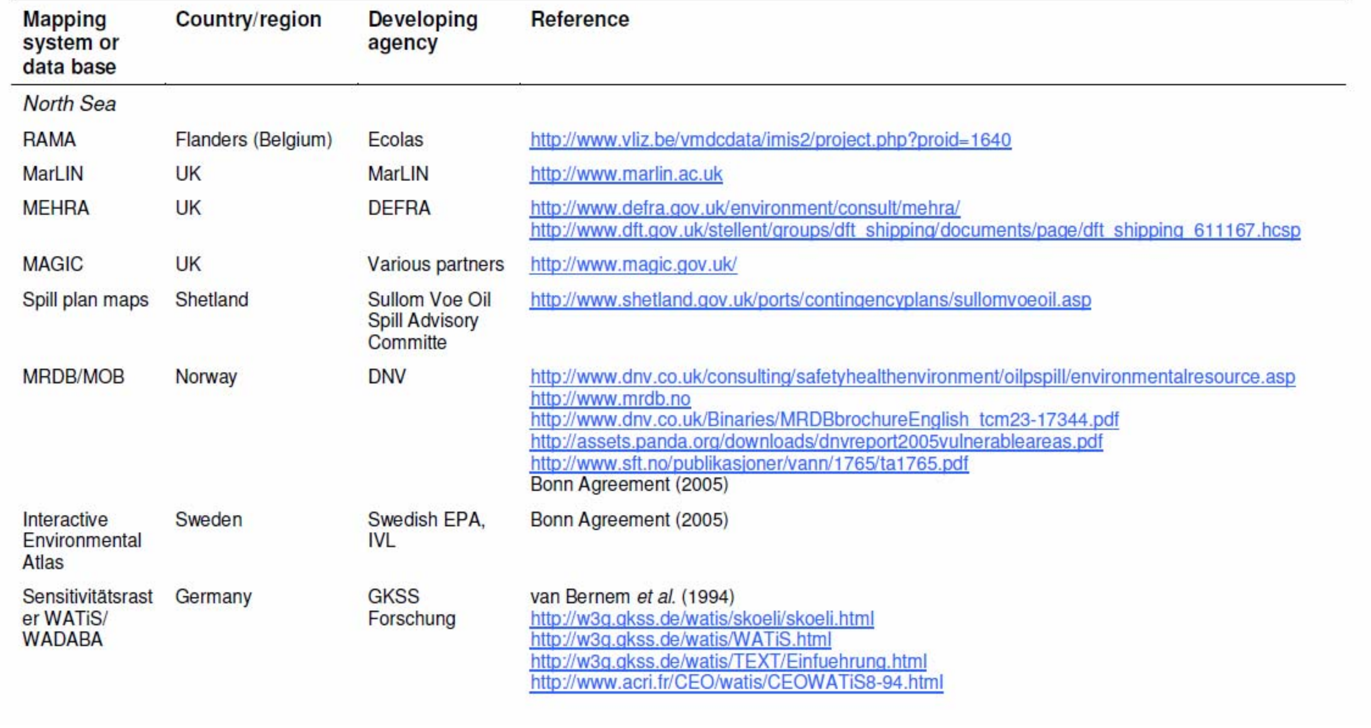


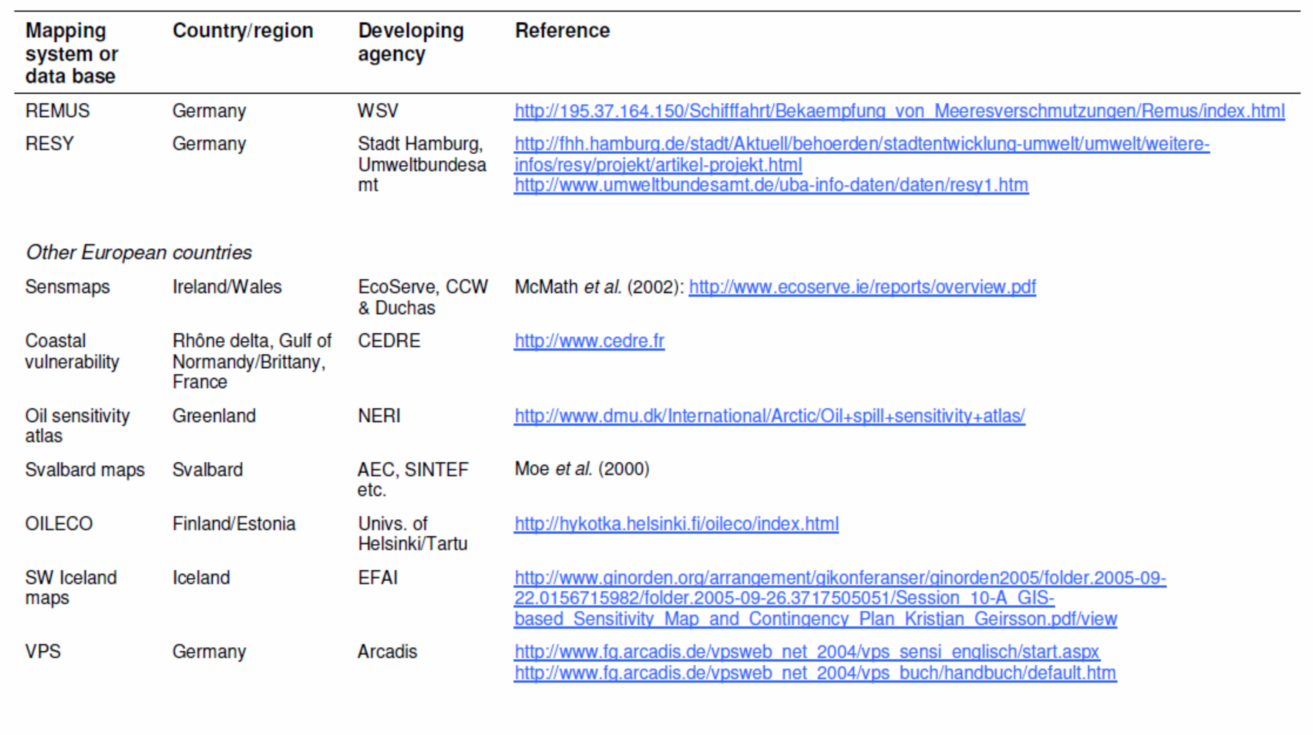
Figure 15 Set of V-maps for oil. The periods correspond to two months (from Lahr et al, 2007)

Different stages have been identified in dealing with the risk due to pollution from sea-based sources. The first is the prevention stage, followed by the preparation stage, the evaluation, the contingency planning stage and the actual cleaning operations stage. Within the Interregional project Safety at Sea, all these stages fall under strategic and operational risk management. RWS is involved in all these stages. According to the definition of Safety at Sea, Strategic Risk Management can be thought of as work that leads towards recommendations for future changes, whilst Operational Risk Management can be thought of as day-to-day actions.

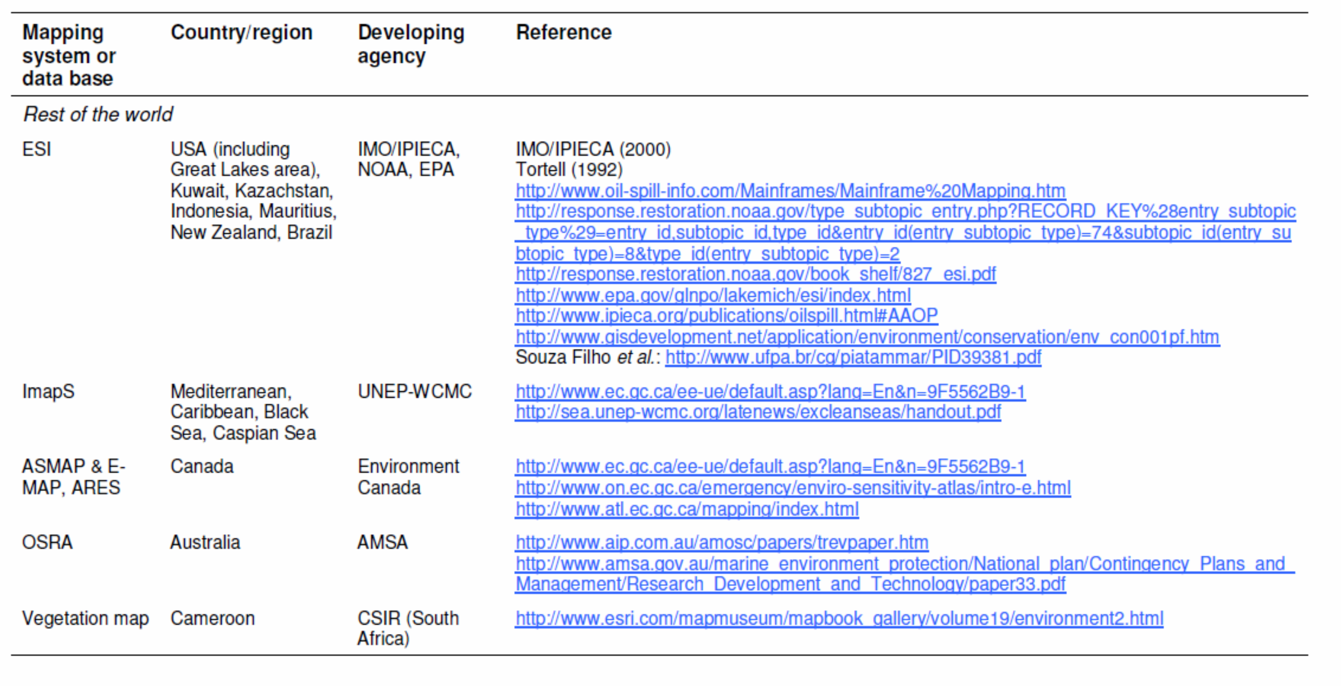
Table 3 Existing methods for ecological sensitivity/vulnerability mapping (Offringa and Lahr, 2007)



Mapping system or data base	Country/region	Developing agency	Reference
North Sea			
RAMA	Flanders (Belgium)	Ecolas	http://www.vliz.be/vmdcdata/imis2/project.php?proid=1640
MarLIN	UK	MarLIN	http://www.marlin.ac.uk
MEHRA	UK	DEFRA	http://www.defra.gov.uk/environment/consult/mehra/ http://www.dft.gov.uk/stellent/groups/dft_shipping/documents/page/dft_shipping_611167.hcsp
MAGIC	UK	Various partners	http://www.magic.gov.uk/
Spill plan maps	Shetland	Sullom Voe Oil Spill Advisory Committe	http://www.shetland.gov.uk/ports/contingencyplans/sullomvoeoil.asp
MRDB/MOB	Norway	DNV	http://www.dnv.co.uk/consulting/safetyhealthenvironment/oilpspill/environmentalresource.asp http://www.mrdb.no http://www.dnv.co.uk/Binaries/MRDBbrochureEnglish_tcm23-17344.pdf http://assets.panda.org/downloads/dnvreport2005vulnerableareas.pdf http://www.sft.no/publikasjoner/vann/1765/ta1765.pdf Bonn Agreement (2005)
Interactive Environmental Atlas	Sweden	Swedish EPA, IVL	Bonn Agreement (2005)
Sensitivitätsraster WATiS/ WADABA	Germany	GKSS Forschung	van Bernem *et al.* (1994) http://w3g.gkss.de/watis/skoeli/skoeli.html http://w3g.gkss.de/watis/WATiS.html http://w3g.gkss.de/watis/TEXT/Einfuehrung.html http://www.acri.fr/CEO/watis/CEOWATiS8-94.html



