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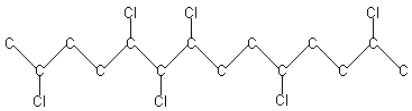
Risk Assessment Report

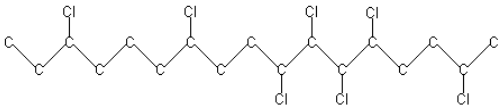
CAS: 85535-85-9 **EINECS No: 287-477-0**

ALKANES, C14-17, CHLORO

Addendum to the final report (2007) of the risk assessment - Environment part



$C_{14}H_{24}Cl_6$



$C_{17}H_{29}Cl_7$

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The mission of the JRC-IHCP is to protect the interests and health of the consumer in the framework of EU legislation on chemicals, food, and consumer products by providing scientific and technical support including risk-benefit assessment and analysis of traceability.

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Foreword

I am pleased to present this updated Risk Assessment Report on ALKANES, C_{14-17}, chloro (MCCP) which is the result of in-depth work carried out by experts in United Kingdom, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.

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

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

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

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

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

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

Elke Anklam
Director
Institute for Health and
Consumer Protection

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[1] O.J. No L 084, 05/04/199 p.0001 – 0075

[2] O.J. No L 161, 29/06/1994 p. 0003 – 0011

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

UPDATED RISK ASSESSMENT
OF
ALKANES, C_{14-17}, CHLORO
(MEDIUM-CHAIN CHLORINATED PARAFFINS)

CAS Number: 85535-85-9
EINECS Number: 287-477-0

Environment Addendum of August 2007

Executive summary

An environmental risk assessment of alkanes, C_{14-17}, chloro (medium-chain chlorinated paraffins or MCCPs) produced in accordance with Council Regulation (EEC) 793/93 was published in December 2005. This report provides the updated risk assessment dealing with new data and the consequences of the new data for the conclusions in the original report. The report has been prepared by the United Kingdom in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

This report considers the secondary poisoning assessment and the exposure of man via the environment based on new information. This update includes also the PBT assessment which was not addressed in the original report for medium-chain chlorinated paraffins.

The updated environmental risk assessment concludes that risks are identified for the earthworm food chain due to various uses of MCCPs. Risks are not identified any longer for the fish food chain, with the exception of the use in leather fat liquors. The exposure of man via environmental routes has been revised with new information. It is now concluded that there is no longer concern for this route of human exposure. The PBT assessment concludes that further information is needed in order to confirm whether or not the substance should be considered as a PBT substance or not. A testing strategy is discussed in the report.

Introduction

An environmental risk assessment of alkanes, C_{14-17}, chloro (medium-chain chlorinated paraffins or MCCPs) produced in accordance with Council Regulation (EEC) 793/93[1] was published in December 2005[2]. Subsequently, further information on the toxicity of medium-chain chlorinated paraffins to mammals has become available in relation to the human health risk assessment which has an impact on the PNEC used for the assessment of secondary poisoning. In addition, new data on the uptake of the chemical from soil by root crops has become available which should be considered in relation to man exposed via the environment.

This updated risk assessment considers the consequences of these new data for the conclusions drawn in the original risk assessment. In addition a PBT assessment has been performed.

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The scientific work on the environmental sections was carried out by the Building Research Establishment Ltd (BRE) under contract to the rapporteur.

1 O.J. No. L 084, 05/04/1993 p. 0001-0075.
2 European Union Risk Assessment Report: Alkanes, C_{14-17}, chloro-. 3rd Priority List, Volume 58. European Commission Joint Research Centre, EUR 21640 EN.

0 OVERALL RESULTS OF THE RISK ASSESSMENT

This update considers three main aspects of the environmental risk assessment for medium-chain chlorinated paraffins that was published in 2005 (EU, 2005). The resulting conclusions are summarised below.

Secondary poisoning

A new $PNEC_{oral}$ of 10 mg/kg food has been derived using new data on the toxicity of medium-chain chlorinated paraffins which have become available since the original environmental risk assessment was published. This has significantly affected the conclusions drawn for secondary poisoning via both the fish and earthworm food chains.