Mapping system or data base	Country/region	Developing agency	Reference
REMUS	Germany	WSV	http://195.37.164.150/Schifffahrt/Bekaempfung_von_Meeresverschmutzungen/Remus/index.html
RESY	Germany	Stadt Hamburg, Umweltbundesamt	http://fhh.hamburg.de/stadt/Aktuell/behoerden/stadtentwicklung-umwelt/umwelt/weitere-infos/resy/projekt/artikel-projekt.html http://www.umweltbundesamt.de/uba-info-daten/daten/resy1.htm
Other European countries			
Sensmaps	Ireland/Wales	EcoServe, CCW & Duchas	McMath *et al.* (2002): http://www.ecoserve.ie/reports/overview.pdf
Coastal vulnerability	Rhône delta, Gulf of Normandy/Brittany, France	CEDRE	http://www.cedre.fr
Oil sensitivity atlas	Greenland	NERI	http://www.dmu.dk/International/Arctic/Oil+spill+sensitivity+atlas/
Svalbard maps	Svalbard	AEC, SINTEF etc.	Moe *et al.* (2000)
OILECO	Finland/Estonia	Univs. of Helsinki/Tartu	http://hykotka.helsinki.fi/oileco/index.html
SW Iceland maps	Iceland	EFAI	http://www.ginorden.org/arrangement/gikonferanser/ginorden2005/folder.2005-09-22.0156715982/folder.2005-09-26.3717505051/Session_10-A_GIS-based_Sensitivity_Map_and_Contingency_Plan_Kristjan_Geirsson.pdf/view
VPS	Germany	Arcadis	http://www.fg.arcadis.de/vpsweb_net_2004/vps_sensi_englisch/start.aspx http://www.fg.arcadis.de/vpsweb_net_2004/vps_buch/handbuch/default.htm



Mapping system or data base	Country/region	Developing agency	Reference
Rest of the world			
ESI	USA (including Great Lakes area), Kuwait, Kazachstan, Indonesia, Mauritius, New Zealand, Brazil	IMO/IPIECA, NOAA, EPA	IMO/IPIECA (2000) Tortell (1992) http://www.oil-spill-info.com/Mainframes/Mainframe%20Mapping.htm http://response.restoration.noaa.gov/type_subtopic_entry.php?RECORD_KEY%28entry_subtopic_type%29=entry_id,subtopic_id,type_id&entry_id(entry_subtopic_type)=74&subtopic_id(entry_subtopic_type)=8&type_id(entry_subtopic_type)=2 http://response.restoration.noaa.gov/book_shelf/827_esi.pdf http://www.epa.gov/glnpo/lakemich/esi/index.html http://www.ipieca.org/publications/oilspill.html#AAOP http://www.gisdevelopment.net/application/environment/conservation/env_con001pf.htm Souza Filho *et al.*: http://www.ufpa.br/cg/piatammar/PID39381.pdf
ImapS	Mediterranean, Caribbean, Black Sea, Caspian Sea	UNEP-WCMC	http://www.ec.gc.ca/ee-ue/default.asp?lang=En&n=9F5562B9-1 http://sea.unep-wcmc.org/latenews/excleanseas/handout.pdf
ASMAP & E-MAP, ARES	Canada	Environment Canada	http://www.ec.gc.ca/ee-ue/default.asp?lang=En&n=9F5562B9-1 http://www.on.ec.gc.ca/emergency/enviro-sensitivity-atlas/intro-e.html http://www.atl.ec.gc.ca/mapping/index.html
OSRA	Australia	AMSA	http://www.aip.com.au/amosc/papers/trevpaper.htm http://www.amsa.gov.au/marine_environment_protection/National_plan/Contingency_Plans_and_Management/Research_Development_and_Technology/paper33.pdf
Vegetation map	Cameroon	CSIR (South Africa)	http://www.esri.com/mapmuseum/mapbook_gallery/volume19/environment2.html

Strategic risk assessment involves marine accidents (e.g. contact, collision, etc), the ranges of possible causes (e.g. human error, hardware failure and external events), the safety, environmental, property and economical consequences of accidents and tries to calculate the tolerability of risk and equity of risk control to the stakeholders. The assessment might serve as preparation or evaluation of policy (international and national) and should aid and guide the politicians in taking the right decisions.

Operational risk management is the response to an accident. There are many organisations in The Netherlands that are involved in operational management. In general there is a group of administrators deciding about the necessary measures, such as the deployment of cleaning facilities or the evacuation of an area. They are informed by a group of advisors that look at aspects such as the consequences for the environment, economy, human health, practical and logical considerations, costs, and policy and media attention.

Sensitivity or vulnerability maps may be used to support both strategic and operational planning. It must be stressed however, that the maps simply present geo-spatial information. It is not a decision support system. It is left with the decision makers to take the implications into account or not.

Vulnerability maps encompass the properties of substances (oils and chemicals) that are transported by ships and all components of the ecosystem. There is flexibility in the development of the map. It allows the inclusion of other substances like stress factors in the ecosystem. The basic calculations involved in the process perfectly fit in a simple spreadsheet, so that the user can see which values are used and, when more information becomes available, the spreadsheet can be updated. Currently, no vulnerability maps exist for pollution in freshwater bodies.

The maps developed indicate which areas are more vulnerable to a type of oil spill than others. The degree of vulnerability is dependent on the potential damage and the expected recovery of the selected ecosystem components present in that area. Ecosystem components include species, habitats and ecological functions in the water system. These components are strictly being controlled by RWS and are also protected by current (inter-) national policies and laws. The ecosystem components could also be of commercial interest (predominantly fish and shellfish). From the list of components the most prominent of them in the marine waters with sufficient data and basic information are selected. These reports present selected species from the North Sea ecosystem and they are used for testing the V-maps methodology. Other species and habitats may be added to the list in future.

In the development of the V-maps, the behaviour and the effects of substances are labelled, following international standards, for instance the SEBC and GESAMP codes for behaviour and effects of the substance. The V-maps' approach calculates the Substance Vulnerability Point as a function of exposure rate × sensitivity / recovery. Multiplied with the occurrences of the corresponding species, these yields the geographical vulnerability maps (see equation 1).

$$V = E \times \frac{S}{R} \qquad (1)$$

Where
V = vulnerability
E = potential exposure
S = sensitivity, and
R = recoverability.

In the future this set of preliminary maps may be improved and extended with:

- data on other species
- habitats
- additional areas such as the Wadden Sea and the Western Scheldt
- areas of special concern such as marine conservation areas, shellfish banks and spawning areas
- the coastal waters (including sensitive objects that are important for society)
- other relevant hazardous chemicals that are transported at sea

The V-maps use a 'bottom-up approach (Figure 16). However, other important existing methods for the construction of ecological sensitivity maps use more of a 'top-down' approach. Three of these methods are:

- Sensitivitätsraster
- Environmental Sensitivity Index, ESI
- SensMaps/MarLIN

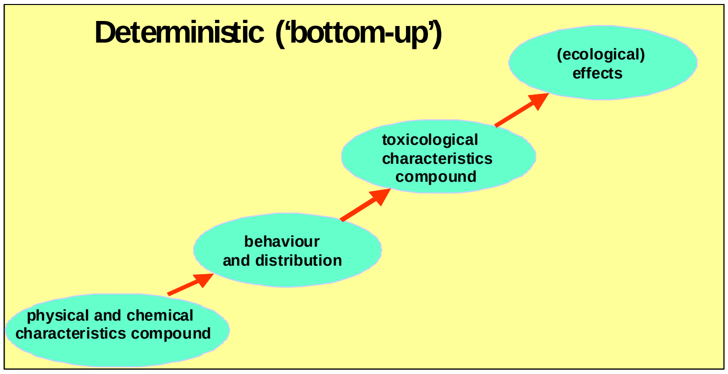


Figure 16 Scheme of a deterministic or 'bottom-up'approach for making ecological sensitivity maps for calamities (adopted from RIKZ, 2003).

4 River Basin Management Plans (RBMP's)

4.1 Introduction

The RBMP's provide useful information for ECODIS on how and which ecosystem characteristics have to be taken into account when attempting to assess environmental effects of a chemical disaster event. RBMP's also provide monitoring programmes and have a well described step-by-step approach. The fundamental difference compared to a disaster event is that that the monitoring and measures of a RBMP is by nature slow while a disaster requires immediate action. Below a short summary is given on how RBMP's are applied based on a report dealing on the implications of the WFD for water management of the Sea of Marmara (Gotjé et al., 2007). Only the RBMP steps which are relevant for ECODIS are shown and explained in more detail.

4.2 River Basin Management Plan (RBMP): remediation measures

The implementation of the WFD in a certain river basin requires the development of a River Basin Management Plan (RBPM). In such a RBMP, water issues (problems as well as measures) are addressed in an integrated way, on the scale of a river basin, from source to coastal area. The WFD gives guidelines for the contents and format of the RBMP. The concept of the WFD and a RBMP comes down to the following scheme (Figure 17).

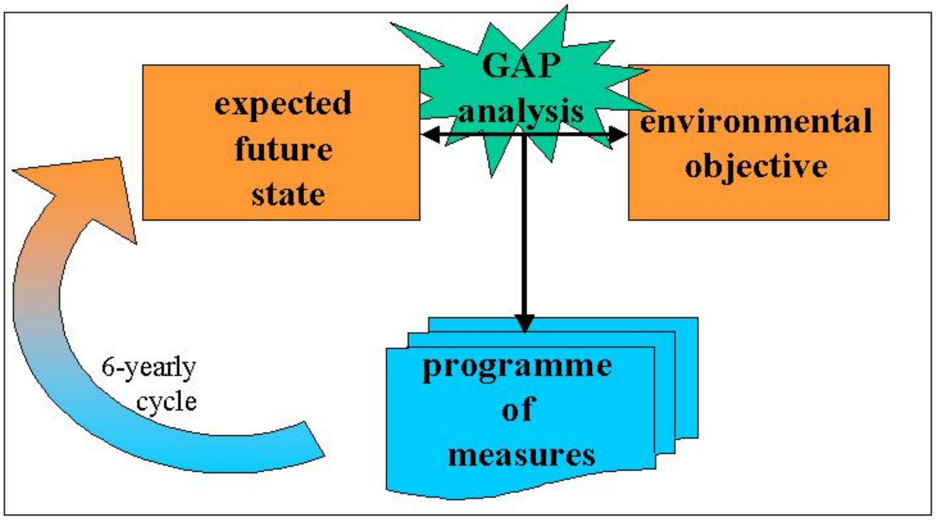


Figure 17 Concept of the WFD (from Gotjé et al., 2007)

First an expectation of the future (chemical and biological) status of the water bodies must be made based on the current state. For this the current state must be known very well. In a gap-analysis, the expected state is compared with the environmental objectives. Objectives are set for each individual type of water. If the objective is not likely to be met, measures should be taken. Every six years, one should investigate the outcome of the programme of measures.

The WFD prescribes the elements that a River Basin Management Plan must contain. These are the following eleven elements:

1. Characterisation of the river basin;
2. Summary of significant pressures and impacts of human activities;
3. Identification and mapping of protected areas;
4. Map of monitoring network(s);
5. List of environmental objectives;

6. Summary of economic analysis;
7. Program of measures;
8. Register of more detailed programs including summary;
9. Summary of measures and results for public information and consultation;
10. List of competent authorities;
11. Contact points and procedures for obtaining background info and comments from the public.