For the fish food chain, the original risk assessment concluded that production and all uses other than formulation and use of sealants, and domestic application of paints, presented a potential risk from secondary poisoning. These conclusions were based on a $PNEC_{oral}$ of 0.17 mg/kg food. Using the new $PNEC_{oral}$ of 10 mg/kg food, all scenarios considered in the risk assessment, with the exception of use in leather fat liquors – processing of wet blue, lead to a PEC/PNEC <1, and hence it is now concluded that the risks of secondary poisoning from production and most uses of medium-chain chlorinated paraffins are low for the fish food chain.

For the earthworm food chain, the original risk assessment concluded that the risk from secondary poisoning was low from production sites (where no sewage sludge is applied to land), formulation and use of sealants, and domestic application of paints. All other uses of medium-chain chlorinated paraffins were found to present a potential risk from secondary poisoning for the earthworm food chain. Again these conclusions were reached using a $PNEC_{oral}$ of 0.17 mg/kg food. Using the new $PNEC_{oral}$ of 10 mg/kg food, several other scenarios now lead to PEC/PNEC <1, but potential risks are still identified for fifteen of the thirty two scenarios considered in the assessment.

Result

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

This applies to the assessment of secondary poisoning via the fish food chain from production and all uses of medium-chain chlorinated paraffins except for use in leather fat liquors – processing of wet blue. This also applies to the assessment of secondary poisoning via the earthworm food chain for the following scenarios.

- Production sites (where sewage sludge is not applied to agricultural land).
- Use in PVC – plastisol coating – compounding sites.
- Use in PVC – plastisol coating – conversion sites.
- Use in PVC – extrusion/other – compounding sites using open or closed systems.
- Use in plastics/rubber – compounding sites.
- Use in plastics/rubber – conversion sites.
- Use in sealants – formulation and use.
- Use in paints – formulation sites.
- Use in paints – industrial application and domestic application.
- Use in metal cutting/working fluids – use in emulsifiable fluids.
- Use in leather fat liquors – formulation sites.
- Use in carbonless copy paper – paper recycling.

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

This applies to the following uses for the earthworm food chain:

- Use in PVC – plastisol coating – combined compounding/conversion sites*.
- Use in PVC – extrusion/other – compounding sites using partially open systems.
- Use in PVC – extrusion/other – conversion sites and combined compounding/conversion sites.
- Use in plastics/rubber – combined compounding/conversion sites*.
- Use in metal cutting/working fluids – formulation sites.
- Use in metal cutting/working fluids – use in oil-based fluids at large and small sites.
- Use in metal cutting/working fluids – use in emulsifiable fluids – intermittent release.
- Use in leather fat liquors – processing of raw hides and wet blue.

It should be noted that for the two scenarios for the earthworm food chain marked as * above, the risk identified depends on whether EUSES 1 or EUSES 2.0.3 is used for the calculation. However it should be born in mind that PEC/PNEC ratios >1 were identified for these two scenarios in EU (2005) for the sediment compartment and so risk management is already considered to be necessary for them. Therefore it is recommended that this risk management should also consider the possible risk of secondary poisoning through the earthworm food chain identified here.

In addition, this conclusion also applies to fish food chain for use in leather fat liquors – processing of wet blue. A PEC/PNEC ratio >1 is obtained for this scenario when a BMF of 3 is considered but a PEC/PNEC ratio <1 is obtained when a BMF of 1 is considered. This finding is independent of whether EUSES 1 or EUSES 2.0.3 is used. Although there is, therefore, some uncertainty over whether or not this scenario actually presents a risk of secondary poisoning via the fish food chain, it should be noted that PEC/PNEC ratios >1 for this scenario have already been identified for surface water, sediment and soil in EU (2005) and so risk management is already considered to be necessary for this use. Therefore it is recommended that this risk management should also consider the possible risk of secondary poisoning through the fish food chain identified here.