4.3 Characterisation of the river basin

General description

For the water Frame Directives a general description of the environment and its present state must be given.

This includes:

- Review of all protected area's;
- Review of existing monitoring locations;
- Review of existing monitoring data;
- List of basic data on respective waterbody;
- Description of existing nature;
- Each obligatory quality parameter must be described.

Description of surface water

The surface water must be described based on the following aspects:

- Determination of the river catchment area;
- Determination of water bodies: categorisation;
- Determination of water types inside the distinguished water bodies; criteria for identifying the water types are:
    - category (river, lake, transitional water, coastal water);
    - altitude;
    - slope (rivers);
    - geology;
    - size (width of channel / surface area);
    - salinity;
    - connection to a river (lakes).
- Identification of human impact for determination the state of the water body.

4.4 Summary of significant pressures and impacts of human activities

Introduction

The pressure and impact analysis is performed to investigate the chance and causes of not meeting the environmental objectives. It is an important and effective way to assess the main 'threats' and problems of the water system. By prioritising these threats and problems, the most effective measures can be chosen.

Pressures and impacts

The pressure and impact analysis as required by the WFD is a new way of analysing a water system and introduces new concepts. Table 4 explains the most important definitions used in the pressure and impact analysis.

Table 4 Definitions used in the pressure and impact analysis (source: EU Guidance on Pressure and Impact analysis, version 3.0).

Term	Definition
Driver	An anthropogenic activity that may have an environmental effect (e.g. agriculture, industry)
Pressure	The direct effect of the driver (e.g. change in flow , a change in the water chemistry)
State	The condition of the water body resulting from both natural and anthropogenic factors (i.e. physical, chemical and biological characteristics)
Impact	The environmental effect of the pressure (e.g. fish killed, ecosystem modified)

The pressure and impact analysis will be an iterative process with two starting points, as shown in Figure 18.

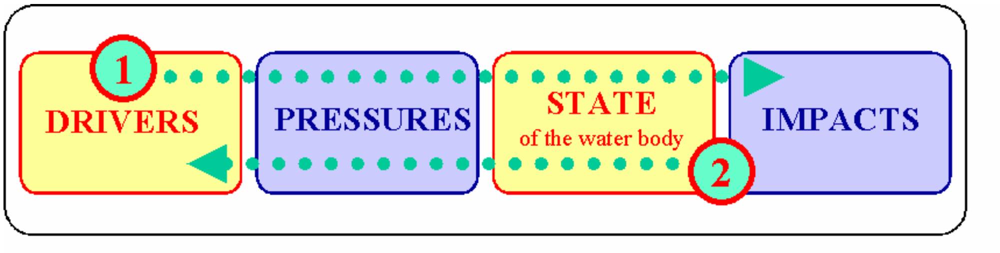


Figure 18 Scheme of the pressure and impact analysis with two possible starting points (1 and 2).See the text below for an explanation (from Gotjé et al., 2007).

The first way starts at the 1 on left side of the scheme of Figure 18. The following steps will be taken.

A. First, relevant drivers are identified and described, for example agriculture, industry, households etc.
B. Then each driver will be analysed in terms of pressures, for example abstraction for domestic use, discharge of industrial wastewater. It is important to clearly and quantitatively describe the link between the driver and the pressure.
C. After step B, the pressure will be translated into the state of the water body / water system.
D. The state of the water body is translated into an impact on the aquatic *eco*system: change in abundance of species, decrease in biodiversity, loss of habitats etc.

A second way starts at the 2 on the right side of the scheme:

A. The process starts with field observations. For example monitoring results show that a water body has a bad state: too few fish, a high nitrate concentration etc.
B. Then a search for the causes of this bad state starts. This is the search for the pressures. One could discover for example that the high nitrate concentration is a result of discharge of untreated wastewater.
C. When the cause of the bad state is found, this pressure can be linked to a driver.

In practice, probably both ways will be used. Some information about drivers will be available and some monitoring results. First you will try to link the information about the drivers with the monitoring results. Most likely, some 'gaps' will remain: drivers of which the impact is unclear, an observed state that cannot be explained yet. Then more research and monitoring will be needed to fill the gaps: to get a complete picture of all relevant drivers, their pressures and impacts.

Potential relevant sources and effects

Diffuse pollution:
Diffuse pollution originates mainly from agriculture. The two main pressures are:

- fertilisers, pesticides and herbicides used in irrigated agriculture;
- drainage water containing salt and sodium.

This type of pollution is not relevant for ECODIS as disasters normally originate from only one source:

Point source pollution:
An inventory of point sources for pollution (industrial, agricultural and domestic) must be made. It is necessary to provide quantitative information of point source pollution: *who* is discharging *what* in *which* amount.

Prioritising pressures

When the pressures and impact analysis is finished, it should give a clear view on the main problems and pressures. By prioritising these threats and problems, the most urgent measures can be chosen to reach Good Ecological Potentials as will be mentioned below.

4.5 Identification and mapping of protected areas

A register and map(s) of protected areas must be made. With 'protected areas' the WFD means areas that are protected under existing Community legislation such as:

- Drinking water protection zones;
- Bathing water locations;
- Areas protected under the Bird- and Habitat directive, of which the protection may depend significantly from maintaining or improving the water quality status.

4.6 Map of monitoring networks

The next step is to map the existing monitoring network(s).

4.7 Environmental objectives

Next, a process is initiated leading to environmental objectives for each individual water body. When all water bodies are characterised and thus given a code representing their 'type', reference conditions must be defined for each individual type. These reference conditions (described in quantitative terms) form the basis of a scale of classes (ecological scale) to define the environmental objectives for and the status of a water body.

Identification of reference conditions

The identification of reference conditions is the link between the typology and the objectives. For each water type ecological reference conditions have to be defined. The reference conditions reflect the undisturbed state of a water type with no or "very minor" human impacts and thus reflects the high status on the ecological scale. All the other statuses of the ecological scale will be derived from this high status including good status. The reference condition will be based on the type-specific biological quality elements, hydro-morphological and physicochemical conditions.

Reference conditions can be found:

1. In the past (temporally based); in some cases the reference conditions can be reconstructed from historical databases.
2. If the first is not possible, then it can be found in the present in another water body or over the border (spatially based);
3. If the second is also not possible, it can be found with the help of models and expert judgement: The models use data from existing undisturbed water bodies.

Reference conditions must be described for the quality elements assigned to each water category (see Table 5).

Table 5 Quality elements to describe reference conditions (from Gotjé et al., 2007).

Quality elements	Rivers	Lakes	Transitional waters	Coastal waters
Phytoplankton		X	X	X
Phytobenthos	X	X		
Macrophytes	X	X		
Macroscopic algae			X	X
Angiosperms			X	X
Macro invertebrates	X	X	X	X
Fish	X	X	X	
Hydro morphology	X	X	X	X
Physic-chemistry	X	X	X	X

In some cases there are not enough data to determine reference conditions based on all the above mentioned quality elements. In such cases it is allowed to determine preliminary reference conditions and start an additional monitoring program in order to collect the missing data. The reference conditions are not always “perfect” values; they are the values of a nearly undisturbed state. In some cases the background concentration of a chemical can be high from nature. But then again, such a situation will still be a reference condition as the term “undisturbed” reflects no or “very minor” human impact. Member states do not have to establish chemical reference conditions. However, they do have to establish appropriate standards for physic-chemical quality elements at good status.

Ecological scales and its boundaries

Based on the different reference conditions for each water type an ecological scale should be made. With these scales the status of a water body can be determined in terms of the Ecological Quality Ratios (EQRs). In this ratio the values of all quality elements of a water body are assembled to one observed value and compared with its reference value (see Figure 3).

Setting environmental objectives

Environmental objectives are goals set for water bodies, consisting of chemical, morphological as well as biological elements. It is important to set realistic goals and realistic objectives. The environmental objectives will be used to develop a program of measures. It is important to have knowledge on measure-effect processes.

Chemical objectives for surface waters

The WFD sets objectives for the chemical status of aquatic ecosystems by defining concentration thresholds for specific substances such as pesticides and heavy metals. For the priority substances, a reduction of the output must be established. For a subgroup of the list of priority substances, the priority hazardous substances, the goal will be to phase out the use or production and stop the discharge into the river altogether. The European Commission has set the standards for the first cohort of priority substances (WFD 2008) and will update legislation regularly.

There are other pieces of legislation providing threshold values corresponding to good status which can be used for setting of chemical objectives. Three examples of EU directives are presented below:

- directive about the required quality of surface water meant for the production of drinking water (75/440/EEG);
- directive about the quality of surface water needing protection of enhancement to be able for fish life (78/659/EEG);
- directive about discharges of dangerous substances (76/464/EEG).

Ecological objectives for surface waters

The ecological objectives are to achieve a Good Ecological Status for natural water bodies or Good Ecological Potential for heavily modified water bodies. For heavily modified water bodies the Good Ecological Potentials can be achieved in two ways (see Figure 20):

1. top-down i.e. from the reference situation
2. bottom-up i.e. from the present situation including the effects of programs of measures (the so called ‘Prague method’, also called pragmatic method).

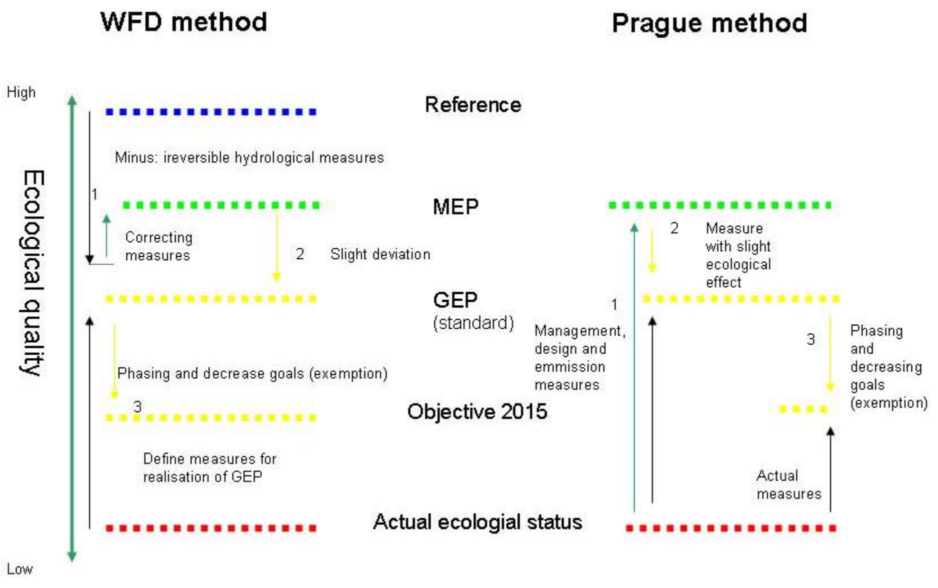


Figure 20 Two pathways to MEP and GEP (maximal and good ecological potential) and the objectives for 2015. Left: top-down approach starting from the reference conditions and right bottom-up approach starting from de actual ecological status (from Gotjé et al., 2007).

The first method is difficult in case the knowledge of the reference conditions is insufficient. The second method is pragmatic. In this method the result of all feasible measures for improving the present state of the environment will set the standard for the Good Ecological Potentials of water bodies. In most cases this method is used for setting objectives for the Water Frame Directives.