Man exposed via the environment

A new study investigating the uptake into carrot roots from soil is available. This showed that the uptake of medium-chain chlorinated paraffins into root crops is substantially lower than is predicted using the default methods in the Technical Guidance Document. This new value has been used to revise the calculations for man exposed via environmental routes and has resulted in substantially lower estimates for the daily human exposure via environmental routes. These data have been discussed by the human health experts at TCNES and a conclusion ii) was agreed.

Result

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

PBT assessment

No assessment of the PBT properties of medium-chain chlorinated paraffins was carried out in the original environmental risk assessment. The analysis carried out here concludes that the substance meets the T-criterion and meets the screening criterion for P or vP. However there are no data from simulation tests that can be used to unambiguously confirm that the substance is a P or vP substance. With regards to the B-criterion, the highest BCF available for a medium-chain chlorinated paraffin in fish is 1,087 l/kg and so, on this basis, the substance does not meet the specific criteria for either B or vB laid down in the Technical Guidance Document. However, there are a number of other factors that need to be considered in this respect and the balance of evidence is that the substance could be considered as meeting the screening criteria for bioaccumulation. In

particular, uptake via food appears to be important for medium-chain chlorinated paraffins (possibly resulting in higher concentrations in organisms than may be expected based on the BCF alone), and it is also possible that the actual BCF for some components of the technical medium-chain chlorinated paraffin products could be >2,000 l/kg (these same components are also considered to meet the T-criterion and the screening criterion for P or vP).

Overall, although medium-chain chlorinated paraffins are not shown to meet the specific criteria for a PBT substance, there are other data available to suggest that medium-chain chlorinated paraffins (or components of medium-chain chlorinated paraffins) may have the properties of a PBT substance. There are uncertainties over both the persistence and bioaccumulation potential for medium-chain chlorinated paraffins, and the available database of reliable laboratory studies and field monitoring data is fairly limited. Therefore further information would be needed in order to confirm whether or not the substance should be considered as a PBT substance or not.

Result

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

A simulation test for biodegradability could be performed to determine the half-life in the marine environment in order to confirm whether or not the substance meets the actual criteria for persistence. However it is considered that such a test would be technically very difficult to carry out, and may not even then be sufficient to show definitively that medium-chain chlorinated paraffins are not persistent. Such a test has recently been completed for the related short-chain chlorinated paraffins. This test confirmed that short-chain chlorinated paraffins are persistent, but read-across of these results to medium-chain chlorinated paraffins is not straight forward as the chlorine content of the short-chain chlorinated paraffins tested was much higher (around 65% by weight) than typically found in the commercial medium-chain chlorinated paraffins (typically around 45-52% by weight) and there is some evidence that the rate of biodegradation of medium-chain chlorinated paraffins may increase with decreasing chlorine content. However, the mineralisation half-lives found with short-chain chlorinated paraffins were sufficiently long (around 1,630-1,790 days in freshwater sediment and 335-680 days in marine sediment) that it is considered likely that medium-chain chlorinated paraffins would also be persistent within the meaning of the PBT assessment and that it is unlikely that further testing with medium-chain chlorinated paraffins themselves would change this interpretation.

The assessment of this substance against the B- or vB criteria is not straight forward. The available evidence suggests that some components of the technical products meet the screening criteria for B. It should be noted that the available database is relatively limited and extrapolation and modelling have been used in order to assess the likely bioaccumulation potential of some components. Therefore uncertainty exists over the actual bioaccumulation potential. Further work is needed order to provide a more solid conclusion for this endpoint. In this respect it is thought that modelling methods have been taken as far as possible (there will always be some uncertainty associated with modelled data) and there would appear to be little more to be gained by investigating other modelling approaches at this stage. The modelling approaches investigated do not allow an unambiguous estimate of the bioaccumulation potential relative to the B criterion to be made and thus a confirmatory experimental approach is proposed. As there are a number of issues that need to be considered, a tiered approach is recommended. This should include the following.

1. Further information to assess the bioaccumulation potential of relevant components of medium-chain chlorinated paraffins, e.g. a further fish bioconcentration study using a C_{14}-chain length chlorinated paraffin of low-moderate chlorine content (e.g. 45% wt. Cl and/or 52% wt. Cl). The available evidence suggests that the accumulation potential of medium-chain chlorinated paraffins probably decreases with increasing carbon chain length and degree of chlorination (although some predictions indicate an opposite trend with chlorine

content). The available fish BCF of 1,087 l/kg for medium-chain chlorinated paraffins was determined with a C_{15}, 51% wt. Cl substance and so it is possible that the fish BCF for a C_{14} chlorinated paraffin may be higher than this value. Estimates suggest that a BCF of >2,000 l/kg could be expected for a C_{14}, 45% wt. Cl and C_{14}, 52% wt. Cl substance.

The need for further information should then be reviewed based on the outcome of this testing. It must be recognised that the bioaccumulation potential of medium-chain chlorinated paraffins may remain uncertain even after the above testing. In such circumstances it may be necessary to consider the need to generate further data. These data could include the following:

2. A further fish feeding study to obtain a reliable BMF value. However, it should be noted that there is, as yet, no agreed methodology for carrying out such a study, and no agreed way to take account of the results of such a study in the risk assessment. Several fish feeding studies are already available for medium-chain chlorinated paraffins, and the problems with interpreting these data are outlined in EU (2005). It is thought that any new fish feeding study would be subject to similar problems and uncertainties until an agreed method for carrying out and interpreting such studies is available.
3. Monitoring of biota. The available monitoring data for medium-chain chlorinated paraffins in biota are generally limited. Medium-chain chlorinated paraffins are complex substances and this provides serious challenges for the analysis of the substances in environmental media (the problems with the analysis are discussed in EU (2005)). Many of the methods used in the past did not unambiguously determine medium-chain chlorinated paraffins (e.g. interference from short-chain chlorinated paraffins in particular could have occurred in many of these studies), but more recent studies have confirmed that medium-chain chlorinated paraffins are present in human breast milk, cows milk, and in some cases marine fish and marine mammals. The number of reliable data available, particularly for fish and marine mammals, is currently very limited and so it could be considered to carry out further monitoring of such organisms to verify whether or not medium-chain chlorinated paraffins show a wide-spread occurrence in such biota, and possibly provide some information on the trends in these levels. This would provide useful information in relation to the conclusions on bioaccumulation potential for the PBT assessment, and also possibly the long-range transport potential. However, it should be stressed that the analysis of medium-chain chlorinated paraffins is not straight forward in such samples.

When considering the need for further testing it should be born in mind that the substance has already been detected in marine biota (including marine mammals), although the number of reliable monitoring studies is very limited. The trends in levels are unknown, and they may be due (in part at least) to a local source or uses that take place in other regions, or uses that are now better controlled in the EU. It is therefore possible that levels may decrease if the current level of emission does not increase. However, the possibility of long range transport can not totally be excluded. Whilst it is not possible to say whether or not on a scientific basis there is a current or future risk to the environment, in light of:

- data indicating presence in marine biota;
- the apparent persistence of the substance (i.e. absence of significant degradation in laboratory screening tests);
- the time it would take to gather the information; and
- the fact that it could be difficult to reduce exposure if the additional information confirmed a risk;

consideration could be given at a policy level to the need to investigate precautionary risk management options now in the absence of measured environmental half-life data and confirmatory bioaccumulation data, to reduce the inputs to water (and soil from the application of sewage sludge), including from "waste remaining in the environment".

In this respect it should also be taken into account that an assessment of secondary poisoning for medium-chain chlorinated paraffins has already been carried out, and this leads to the identification of risks from several uses of medium-chain chlorinated paraffins for the earthworm food chain, but possible risks are identified only for one scenario for the fish food chain. A key consideration is therefore whether or not there is any added concern for medium-chain chlorinated paraffins over and above that already identified based on a PEC/PNEC approach[3], given that the PEC/PNEC approach already considers that uptake into aquatic organisms may occur from both exposure via water and via food. Such considerations could include uncertainties around the BCF values for all components of the technical products, and also the very long apparent depuration half-life that has been found recently in mammalian systems. These may introduce uncertainties into the risk assessment of secondary poisoning when extrapolating from the results of laboratory tests to PECs and PNECs related to exposure over an organism's lifetime.