Protected areas: For protected areas, objectives should be derived from the WFD and from the directives or other regulations by which they are assigned as a protected area. The objectives for the water bodies in protected areas should ensure that the state of the area as a whole will not decrease. The rule is that from the WFD-objectives and the objectives from other regulations, the most severe objective is valid.

Program of measures: From the list of significant pressures a program of measures has to be developed. With the aid of these measures the Good Ecological Potentials of the water bodies must be met.

Monitoring of surface water: Three different types of monitoring can be distinguished, surveillance (detecting long term trends in water bodies), operational (surveying the status of water bodies ‘at risk’ and the effects of taken measures to improve the status), and investigative (monitoring with the aim to identify the factors responsible for the risk).

Intermezzo

Reference condition, exceedance of thresholds & future environmetal objectives?

When dealing with a disaster pollution event three important steps can be discriminated (see Figure 21):

Step 1:

After a disaster pollution event it is important to estimate what the chemical and biological situation was *prior* to the disaster. The situation may be such that the waterbody already had a poor ecological status and/or exceedence of thresholds of priority compounds due to anthropogenic and/or natural causes. In this case it is obviously not the goal of the proposed measures to bring the environmental state back to a good one within a couple of years. Naturally the standard actions of the RBMP are in effect (good ecological status by 2015).

Step 2:

Determination of the relevant chemical and ecological thresholds which are in effect in the specific waterbody (e.g. WFD, Drinking Water Directive etc.). Next, establish if these thresholds are exceeded and if this exceedence is the result of the pollution disaster event.

Step 3

Establish the future chemical and ecological objectives of the polluted waterbody with the respective measures.

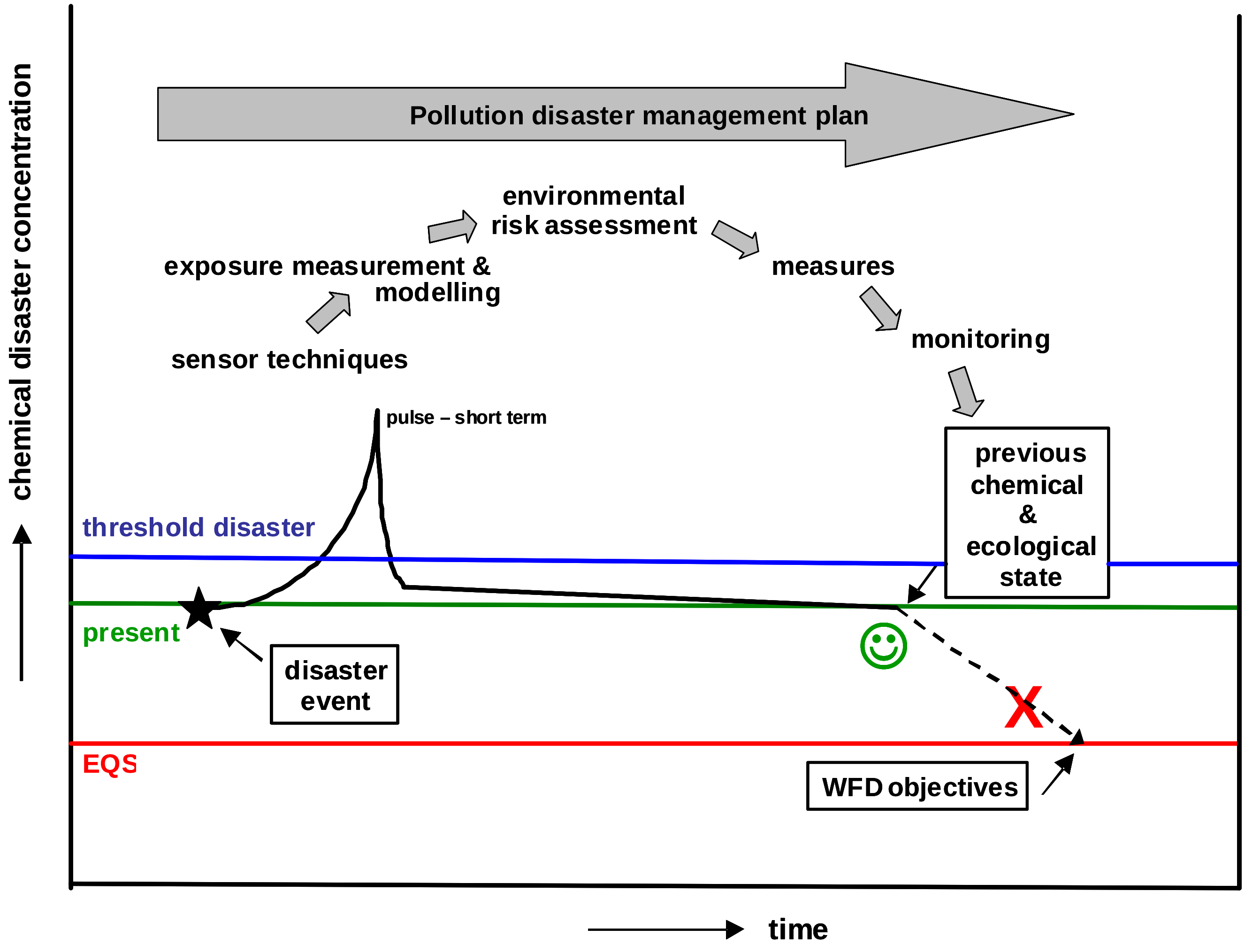


Figure 21 Schematic overview of a proposal on how to deal with a pollution disaster event.

Part C: Major accidents registered in the EC MARS database: A review of water polluting accidents (1986 to 2005)

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1 Analysis of accidents

1.1 Introduction

The present report has been prepared within the framework of the ECODIS project (full title: Dynamic Sensing of Chemical Pollution Disasters and Predictive Modelling of their Spread and Ecological Impact). ECODIS develops sensor technologies for monitoring the physicochemical reactivity and biological impact of inorganic and organic pollutant species in aquatic systems. The project also applies these technologies to the study of the short and long-term chemical and biological status of aquatic ecosystems following a pollution disaster. Exposure conditions experienced by organisms are defined by the temporal profiles of concentration and speciation of pollutants. These profiles will be quantitatively linked to biological effects via an innovative dynamic approach based on the flux of pollutant species as a key parameter in effective ecosystem quality.

ECODIS also opens the way for developing sophisticated strategies for dynamic risk assessment and disaster management policies.

One of the ultimate goals in the project action plan is the formulation of a set of guidelines for monitoring, management and interpretation of aquatic pollution disasters. To such purpose, it is essential to analyse this matter in depth and identify an action strategy, by taking into consideration:

1. the key factors (biological, chemical and physical), determining the fate and impact of pollutants at disaster sites;
2. the tools for on-site determination of these parameters, which can provide the best indication of the immediate and long term risks;
3. the systems for a rapid knowledge and mapping of the ecological risks and relative involved sites, as a function of location and time;
4. the provision of models, which may describe the temporal and spatial spread of pollutants and risks.

The recommended procedure will also account for the type of water body impacted, i.e. freshwater (river, lake), estuarine, marine.

In such a context, a wide and detailed analysis of the water polluting major accidents, which have occurred in the last decades may give valuable elements towards the identification of lessons learned regarding critical steps in environmental monitoring and risk management. Besides the open literature, relevant information about these accidents is mainly available on databases set up by Institutions, Enterprises and NGOs. We can cite, as an example, the databases set up by the UK Health Safety Executive[64], the US Environmental Protection Agency[65], by competent Ministries of most States and by international Organizations, such as the World Health Organisation, the United Nations Environment Program UNEP[66] and the Commission of the European Union.

The latter, in 1986, has established the Major Accident Reporting System, MARS[67], based on the requirements of EU directives 82/501[68] (Seveso I) and 96/82[69] (Seveso II or COMAH directive). It is dedicated to collecting data on major industrial accidents from the Member States of the European Union (mandatory) and from other OECD countries (on a voluntary basis).

A major accident is defined, in the Seveso II directive, as “an occurrence such as a major emission, fire, or explosion resulting from uncontrolled developments in the course of the operation of any establishment covered by this Directive, and leading to serious danger to human health and/or the environment, immediate or delayed, inside or outside the establishment, and involving one or more dangerous substances”. However, also near misses, i.e. accidents causing no harm or no serious harm are taken into account and recorded in the MARS database. It is managed by the Major Accident Hazards Bureau (MAHB), a special Unit within the Joint Research Centre's Institute for the Protection

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[64] http://www.hse.gov.uk

[65] http://www.epa.gov/

[66] http://www.natural-resources.org/environment/regulators/index_reg.htm

[67] http://mahbsrv.jrc.it

[68] Directive 82/501/EEC on the major-accident hazards of certain industrial activities. O.J. L 230, of 5 August 1982.

[69] Council Directive 96/82/EC, of 9 December 1996, on the control of major-accident hazards involving dangerous substances. Official Journal L 10, of 14 January 1997 and Directive 2003/105/EC of the European Parliament and of the Council, of 16 December 2003, amending Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances. O.J. L 345, of 31 December 2003.

and Security of the Citizen, founded in 1996, with a remit "to offer scientific and technical support to other services of the Commission (principally DG Environment), in the successful implementation of European Union policy on the control of major industrial hazards and the prevention and mitigation of major accidents" (Kirchsteiger 2001)[70]

Briefly, the information contained in the MARS database is organised in 3 main sections. The Report Profile is designed to provide sufficient information to identify an accident from some basic details. These are, among others, the date of the accident, the identification data of the industrial establishment where the accident occurred, the name and address of the Member State Competent Authority, which has the task of communicating the event, the type of event and related legislation. It also assigns a unique identification code to the accident.

The Short Report is designed to assemble the most important data about the accident and its consequences. So, it may work as a synopsis of the accident and give a concise overview of all the important characterising elements of the accident itself. The Short Report moreover, is available for querying by the public online.

Lastly, the Full Report (in its turn subdivided into 3 sections: occurrence, consequences, response) is generally elaborated by experts, when the dynamics of the accident have been thoroughly elucidated and often also contain confidential information.

The following report contains a review of the major accidents recorded in the MARS database in the period from 1986 to 2005. Only the information freely available on the Short Report has been consulted. However, it is outside the scope of this analysis to provide an exhaustive list of accidents, or to give long and detailed descriptions. The main aim of this report is to derive the main aspects of this phenomenon and draw lessons for implementing appropriate prevention and mitigation plans of action.

1.2 Characteristics of major accidents

Forty-four accidents, involving water pollution[71], have been selected for analysis, in order to fulfil the scope and requirements of the ECODIS project. Their geographical distribution covers the whole of the European Union, while information from non-EU countries, namely Norway and the USA, has been analysed. In general there was more information available from accidents in France, the Netherlands, Germany and Italy, while accidents in Spain, UK, Belgium, Czech Republic, Denmark, Greece, Ireland, Portugal and Sweden also contributed to the analysis. It should be noted that the detail of reporting of environmental consequences varies significantly across Member States due to different attitudes and interests of the reporting authorities.

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[70] Kirchsteiger (2001) Major Accident Reporting System (MARS) Technical Guideline on Reporting Accidents to the MARS Database, download via http://mahbsrv.jrc.it/MARS/MARS-Technical-Guideline-February 2001.pdf

[71] With respect to the immediate damage to the aquatic environment any accident having at least one of the following consequences has to be notified to the European Commission (Kirchsteiger 2001):
- significant or long-term damage to freshwater and marine habitats
    - 10 km or more of a river or canal
    - 1 ha or more of a lake or pond
    - 2 ha or more of a coastline or open sea
- significant damage to an aquifer or underground water (1 ha or more)

1.2.1 Type of Industry

Table 1 shows the number of major water polluting disasters caused by various types of industrial activities. General Chemicals Manufacture is the industry most frequently involved in such accidents (9 accidents, 20 %), followed by factories producing pesticides, pharmaceuticals and other fine chemicals (6 accidents, 14 %) and by petrochemical, refining, processing and wholesale and retail storage and distribution, with 5 accidents respectively. Food and drink, waste treatment and disposal are also responsible for some accidents. Agricultural firms, though not using or producing dangerous substances, may cause ecological problems when a huge quantity of biological materials such as molasses or wine residues accidentally spills and reaches water courses. Other industries affected are handling and transportation centres, paper manufacture, printing, publishing, plastics and rubber manufacture, ceramics and textiles, clothing and footwear. Special attention has to be given to tanker shipwrecks, which represent a very frequent and serious source of ecological disasters.

Table 1. Distribution of the selected 44 major accidents (MA) for "Type of Industry"

TYPE of INDUSTRY	N. MA
General Chemicals Manufacture	9
Pesticides, Pharmaceuticals, other fine chemicals	6
Petrochemical, Refining, Processing	5
Wholesale and Retail Storage and Distribution	5
Food & Drink	4
Waste Treatment, Disposal	3
Not known / not applicable	3
Agriculture	2
Handling and Transportation Centres	2
Paper Manufacture, Printing, Publishing	2
Ceramics	1
Plastics and Rubber Manufacture	1
Textiles, Clothing and Footwear	1
Total	**44**

In the following the 44 accidents are examined according to the classification parameters, adopted in the MARS database that is "type of accident"," substances directly involved"," immediate sources"," causes", "effects", "emergency measures" and "lessons learned". Three accidents are reported in detail, as examples, in the Part 2 to this Annex.

1.2.2 Type of accident

Accidents are categorised as "Release", "Water contamination", "Fire" and "Explosion". As already mentioned, every selected accident has caused water contamination. In nineteen accidents, water contamination is accompanied and/or caused by a release of substances, whilst in eighteen cases of water pollution the type of accident was a fire often leading to a water contamination due to the foams used to extinguish fires. Thus, a frequent sequence of events leading to water pollution is release of flammable and explosive substances, fire and explosion, with resulting wide-spreading of pollutants in the environment.

In reality water contamination can not occur without a release of pollutants. This contradiction is due to the fact that the person inserting the report into the database had the choice between the different types of accidents. Probably the release was considered as a secondary process in some cases and not selected as a type of accident.

Table 2. Distribution of the selected 44 Major Accidents (MA) for "Type of Accident"

TYPE of ACCIDENT	**N. MA**
Water Contamination (only)	5
Water Contamination and Release	19
Water Contamination and Release and Fire and Explosion	11
Water Contamination and Release and Fire	4
Water Contamination and Fire and Explosion	2
Water Contamination and Release and Other	1
Water Contamination and Fire	1
Water Contamination and Other	1
Total	**44**
Total Release	35
" Fire	18
" Explosion	13

1.2.3 Substances directly involved in the accident

The chemicals directly involved in accidents are classified, in the MARS database, on the basis of physicochemical and toxicological properties, as "Toxic", "Ecotoxic", "Flammable", and "Explosive". As expected, most accidents involve ecotoxic (28 accidents) or toxic (24 accidents) substances. Major accidents, however, generally involve many substances, with different properties (Table 3) and this is likely to amplify their effects. Substances involved in the selected water polluting accidents, divided into inorganic and organic chemicals, pesticides and miscellaneous are listed in text box 1.

As shown in the text box, simple and very commonly used substances may represent a cause of important adverse events. One can underline the warning presence of some pesticides and derivatives of petrol, which are very dangerous substances both to the environment and human health. So, as regards pesticides, we may observe that most of them (e.g. carbofuran, methiocarb, pendimethalin, methyl-parathion, thiram) have been classified as N, R50 - 53 (very toxic to aquatic organisms / may cause long-term adverse effects in the aquatic environment). Crude oil spilled from wrecked tankers, then, represents a peculiar stressor for marine birds and mammals: dangerous substances, mostly PAHs, engulfed into sediments, may be up-taken by benthic organisms, accumulated in their tissues and, lastly, transmitted to wildlife animals, foraging in the contaminated area. Oiling then, may weather feathers or fur of sea birds and marine mammals, and so, it may provoke harms, as hypothermia, smothering, drowning and ingestion of toxic substances. Accidents involving such chemicals should be monitored over a long period.

Special care should also be taken with every substance given the risk phrases N, R 50/51/52/53 (e.g. ammonia, chlorine, glutaraldehyde, HCN, Na hypochlorite, PCBs, thiourea), because of their dangerous potentialities to the environment.

Table 3. Distribution of the selected 44 Major Accidents (MA) for "Substances directly Involved"

SUBSTANCES PROPERTIES	**N. MA**
Eco-toxic	7
Eco-toxic and Toxic and Flammable and Explosive	7
Eco-toxic and Toxic,	6
Toxic	5
Flammable and Explosive	4
Flammable	3
Eco-toxic and Toxic and Flammable	3
Toxic and Flammable and Explosive	2
Eco-toxic and Flammable and Explosive	2
Other	2
Eco-toxic and Other	1
Eco-toxic and Flammable	1
Eco-toxic and Toxic and Flammable and Explosive and Other	1
Total	**44**
Total Eco-toxic	28
Total Toxic	24
Total Flammable	23
Total Explosive	16

Foodstuff, as already mentioned, may also become a cause of ecological harm (death of fish and other aquatic organisms, loss or damage of natural heritage), when discharged in abnormal quantities. Estimates of the quantity involved always constitute an important parameter in order to foresee the immediate and long-term consequences of an accident and plan appropriate prevention and recovery measures. Furthermore, some substances are very dangerous to human health. Among these, probable (R45) or suspect (R40) carcinogens, such as crude oil Arabian light, gasoline, naphta, sulphur dioxide, o-toluidine; mutagens (R68), as phenol, or toxic to reproduction (R61/63), such as CO, toluene, thiourea.

1.2.4 Immediate Sources

This section refers to the immediate cause of an accident, without direct regard to the overall activities of the plant. The possible choices are "process", "storage" and "transfer". Generally, "process" refers to the series of technological actions, which lead to the end products; "transfer" refers to the internal transport of substances and "storage" to the presence of a large amount of dangerous substances for the purposes of warehousing, depositing in safe custody or keeping in stock. The results are reported in Table 4.

As can be seen in the table, improper storage or a lack or insufficient knowledge of the process represent the major immediate cause of accidents. Transfer mainly involves the outpouring of crude oil and its derivatives from a tanker.

Text box 1 Substances involved in the selected major accidents.

Inorganic Chemicals:
Acetone cyanohydrin, Calcium hypochlorite, Calcium peroxide, Carbon Disulphide, Carbon Monoxide, Chlorine, Halogens, Mercaptans, Nitrogen, Oxigen, Potassium and Sodium Hydroxide, Sodium chlorite, HCl, HCN, HF, K_2CO_3, NO, N_2O, NO_2, NH_4+, HNO_3, H_2SO_4.

Organic Chemicals:
Anthrachinone, Butanol, Cellulose Nitrate, Chlorobenzene, Crude oil, Cyclohexylene, Dicyclopentadiene, Diesel Oil & Gasoil, Dioxins, Dyes, Formaldehyde, Furfuraldehyde, Gasoline, Glutaraldehyde, Heavy & Aviation Fuel oil n°2, Isopropanol, Methanol, Methylene Dichloride, Methyl Ethyl Ketone, Naphtha, Naphthalene, Phenol, Polypropylene Glyicol, Toluene, o-Toluidine, N-methyl-1-methyl-Thio-2-nitro-Ethenanamine, 1,1-Bis-(Methyl-thio)-2-nitroethene; Dipotassium Salt 1,1 Dithio-2-Nitroethene, PCBs, Resins as Unsaturated Hydrocarbons C9, Resins as Saturated Hydrocarbons C9, Unleaded Petroleum Additives.

Pesticides:
Carbofuran, 2,4-Dichlorophenoxyacetic Acid, Dimethoate, Dimethoate [Rogor], Hymexazol, Iprodione, Methiocarb, Nitro-Pendimethalin, Nitroso-Pendimethalin, Parathion-Methyl, Pendimethalin, Thiram.

Miscellaneous:
Eucalyptus bark, Molasses, Saw dust, Seed, Slaughterhouse slurry, Starch glue, Textiles, White wine, Wine harvest residues.

Table 4. Distribution of the selected 44 Major Accidents (MA) for "Immediate Sources"

IMMEDIATE SOURCES	N. MA
Process	15
Storage	13
Process and Storage	5
Other	4
Storage and Transfer	3
Transfer	2
Process and Transfer	1
Process and Storage and Other	1
Total	**44**
Total Process	22
Total Storage	22
Total Transfer	6
Total Other	5

1.2.5 Causes

As regards the suspected causes, selections can be made between "plant equipment", "human", and "environmental".

Table 5 Distribution of the selected 44 Major Accidents (MA) for "Suspected Causes"

SUSPESCTED CAUSES	**N. MA**
Human	11
Plant Equipment	10
Plant Equipment and Human	10
Other	6
Plant Equipment and Other	2
Plant Equipment and Environmental	2
Human and Environmental	1
Human and Other	1
Unknown	1
Total	**44**
Total Plant Equipment	24
Total Human	22
Total Environmental	7
Total Other	3

"Human error" is the only cause of 11 accidents (25 %) and the concomitant cause of 22 of them and is the Suspected Cause with the highest frequency. A human error may be the consequence of insufficient care of delegated workers or lack of proper training and supervision.

"Plant Equipment" represents a frequent cause of accidents too. However, it includes different situations: failure or malfunction of the various pieces of machinery or components; failure due to the corrosion or mechanical fatigue of a material; the blockage of a valve or a pipe.

"The Environment", lastly, constitutes a minor but not negligible cause. It regards, generally, adverse weather conditions (e.g. extreme values of temperature, wind speed), natural events (flooding, earthquake) or the so called domino-effect from another accident.

1.2.6 Immediate Effects

Effects are categorized in "Human Deaths", "Human Injuries", "Ecological Harm", "Natural Heritage Loss", "Material Loss", "Community Disruption" and "Other".

"Ecological Harm" is always present (in one accident only probable) and is therefore the most frequent effect of accidents. However, this field is very large and generic, designed to record information on the effect of the accident on every component of the environment. Therefore, ecological harm includes chemical pollution, increases of chemical and biological oxygen demand due to degradation of discharged organic substances, whitening of plants, death of fish and other aquatic organisms and contamination of marine birds often followed by death. The latter, generally affected in the case of tank ship spills, are the object of intensive studies to determine both the nature and degree of water pollution and the acute and long-term effects on living organisms. To discover appropriate bioindicators is also a main goal.

“Human Deaths and Injuries” concern people inside and outside the establishment. Special mention should be made of emergency personnel, both official (e.g. fire-fighters, police officers, etc.) and voluntary, who take part in emergency action, in response to the accident. These people are often the main victims of the accident. Other than death, which is not a very frequent event, they may suffer burns, traumas, poisoning and other physical or psychological injuries, sometimes requiring hospitalization or medical treatment.