[3] It should also be born in mind that the original risk assessment also identified risks to sediment from many uses of medium-chain chlorinated paraffins (and risks to surface water and soil were also identified from some scenarios) and any risk reduction measures implemented as a result of these conclusions for water, sediment and soil will also have an impact on the amount of medium-chain chlorinated paraffins that would be released to environment in the future.

1 SECONDARY POISONING

1.1 REVIEW OF NEW MAMMALIAN TOXICITY DATA

This Section revises Section 3.2.4.3 (Mammalian toxicity) of EU (2005).

In the existing published environmental risk assessment (EU, 2005) the $PNEC_{oral}$ for secondary poisoning is based on a NOAEL of 5 mg/kg food (equivalent to 0.4 mg/kg bw/day) from a 90-day feeding study in rats carried out by Poon *et al.* (1995). Using this value and an assessment factor of 30 a $PNEC_{oral}$ of 0.17 mg/kg food was derived and used as the basis for the conclusions drawn in EU (2005). It was noted in EU (2005) that the dose response curve for this study was shallow, and the effects seen at the next highest dose tested (50 mg/kg food) were slight.

Industry has now voluntarily conducted a further 90-day study with rats (CXR, 2005c). This study has been reviewed in detail in the human health risk assessment[4] and the assessment concluded that the results from this study should be used in preference to the Poon *et al.* (1995) study. The NOAEL from this new study was 300 mg/kg food.

In addition to this, further studies have become available recently on the toxicity of medium-chain chlorinated paraffins to reproduction. These data also need to be considered in relation to the $PNEC_{oral}$.

The results from the relevant mammalian toxicity studies are summarised in **Table 1**. The values are taken from the human health risk assessment[5], which should be consulted for further details.

For repeated dose toxicity, the lowest reliable NOAEL for rats is 300 mg/kg food (equivalent to 23-25 mg/kg bw/day) from the CXR (2005c) study based on effects on kidneys. In addition to this, there is a poorly reported study with dogs where a NOAEL of 10 mg/kg bw/day was found (Birtley *et al.*, 1980). Using the conversion factor given in the Technical Guidance Document (for *Canis domesticus* the conversion factor is 40 kg bw d/kg_{food}), a dose of 10 mg/kg bw/day is equivalent to a concentration of 400 mg/kg food, which is comparable to the value derived for rats.

[4] Document version R331_0612_hh

[5] Document version R331_0612_hh

Table 1 Summary of relevant mammalian toxicity studies

Duration/study type	Species	Substance tested	Administration route	Concentrations/ doses tested	Result	Reference
Standard repeated dose studies						
14-day	F344 rats	C_{14-17}, 52% wt. Cl	Dietary	0, 150, 500, 1,500, 5,000 and 15,000 mg/kg food (equivalent to 0, 18, 58, 170, 550 and 1,540 mg/kg bw/day in males and 0, 18, 58, 180, 580 and 1,290 mg/kg bw/day in females).	Not possible to draw firm conclusions.	Spicer, 1981
90-day	F344 rats	C_{14-17}, 52% wt. Cl	Dietary	0, 30, 100, 300 and 3,000 mg/kg food (equivalent to 0, 2.4, 9.3, 23 and 222 mg/kg bw/day in males and 0, 2.5, 9.7, 25 and 242 mg/kg bw/day in females).	NOAEL = 300 mg/kg food (equivalent to 23 mg/kg bw/day in males and 25 mg/kg bw/day in females).	CXR, 2005c
90-day	Sprague-Dawley rats	C_{14-17}, 52% wt. Cl	Dietary	0, 5, 50, 500 and 5,000 mg/kg food (equivalent to 0, 0.4, 4, 36 and 360 mg/kg bw/day in males and 0, 0.4, 4, 42 and 420 mg/kg bw/day in females).	Concluded that study is not representative of the repeated dose toxicity profile for MCCPs and so should no be used for risk characterization purposes.	Poon *et al.*, 1995
90-day	F344 rats	C_{14-17}, 52% wt. Cl	Dietary	0, 10, 100 and 625 mg/kg bw/day.	NOAEL = 100 mg/kg bw/day.	IRDC, 1984a
90-day	Rats	C_{14-17}, 52% wt. Cl	Dietary	0, 500, 2,500 and 5,000 mg/kg bw/day (equivalent to 0, 33, 167 and 333 mg/kg bw/day in males and 0, 32, 160 and 320 mg/kg bw/day in females).	Not possible to draw firm conclusions.	Birtley *et al.*, 1980
90-day	Beagle dogs	C_{14-17}, 52% wt. Cl	Dietary	0, 10, 30 and 100 mg/kg bw/day.	Effects seen in liver at 30 mg/kg bw/day and above but not possible to draw firm conclusions.	Birtley *et al.*, 1980
Toxicity for reproduction						
Range finding study for a 2-generation reproduction study	Wistar rats	C_{14-17}, 52% wt. Cl	Dietary	0, 100, 1,000 or 6,250 mg/kg food (equivalent to 0, 6, 62 and 384 mg/kg bw/day in males and 0, 8, 74 and 463 mg/kg bw/day in females).	NOAEL = 100 mg/kg food (equivalent to 8 mg/kg bw/day) – based on effects in offspring (pre- or post-natally). The effects seen at the LOAEL (1,000 mg/kg food) were not statistically significant and so the true NOAEL may be close to the LOAEL.	IRDC, 1985

Table 1 continued

Duration/study type	Species	Substance tested	Administration route	Concentrations/ doses tested	Result	Reference
One generation reproduction study	Rats	C_{14-17}, 52% wt. Cl	Dietary	0, 300, 600 and 1,200 mg/kg food (equivalent to 0, 23, 47 and 100 mg/kg bw/day).	NOAEL • 1,200 mg/kg food (equivalent to • 100 mg/kg bw/day).	CXR, 2006
Developmental study	Rats	C_{14-17}, 52% wt. Cl	Oral gavage	0, 500, 2,000 or 5,000 mg/kg bw/day.	NOAEL = 500 mg/kg bw/day (maternal toxicity) NOAEL • 5,000 mg/kg bw/day (developmental effects).	IRDC, 1984b
Developmental study	Rabbits	C_{14-17}, 52% wt. Cl	Oral gavage	0, 10, 30 or 100 mg/kg bw/day.	NOAEL • 100 mg/kg bw/day (maternal toxicity and developmental effects).	IRDC, 1983

For toxicity to reproduction, a NOAEL of 100 mg/kg food (equivalent to 8 mg/kg bw/day) has been generated from the range finding study of a 2-generation reproduction study with rats based on effects mediated via lactation (IRDC, 1985). However, it should be noted that the effects seen at the next highest exposure level (LOAEL = 1,000 mg/kg food) were not statistically significant and so it was thought that the true NOAEL would lie close to the LOAEL. Results of a further dietary one generation study in rats have become available recently (CXR, 2006). Full details of the study are reported in the human health risk assessment[6]. This study showed no effects on pup mortality at any of the three concentrations tested (300 mg/kg food, 600 mg/kg food and 1,200 mg/kg food).

When the results from the two available reproduction studies are taken together, an overall NOAEL for these effects can be set as 600 mg/kg food (47 mg/kg bw/day), taking into account that effects (non-statistically significant) on pup mortality have been seen at 1,000 mg/kg food in the IRDC (1985) study. This NOAEL of 600 mg/kg food (47 mg/kg bw/day) has been agreed by TCNES human health experts.

1.2 REVISION OF $PNEC_{ORAL}$

This Section revises Section 3.2.4.4 (Predicted no effect concentration (PNEC) for secondary poisoning) of EU (2005).