“Material loss” aims at quantifying monetary costs of property damage and associated restoration efforts, whilst “Natural Heritage Loss” is devoted to record the loss of sites or monuments of great historical importance. Fortunately, this rarely happens (2 accidents).

Table 6. Distribution of the selected 44 Major Accidents (MA) for “Immediate Effects”

IMMEDIATE EFFECTS	**N. MA**
Ecological Harm	12
Ecological Harm and Material Loss	7
Ecological Harm and Material Loss and Community Disruption	5
Ecological Harm and Human Injuries and Material Loss	4
Ecological Harm and Human Injuries and Human Deaths and Material Loss	3
Ecological Harm and Human Injuries and Material Loss and Community Disruption	3
Ecological Harm and Other	2
Ecological Harm and Community Disruption	2
Ecological Harm and Human Deaths and Human Injuries and Material Loss and Community Disruption	2
Ecological Harm and Natural Heritage Loss and Material Loss	1
Ecological Harm and Human Injuries and Human Deaths	1
Ecological Harm and Human Injuries and Natural Heritage Loss and Material Loss	1
Material Loss	1
Total	**44**
Total Ecological Harm	43
Total Material Loss	27
Total Community Disruption	14
Total Human Injuries	10
Total Human Deaths	6
Total Natural Heritage Loss	2

“Disruption of Community Life” is a field designed to provide information on the effect of the accident on community life, such as disruptions to buildings, interruption of utilities (gas, electricity, sewage treatment works, telecommunications, roads, railways, and so on). This field, moreover, intends to explore whether there was concern about the accident among the population, outside the establishment, the media and policy-makers.

1.2.7 Emergency measures taken

This field includes many components. They have to be selected among “On Site Systems”, “External Services”,” Sheltering”, “Evacuation”, “Decontamination”, “Restoration” (Table 7).

Table 7. Distribution of the selected 44 Major Accidents (MA) for “Emergency Measures”

EMERGENCY MEASURES TAKEN	**N. MA**
External Services and On Site Systems	11
Other	6
External Services and On Site Systems and Decontamination	4
External Services	3
External Services and On Site Systems and Evacuation and Decontamination	3
Decontamination	2
External Services and On Site Systems and Sheltering and Evacuation and Decontamination	2
Restoration	1
On Site Systems	1
External Services and Sheltering	1
External Services and Other	1
External Services and Decontamination	1
On Site Systems and Restoration	1
External Services and On Site Systems and Restoration	1
External Services and Decontamination and Restoration	1
External Services and Decontamination and Other	1
On Site Systems and Sheltering and Evacuation	1
External Services and On Site Systems and Sheltering and Decontamination	1
External Services and On Site Systems and Evacuation and Restoration	1
External Services and On Site Systems and Evacuation and Decontamination and Restoration	1
Total	**44**
Total External Services	28
Total On Site Systems	27
Total Decontamination	16
Total Evacuation	8
Total Restoration	6
Total Sheltering	5

As the table shows, every accident (with one exception) requires the utilization of on-site systems and/or external services. The first includes e.g. drenching or extinguishing systems, internal emergency teams, secondary containment, the second may comprehend external fire-fighting and ambulance/victim recovery services, police or military intervention, crowd and traffic control and also voluntary organisations mobilization. These measures generally have to be associated with other more specific measures, such as evacuation of internal personnel, sheltering (i.e. public alerted directly by emergency services or by media), decontamination (i.e. measures aimed at eliminating or containing the spread of the dangerous substances, usually by chemical means) and restoration (i.e. the re-establishment of the pre-accident state, by cleaning, rebuilding, removing, and so on). In addition, other measures may be adopted, such as psychological support or financial help.

1.2.8 Lessons learned

This field of the MARS database may give an important contribution to avoiding or at least mitigating the problem of ecological disasters. The possible choices are to be selected among "Prevention", "Mitigation" and "Other" (Table 8).

"Prevention" is advocated in more than half of the cases, while "Mitigation" only in 13 %. However, these two terms are very generic, and encompass many different conditions. Every accident, in fact, presents its own peculiar characteristics. Therefore, many "learned lessons" are categorised under "Other". They come from the necessity of performing a risk assessment for all modifications, concerning operational procedures or designs, to the usefulness of having a thorough environmental risk analysis, to comply with regulations of storage of dangerous goods, to take into consideration also possible extreme weather conditions (e.g. the possible rupture of pipes from freezing). Moreover, one should not forget the importance of wearing proper and appropriate personal protective devices. Prompt and suitable communication between company managers, local authorities and external emergency services has been proved to be very important in reducing the effects of these accidents.

Table 8. Distribution of the selected 44 Major Accidents (MA) for "Immediate Lessons Learned"

LESSONS LEARNED	**N. MA**
Other	17
Prevention	14
Prevention and Mitigation	8
Prevention and Mitigation and Other	4
Mitigation	1
Total	**44**
Prevention	26
Mitigation	13
Other	21

1.3 Conclusions

Major ecological accidents represent a serious problem to be faced up. Their frequency has been continuously increasing in the last decades, due to many reasons, such as the extensive industrialisation process, the huge number of chemicals available in almost every sector of the working and general environment, new technological processes often not thoroughly known to delegated staff and a not adequate culture of human and environmental safety.

Following some very grave accidents which occurred in the 70s, many important measures, both at scientific and institutional level, have been taken, with the aim of preventing or, at least, mitigating their effects. Among the first, we can mention research programs to identify and study the real causes and the acute and long-term effects of these accidents. At the institutional level, paramount measures are represented by provisions, such as regulations, directives and other legislative acts, promulgated at international or state level.

Within this framework, a pivotal role is played by the so-called Seveso directives, I and II, which have placed the bases of current European ecological politics, Directive I, mainly focusing on health and safety protection, and Directive II, extending to environmental quality defence. Some support tools have been planned, aimed at improving prevention and protection measures. The MARS database may be considered as one of these instruments. Recording major accidents, in fact, and their follow-up, is essential for monitoring and tackling this phenomenon.

The above-reported brief review of water polluting accidents, registered in the MARS database between 1986 and 2005, offers an interesting picture of the European situation. In about two decades, 44 accidents have been reported and published in the database. These have involved different types of industry, such as general and specific (e.g. pesticides, drugs) chemicals manufacture, petrochemical refineries, food & drink factories, waste treatment and disposal plants. Agricultural firms have been responsible for some accidents too. Tank shipwrecks, as already mentioned, also require special care due to their heavy polluting loads.

As regards the dangerous substances involved in these accidents, one can firstly observe that they are very heterogeneous, belonging to several different chemical classes (acids, aldehydes, organophosphates, carbamates) and different uses (pesticides, solvents, auxiliaries). The environmental fate of chemicals constitutes matter for study and debate over a long period. As is well-known, many chemicals are conservative and remain in the sediments even when their sources are reduced or removed. Generally, their effects are long-term, and this increases warning in people and authorities. Moreover, chemicals such as dioxins, endocrine disrupters, organophosphate pesticides and PAHs may cause adverse effects already at very low levels (EUR 19651 EN).

The causes may generally be attributed to human error or to problems of plant equipment (e.g. malfunction of machines, corrosion of materials, blockage of gearings). The accident consequences depend on many different factors, such as the type of industry, the quantity of dangerous substances involved, the location of the plant, the weather conditions. Therefore, apart from injury and death and damage to buildings and other structures, the effects of an accident may be ecological (destruction or alteration of communities of living organisms, abnormal increase in vegetal life), toxic, both immediate and long-term (the spreading of substances which are potentially dangerous to man and the environment), and also disruptive for the plant personnel and of the surrounding area. In this regard, emergency measures are very important, because they can mitigate, or even remit the adverse effects of an accident. They are various: from the intervention of internal and public emergency systems (fire-fighters, police voluntary organisations), to decontamination of the site, sheltering and evacuation of the involved population and restoration.

However, in any database, the ultimate scope is to generate lessons learnt. Lessons can be learned from near-misses as well as actual accidents, and the information in the database should help identify notable areas of concern and facilitate the development of future priorities. In order to improve the safety of an establishment it is important to create a “safety culture” on-site, which is initiated at management level and permeates through all personnel at all levels.

2 Examples for accidents registered in MARS

The following examples are directly extracted from the short report of the MARS database.

Example N. 1

Record: Major Accident occurred in an agricultural plant in 2000.
→ **Type of industry**: agriculture

Fertilizer leakage from a storage tank of Midwest Farmers Co-op in Sheldon, Iowa, USA.
→ **Accident type**: release, water contamination.

Ammonia (C.A.S. No: 7664-41-7), fertilizer Nitrogen (C.A.S. 7727-37-9)
→ **Substances directly involved**: toxic, ecotoxic

The material came from the storage tank.
→ **Immediate sources**: storage

The nitrogen containing fertilizer solution spilled onto the ground when a transfer pipe leading to a bulk storage tank froze and then split.
→ **Suspected causes**: plant equipment, environment

The fertilizer reached an area outside of a containment dike designed to prevent accidental releases and then discharged into a storm drain that empties into the Floyd River. The fertilizer contaminated the river water and was spread under the ice cover of the stream. Up to 7,896 gallons of the fertilizer was lost in the spill.
The fertilizer killed all fish for 20 miles downstream from Sheldon to Alton, Iowa. Restriction of water supply for inhabitants.
→ **Immediate effects**: ecological harm, material loss, community life disruption

The City of Sheldon and co-op workers plugged the storm drain, but were not able to stop all the fertilizer before it reached the river.
→ **Emergency measures taken**: other

Need to take into consideration effects of freezing and possible rupture of pipes as a result of freezing.
→ **Immediate lessons learned**: prevention

Example N. 2

Record: Major Accident in a refinery in 1998
→ **Type of industry**: petrochemical, refining, processing.

Accidental spill of crude oil over a rain water drain, followed by a fire and an explosion in the Beach of Aterro, Portugal, near the refinery.
→ **Accident type**: release, water contamination, fire, explosion

Crude oil Arabian Light (density - 0.8614), C.A.S. No: 8002-05-9.