Based on the analysis of the new mammalian toxicity data, the lowest overall NOAEL is now 300 mg/kg food from the 90-day study with rats (CXR, 2005c). According to the Technical Guidance Document, an assessment factor of 90 is appropriate for the results of a 90-day study. However, when choosing the assessment factor it should also be born in mind that the results of several chronic (reproduction) studies are also available, and that these give a higher NOAEL than from the 90 day study. The assessment factor of 90 is designed to take into account subchronic to chronic extrapolation as well as both interspecies variation and lab-to-field extrapolation. Therefore, for this data set it can be argued that an assessment factor lower than 90 could be used as the need for high assessment factors for the subchronic to chronic extrapolation may not be warranted. Therefore it is concluded that an assessment factor of 30 is appropriate (as recommended in the Technical Guidance Document for use on chronic data; this factor takes into account both interspecies variation and lab-to-field extrapolation). This gives a $PNEC_{oral}$ of 10 mg/kg food.

Effects have been seen in a feeding study with fish at concentrations around this value (for example effects were seen on liver at concentrations of 0.78-29 mg/kg food, along with effects on behaviour). These data are from a study by Cooley *et al.* (2001) and are summarised in EU (2005). Erratic feeding was also seen in many of the exposures and it is not clear if the effects seen were due to a true toxic action of the medium-chain chlorinated paraffin or a consequence of the reduced feeding (although the reduction in feeding could itself be considered to be an effect of exposure to medium-chain chlorinated paraffin). No guidance is currently available on the use of this type of study (both for the estimation of a relevant PEC[7] and the estimation of the PNEC). In addition, the Technical Guidance Document indicates that no specific assessment of the risk to fish as a result of the combined intake of contaminants from water and contaminated food is considered necessary as this is

6 See risk assessment version Document version R331_0612_hh.

7 The PEC_{oral} calculated for secondary poisoning represents the internal concentration in a fish near to the top of the aquatic food chain. The concentration in prey (to which the fish would be exposed via food) would be lower than the PEC_{oral} for medium-chain chlorinated paraffins.

assumed to be covered by the aquatic risk assessment and the risk assessment for secondary poisoning of fish-eating predators. In order to test that this is also the case for medium-chain chlorinated paraffins, a provisional comparison (not shown[8]) of the concentrations in diet at which effects on feeding with fish has been seen with the likely concentrations in the diet of predatory fish does not lead to the identification of possible risks for any scenarios other than those for which a risk from the aquatic compartment (surface water or sediment) or secondary poisoning is already identified. Therefore the assumption in the Technical Guidance Document that the assessment of the aquatic compartment and secondary poisoning will also be protective for possible effects on fish from combined exposure via food and water appears to be also relevant for medium-chain chlorinated paraffins. For these reasons this information is not used for the qualitative assessment of secondary poisoning here.

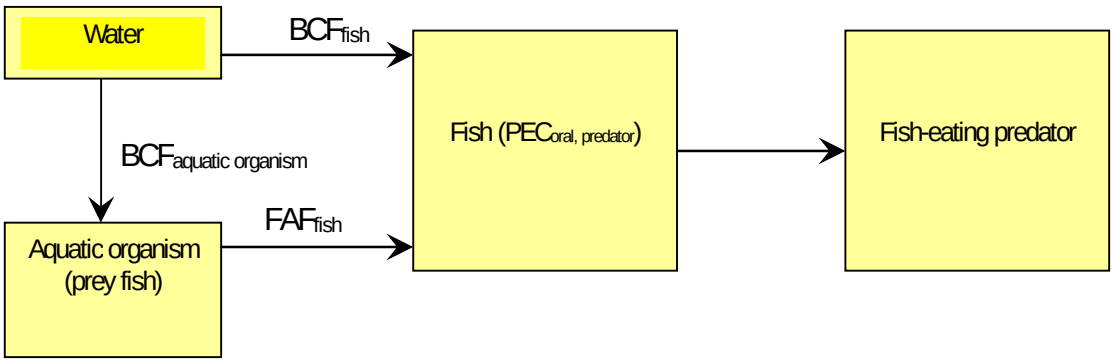
In conclusion, a revised $PNEC_{oral}$ of 10 mg/kg food will be used for this updated risk assessment.