The amount of crude oil involved was estimated as ca. 210 m^3, of which a part was retained in the storm-water basins of the refinery, while the rest was spilled on the beach.
→ **Substances directly involved**: flammable

A spill of crude oil occurred inside the refinery of Porto during a preliminary transfer operation through a pipeline connecting a buoy with the mainland by pumping crude oil from the ship Enalios Thetis to the refinery. The crude oil spilled in the rain water drain, reaching the beach of Aterro where it ignited, causing serious injuries to two persons, one of whom died because of the injuries.
→ **Immediate sources**: transfer

The ship did not respect the pumping program of crude oil previously agreed between the involved parties to start operations; the permitted flow rate was exceeded by ca. 2.4 times.
→ **Suspected causes**: human

Off-site of the establishment serious injuries to two persons, causing the death of one, damage to the rain water outfall, at least 12 m 1200 mm diameter tube needed to be substituted as well as damage to several inspection rooms, contamination of sand and water, particularly on the beach of Aterro.
→ **Immediate effects**: human deaths, human injuries, ecological harm, material loss

When the contamination of the water in the rainwater drain was detected, it was diverted to the storm-water basin of the waste water treatment plant of the refinery and the pumping from the tanker was stopped. The on-site emergency plan was activated when the fire started on the beach of Aterro. The local authorities were also alerted in order to activate the off-site emergency plan. Extinguishing foam was introduced in the rain water outfall to fight the fire at the beach of Aterro and, after the fire was extinguished, the feeding of foam was maintained in order to assure a complete covering with this extinguishing agent, so as to avoid the release of flammable vapours, which could re-ignite. During the extinguishing operations, approximately 50000 l of foaming agent were used to produce the extinguishing foam. Environmental damage caused by the spill of crude oil was not very serious, because of the amount spilled and the immediate start of operations to reduce the consequences and for restoration.
→ **Emergency measures taken**: on-site systems, external services

Achieve the project to motorise all large sized block valves, in order to reduce response times in closing/opening, particularly in case of emergency.
- Assure that for all modifications concerning operational procedures or design modifications, a risk assessment is performed.
- Resize and automate the diversion system of the rain water drain to the waste water treatment plant, so as to assure that no hydrocarbons may be accidentally released to the sea through the rainwater outfall.
- Work out onsite regulations on the use of draining systems, integrating all separate operating instructions which already exist.
- Any operation not specifically mentioned in the manuals or described by operational instructions, will have to be documented with a written procedure, which will have to be approved by all parties involved and, in case of the involvement of a third party, by the management of the refinery.

→ **Immediate lessons learned**: prevention

Example N. 3

Record: The shipwreck of oil tanker “ERIKA” in the Atlantic, 1999.
→ **Type of industry**: not known / not applicable

A Maltese oil tanker, carrying 39000 tonnes of oil, broke in two parts off the French coast. The 26 crew members were airlifted to safety, 6 being hospitalised. At first the two parts of the ship remained afloat, and it was proposed, indeed attempted, to tow them away. Due to adverse weather conditions, the two parts of the ship sank.
→ **Accident type**: release, water contamination

Heavy fuel oil n°2, with sulphur content between 2 and 4 %.
→ **Substances directly involved**: ecotoxic

The product was being transported in the tanks of the ship. At the moment, 10000 tonnes remain in the tanks, and it is proposed to pump them out.
→ **Immediate sources**: other

At this stage of the investigation, the evidence points to mechanical failure as a cause. The question of human error in the checks carried out by various bodies (authorities, owners, etc.) is under study; a report of the Transport Ministry draws attention to a "behavioural failure" in the commercial chain. The final report should be ready in summer 2000.
→ **Suspected causes**: plant equipment, human

Large numbers of birds were killed, perhaps 100,000 - compared to some 2,000 saved by various associations. More than 400 kilometres of coast in 5 "départements" were polluted to a varying degree. Oyster farming has been severely affected: on 31st January, some 150 hectares of oyster farm were closed, in accordance with the precautionary principle. Losses to the local tourist industry are starting to appear (fewer reservations).
→ **Immediate effects**: ecological harm, material loss

A large-scale operation has been launched to clean up the coasts, with the help of the army, the fire service and volunteers. As of mid-January, some 3000 people were involved on the various sites. There are associations trying to treat and save the birds affected. Action is being taken on the wreck to try and stop further leaks.
→ **Emergency measures taken**: external services, decontamination, restoration,

(no explanation reported)
→ **Immediate lessons learned**: prevention

3 Databases providing information on dangerous substances

In the EU, substances are evaluated, classified and labelled on the basis of well-defined criteria, reported in the directive 67/548/EEC (Dangerous Substances Directive) and its subsequent amendments and adaptations to technical progress (ATP). Especially concerning their properties related to environmental effects, the criteria are described in the 18th ATP of Directive 67/548/EEC. Three parameters are taken into consideration for environmental evaluation: biodegradability, acute toxicity to the aquatic environment, and bio-accumulation. In particular, 3 risk phrases are applied to characterise the substance's acute toxicity: **R50**: Very toxic to aquatic organisms; **R51**: Toxic to aquatic organisms and **R52**: Harmful to aquatic organisms. Tests adopted are 96 hr LC50 (for fish) or 48 hr EC50 (for Daphnia) or 72 hr IC50 (for algae).

Concerning the substance's persistence, the following risk phrase is used: **R53:** May cause long-term adverse effects in the aquatic environment, on the basis of its biodegradability or log K_{ow} (log octanol/water partition coefficient) ≥ 3.0 (unless the experimentally determined bio-concentration factor BCF ≤ 100).

Only substances characterised by risk phrases R50, R50/53 and R51/53, labelled with a hazard symbol "N", are considered in the Seveso II directive (Seveso II) and therefore subject to notification when involved in accidents. Carcinogenic, mutagenic and toxic to reproduction substances raise high concern too. The specific risk phrases are **R45** / **49** (category 1 and 2) and **R40** (category 3) carcinogens, **R46** (category 1 and 2) and **R68** (category 3) mutagens, **R60 / 61** (category 1 and 2) and **R62** / **63** (category 3) repro-toxicants.

However, on 20 January 2009, the new "Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures", so-called CLP Regulation, has entered into force. CLP Regulation implements the *United Nations Globally Harmonised System (GHS) of classification and labelling of chemicals*, elaborated at the aim of standardizing and harmonizing the criteria for the evaluation and management of chemical risk, at international level. This regulation will stepwise replace the above mentioned directive 67/548. Therefore, there is presently a transition period from the old to the new regime (until June 2015), to allow producers and/or importers of chemicals to comply with new legislation.

In the following, some databases, specifically regarding chemical hazards, are briefly described. The European chemical Substances Information System[72] (ESIS) is an IT System which provides information on chemicals available in more specific databases such as IUCLID and ORATS. **IUCLID** (International Uniform Chemical Information Data Base) is a collection of chemical data sheets on high production volume substances, as reported by European Industry. Information regarding quantity, uses, major accidents, environmental fate and pathways, ecotoxicity, human toxicity and risk assessment (if performed) is provided. **ORATS** (Online European Risk Assessment Tracking System) gives information on the state of the evaluation of existing substances and provides lists of priority substances to be subjected to risk assessment. Since 1994, 102 final risk assessment reports have been executed.

The **CLASS-LAB** database contains the complete classification and labelling data-set, according to Annex 1 of the above-cited directive 67/548, related to about 8000 substances. The **N-Class** database is specifically dedicated to environmental hazard classification. It is the result of collaboration between ECB and the Nordic Council of Ministers. At present, 7897 substances, both discussed and under discussion by the *ad-hoc* Working Group, are included. Among these: 4736 have been classified as

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[72] http://ecb.jrc.ec.europa.eu/esis/

dangerous for the environment; 1138 not classified as dangerous for the environment, based on data; 996 not classified as dangerous for the environment, due to "lack of data“; the remaining are still under evaluation. This database also reports basic work documents, essential data and brief minutes of meetings.

4 Risk classification datasets of selected substances involved in water contaminating accidents (according to directive 67/548/EEC). For explanation of the symbols and risk phrases, refer to point 6.

No.	CAS RN.	SUBSTANCE NAME	EU CLASSIFICATION
1.	75-86-5	Acetone Cyanohydrin	T+; R26/27/28 N; R50-53
2.	7664-41-7	Ammonia anhydrous	R10, T; R23; C; R34; N; R50
3.	1336-21-6	Ammonia solution 3 %	C; R34; N; R50
4.	71-36-3	Butanol	R10 Xn; R22 Xi; R37/38-41 R67
5.	7778-54-3	Calcium Hypochlorite	O; R8 Xn; R22 R31 C; R34, N; R50
6.	1563-66-2	Carbofuran	T+; R26/28 N; R50-53
7.	75-15-0	Carbon Disulphide	F; R11 Repr. Cat. 3; R62-63 T; R48/23 Xi; R36/38
8.	630-08-0	Carbon Oxide	F+; R12 Repr. Cat. 1; R61 T; R23-48/23
9.	7782-50-5	Chlorine	T; R23 Xi; R36/37/38 N; R50
10.	7440-50-8	Copper	under evaluation
11.	8002-05-9	Crude oil Arabian light	Carc.2; R45
12.	108-94-1	Cyclohexanone	R10 Xn; R20
13.	94-75-7	2,4-Dichlorophenoxyacetic Acid [2,4-D]	Xn; R22 Xi; R37-41 R43 R52-53
14.	77-73-6	Dicyclopentadiene	F; R11 Xn; R20/22 XI; R36/37/38 N; R51-53
15.	8008-20-6	Diesel Oil & Gasoil	Xn; R65
16.	1113-02-6	Dimethoate [Rogor]	T; R25 Xn; R21 N; R50
17.	50-00-0	Formaldehyde	Carc. Cat. 3; R40 T; R23/24/25 C; R34 R43
18.	98-01-1	Furfural (2-furaldehyde)	Carc. Cat. 3; R40 T; R23/25 Xn; R21 Xi; R36/37
19.	8006-61-9	Gasoline	Carc. Cat. 2; R45 Xn; R65
20.	111-30-8	Glutaraldehyde	T; R23/25 C; R34 R42/43 N R50
1	7722-84-1	Hydrogen Peroxide Solution [=< 40 %]	R5 O; R8 C; R35 Xn; R20/22
22.	7647-01-0	Hydrogen Chloride	T; R23 C; R35
23.	74-90-8	Hydrogen Cyanide	T+; R26/27/28 N; R50-53
24.	7664-39-3	Hydrogen fluoride	T+; R26/27/28 C; R35
25.	10004-44-1	Hymexazol	Xn; R22 Xi; R41 R52-53
26.	36734-19-7	Iprodione	Carc. Cat. 3; R40 N; R50-53
27.	67-63-0	Isopropanol	F; R11 Xi; R36 R67
28.	7439-92-1	Lead	under evaluation
29.	67-56-1	Methanol	F; R11 T; R23/24/25-39/23/24/25
30.	78-93-3	Methyl Ethyl Ketone	F; R11 Xi; R36 R66 R67
31.	75-09-2	Methylene Dichloride	Carc. Cat. 3; R40
32	2032-65-7	Methiocarb	T; R25 N; R50-53
33.	108-90-7	Mono-Chlorobenzene	R10 Xn; R20 N; R51-53
34.	8030-30-6	Naphta	Carc. Cat. 2; R45 Xn; R65
35.	7697-37-2	Nitric Acid	O; R8 C; R35
36.	298-00-0	Parathion-Methyl	R5 R10 T+; R26/28 T; R24 Xn; R48/22 N;

			R50-53
37.	40487-42-1	Pendimethalin	R43 N; R50-53
38.	108-95-2	Phenol	Muta. Cat. 3; R68 T; R23/24/25 Xn; R48/20/21/22 C; R34
39.	1336-36-3	PolyChloroBiphenyls (PCBs)	R33, N; R50-53
40.	1310-73-2	Sodium Hydroxide	C; R35
41	7681-52-9	Sodium Hypochlorite	C; R34 R31 N; R50
42.	8006-61-9	Sulphur Dioxide	Carc. Cat. 2; R45 Xn; R65
43.	7664-93-9	Sulphuric Acid	C; R35
44.	62-56-6	Thiourea	Carc. Cat. 3; R40 Repr. Cat. 3; R63 Xn; R22 N; R51-53
45.	137-26-8	Thiram	Xn; R20/22-48/22 Xi; R36/38 R43 N; R50-53
46.	108-88-3	Toluene	F; R11 Repr. Cat. 3; R63 Xn; R48/20-65 Xi; R38 R67
47.	95-53-4	o-Toluidine	Carc. Cat. 2; R45 T; R23/25 Xi; R36 N; R50
48.	87-90-1	Trichloreisocyanuric Acid	O; R8 Xn; R22 Xi; R36/37 R31 N; R50-53

5 Classification of substances selected as priority substances within the ECODIS project.

Nine substances were proposed for coordinated testing and to accomplish the collaboration with other work-packages: 3 heavy metals: Cd, Ni, Pb; 3 PAHs: phenanthrene, pyrene, fluoren; 3 chlorophenols: 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol.

Highlighted are substances which are toxic to the environment, carcinogenic, mutagenic and toxic to reproduction (according to directive 67/548/EEC).

Substance Name	**Classification**	**DataBase**
2,4-Dichlorophenol	T; R24, Xn; R22, C; R34, N; R51-53	ClassLab
2,4,6-Trichlorophenol	Carc. Cat. 3; R40, Xn; R22, Xi; R36/38, N; R5 53	ClassLab
Pentachlorophenol	Carc. Cat 3; R40, T+; R26 Xi; N; R50-53	ClassLab
Cadmium & Cd Oxide	Carc. Cat. 2; R45, Muta. Cat. 3; R68, Repr. Cat. 3; R62-63, N; R50-53	ClassLab
Cd Chloride, Cyanide, Fluride, Fluorosilicate, Formate, Iodide, Oxide, Sulphide, Sulphate	N; R50-53	N-Class
Nickel	Carc. Cat. 3; R40, R43	ClassLab
Ni & Compounds (Carbonate, Dihydroxide, Oxide, Sulphide, Sub-sulphide, Sulphate)	N; R50-53 (proposed)	N-Class
Lead acetate, Alkyls, Azide, Chromate, CI Pigment Yellow 34, CI Pigment Red 104	N; R50-53 (proposed)	N-Class
Benzo[*a*]pyrene	Carc. Cat. 2; R45 Muta. Cat. 2; R46 Repr. Cat. 2; R60-61 R43 N; R50-53	ClassLab N-Class
Benzo[e]pyrene	Carc.2; R45 N; R50-53	ClassLab N-Class
9,9-bis(4-hydroxyphenyl) fluorene	Xi; R36-38 N; R50-53	ClassLab N-Class

6 List of risk phrases and symbols of danger (according to directive 67/548/EEC).

R-phrases
R5: Heating may cause an explosion
R8: Contact with combustible material may cause fire
R10: Flammable
R11: Highly flammable
R12: Extremely flammable
R20: Harmful by inhalation
R21: Harmful in contact with skin

R22: Harmful if swallowed
R23: Toxic by inhalation
R24: Toxic in contact with skin
R25: Toxic if swallowed
R31: Contact with acids liberates toxic gas
R33: Danger of cumulative effects
R34: Causes burns
R35: Causes severe burns
R36: Irritating to eyes
R37: Irritating to respiratory system
R38: Irritating to skin
R40: Limited evidence of a carcinogenic effect
R41: Risk of serious damage to eyes
R42: May cause sensitisation by inhalation
R43: May cause sensitisation by skin contact
R45: May cause cancer
R46: May cause heritable genetic damage
R48: Danger of serious damage to health by prolonged exposure
R49: May cause cancer by inhalation
R50: Very toxic to aquatic organisms
R51: Toxic to aquatic organisms
R52: Harmful to aquatic organisms
R53: May cause long-term adverse effects in the aquatic environment
R60: May impair fertility
R61: May cause harm to the unborn child
R62: Possible risk of impaired fertility
R63: Possible risk of harm to the unborn child
R65: Harmful: may cause lung damage if swallowed
R68: Possible risk of irreversible effects
R23/24/25: Toxic by inhalation, in contact with skin and if swallowed
R26/27/28: Very toxic by inhalation, in contact with skin and if swallowed
R36/37: Irritating to eyes and respiratory system
R37/38: Irritating to respiratory system and skin
R39/23/24: Toxic: danger of very serious irreversible effects through inhalation and in contact with skin
R39/23/25: Toxic: danger of very serious irreversible effects through inhalation and if swallowed
R50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R52/53: Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment

<u>Symbols of Danger</u>
C: corrosive;
Xn: Harmful;
N: Dangerous for the environment;
O: Oxidising;
T: toxic;
T+: very toxic

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ANNEX to Part A: Supporting information: Cadmium related ECODIS results and thresholds set for the protection of the environment and human health

TABLE OF TERMS, ABBREVIATIONS AND DEFINITIONS

Abbreviations

AA-EQS	Annual Average Environmental Quality Standard
AF	Assessment Factor
ARGE	Arbeitsgemeinschaft für die Reinhaltung der Elbe
BCF	Bioconcentration Factor
BR	Body Residues
CALAMARIS	Calamity Preparation Repression and Advice / clean-up
CBR	Critical Body Residues
CGIME	Complexing Gel Integrated Microelectrode
CLE-AdSV	Competitive ligand exchange – adsorptive stripping voltammetry
CLP	Classification, Labelling and Packaging
CMA	Chemical Monitoring Activity under the common implementation strategy of the WFD
CMRs	Carcinogens, Mutagens, and substances toxic to Reproduction
DET	Diffusive Equilibration in Thin films
DGT	Diffusive Gradients in Thin film
DMT	Donnan Membrane Technique
DW	Dry Mass
ECHA	European Chemicals Agency
EQR	Ecological Quality Ratio
ESIS	European chemical Substances Information System
FACE-IT	Fast Advanced Cellular and Ecosystems Information Technologies
FEAT	Flash Environmental Assessment Tool
FIA GIME	Flow injection analysis gel integrated microelectrode
fw	Fresh Water
GIME	Gel Integrated Microelectrode
HMWB	Heavily Modified and artificial Water Bodies
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
IPPC	Integrated Pollution Prevention and Control Directive
ISE	Ion-Selective Electrode
IUCLID	International Uniform Chemical Information Data Base
K_{ow}	Octanol/water partition coefficient
K_p	water/SPM partition coefficient
MAC-EQS	Maximum Allowable Concentration Environmental Quality Standard
MARS	Major Accident Reporting System
MODELKEY	Models for Assessing and Forecasting the Impact of Environmental Key Pollutants on marine and Freshwater Ecosystems and Biodiversity
MOSI	Modular Spectral Imaging system
MPA	Maximum Permissible Addition
NOEC	No Observed Effect Concentration
NOAEL	No Observed Adverse Effect Level
OJ	Official Journal of the European Communities
ORATS	Online European Risk Assessment Tracking System
PAHs	Polycyclic aromatic hydrocarbons
PBTs	Persistent, Bioaccumulative, and Toxic substances
PCBs	Polychlorinated biphenyls
PBPK	Physiology-based pharmacokinetic models
PEC	Predicted Environmental Concentration

PNEC	Predicted No Effect Concentration
PLM	Permeation liquid membrane
PRAGMA	Pragmatic and Integrated Approach for the Evaluation of Environmental impact of oil and Chemicals Spilled at Sea
QSARs	Quantitative Structure-Activity Relationships
RBMP	River Basin Management Plan
RCR	Risk Characterisation Ratio
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RIKZ	Dutch National Institute for Coastal and Marine Management
SARs	Structure-Activity Relationships
SPM	Suspended Particulate Matter.
SPME	Solid-phase Microextraction
SSD	Species sensitivity distribution method
SUBS	Stirred Underwater Biouptake System
UNECE	United Nations Economic Commission for Europe
US-EPA	United States Environmental Protection Agency
vPvBs	Very Persistent, very Bioaccumulative substances
WFD	Water Framework Directive

Definitions

Added risk approach The risk characterisation is performed on the compound concentrations attributable to current anthropogenic activities. Natural background levels and and past anthropogenic (diffuse) inputs are not considered (see “Total Risk Approach”).

AFM Assessment factor method used to extrapolate from results of toxicity tests performed in the lab to toxicity under natural conditions. The general principle is that the highest concentration shown to have no toxic effect in the lab is divided by an appropriate assessment factor. The sparser the available data and the higher the uncertainty of this level, the higher is the assessment factor applied. A detailed description of the AFM for the aquatic compartment is given in ECHA 2008, Part R10, chapter R.10.3.1.2.

BCF bioconcentration factor, the ability of an organism to concentrate a substance from the aquatic environment. Bioconcentration factors [l kg^{-1}] are calculated as the concentration in the organism [mg kg^{-1}, on a wet weight or dry weight basis] divided by the concentration in water [mg l^{-1}] or as the ratio of the uptake rate constant [l kg^{-1} d^{-1}] and the depuration rate constant [d^{-1}].

EQS-AA Environmental Quality Standard expressed as an annual average. For any given surface water body, compliance with EQS-AA requires that for each representative monitoring point within the water body, the arithmetic mean of the concentrations measured at different times during the year is below the standard (WFD 2008).

EQS-MAC Environmental Quality Standard expressed as a maximum allowable concentration. For any given surface water body compliance with EQS-MAC means that the measured concentration at any representative monitoring point within the water body must not exceed the standard.

K_p K_p is the substance specific partition coefficient defined as the concentration in SPM (mg kg^{-1}) divided by the concentration in the filtrate (mg l^{-1}).

NOEC No Observed Effect Concentration, the highest tested concentration at which a certain adverse effect is not found in exposed test organisms where higher concentrations resulted in the adverse effect.

NOAEL No Observed Adverse Effect Level, the highest dose at which a certain adverse effect is not found in exposed test organisms where higher doses or concentrations resulted in the adverse effect

$NOEC_{bird}$ No Observed Effect Concentration expressed as concentration in the food of birds in mg kg_{food}^{-1}.

$NOAEL_{bird}$ No Observed Adverse Effect Level, expressed as a dose in mg $kg_{body\ weight}$ d^{-1}.

PNEC the concentration of a chemical in the respective compartment below which unacceptable effects on the aquatic ecosystem and its organisms will most likely not occur (ECHA 2008, Part B.7.2.1). Methods suitable for the determination of PNECs are described in detail in the "Guidance for the Implementation of REACH", part B – Hazard Assessment (ECHA 2008).

SSD Species sensitivity distribution methods are used to extrapolate from results of toxicity tests performed in the lab to toxicity under natural conditions when reliable toxicity data are available for a sufficiently high number of species and an adaequate spectrum of trophic levels. These methods aim at calculating a concentration, which is assumed to protect a certain percentage (e.g. 95 %) of the species of the ecosystem against toxic effects. A detailed description of this statistical extrapolation technique is given in ECHA 2008, Part R10, chapter R.10.3.1.3 for the aquatic compartment.

Total risk approach The risk characterisation is performed on the total compound concentrations in the environment, i.e. including the natural background and past anthropogenic (diffuse) input (see "Added Risk Approach").

Transitional waters are defined as bodies of surface water in the vicinity of river mouths with partially saline character as a result of their proximity to coastal waters but which are substantially influenced by freshwater flows.

Territorial waters belt of coastal waters extending at most twelve nautical miles from the baseline (usually the mean low-water mark) of a coastal state.

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Abstract

Disasters leading to a release of pollutant(s) into rivers, streams or lakes can have severe short and/or long term effects on the chemical and ecological status of aquatic ecosystems. The aim of the study presented here is to give recommendations for disaster management based on new methods, recent progress in research and advanced sensor techniques developed within the EU-FP6 funded ECODIS project on “Dynamic Sensing of Chemical Pollution Disasters and Predictive Modelling of their Spread and Ecological Impact”.

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