1.3 RISK CHARACTERISATION

This Section revises Section 3.3.4 (Non-compartment specific effects relevant to the food chain (secondary poisoning)) of EU (2005).

The revised PEC/PNEC ratios using the PNEC of 10 mg/kg food are summarised in **Table 2**.

The PEC values used are taken from EU (2005)[9]. The PECs for the earthworm food chain were estimated using the methods outlined in the Technical Guidance Document. The PECs for the fish food chain and were calculated using the following scheme and equation (see EU (2005) for derivation). This assumes that the "aquatic organism" in the food chain is also a fish.



$$PEC_{oral,\ predator} = (0.5 \times PEC_{local\_water} + 0.5 \times PEC_{regional\ \_\ water}) \times BCF_{fish} \times (1 + FAF_{fish})$$

where BCF_{fish} = the fish BCF value.
FAF_{fish} = - the accumulation factor for uptake in fish via food (this term is used here to distinguish it from the BMF given in the equations in the Technical Guidance Document). A FAF of 1-3 was assumed.

8 Further details of this comparison are given in the response to comments from the Netherlands document, July 2007.
9 The PEC values in EU (2005) were calculated using EUSES 1 and so do not agree exactly with the values in the EUSES 2.0.3 printout accompanying this update.

The results are reported using the measured concentration of 0.1 µg/l to represent the regional concentration in surface water and 0.088 mg/kg wet wt. to represent the regional concentration in all soil types. Scenarios that gave PEC/PNEC ratios >1 in EU (2005) but now give PEC/PNEC ratios <1 using the revised PNEC (i.e. where there is a change of conclusion) are indicated by shading and are underlined.

For the aquatic food chain the revised $PNEC_{oral}$ results in all PEC/PNEC ratios now being <1, except for the scenario use in leather fat liquors – processing of wet blue. In the published version of the risk assessment (EU, 2005) the PEC/PNEC ratios for most scenarios were >1. Therefore the revision of the $PNEC_{oral}$ has a significant effect on the outcome of the risk assessment. Based on the new $PNEC_{oral}$ it can now be concluded that the risk of secondary poisoning via the aquatic food chain is low from production and almost all uses of medium-chain chlorinated paraffins.

Table 2 Estimated concentrations in fish and earthworms for secondary poisoning (Note: Scenarios that gave PEC/PNEC ratios >1 in EU (2005) but now give PEC/PNEC ratios <1 using the revised PNEC (i.e. where there is a change of conclusion) are indicated by shading and are underlined)

Scenario	Step	Fish[d] (Using measured regional concentrations)		Earthworms – (Using measured regional concentrations)	
		PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC
Production	Site A	0.22-0.44	0.022-0.044	negligible[c]	<1
	Site B	0.30-0.60	0.030-0.060	negligible[c]	<1
	Site C	0.38-0.76	0.038-0.076	negligible[c]	<1
	Site D	0.22-0.44	0.022-0.044	negligible[c]	<1
Use in PVC – plastisol coating	Compounding - O	0.26-0.52	0.026-0.052	1.7	0.17
	Conversion – O	0.52-1.04	0.052-0.104	9.3	0.93
	Compounding/conversion - O	0.56-1.12	0.056-0.112	10.4	1.04[e]
Use in PVC – extrusion/ other	Compounding - O	0.38-0.76	0.038-0.076	4.8	0.48
	Compounding - PO	1.04-2.08	0.104-0.208	24.1	2.41
	Compounding – C	0.28-0.56	0.028-0.056	2.5	0.25
	Conversion – O	0.68-1.36	0.068-0.136	13.7	1.37
	Conversion – PO	0.72-1.44	0.072-0.144	14.7	1.47
	Conversion – C	0.64-1.28	0.064-0.128	12.6	1.26
	Compounding/conversion – O	0.84-1.68	0.084-0.168	18.1	1.81
	Compounding/conversion - PO	1.54-3.08	0.154-0.308	38.3	3.83
	Compounding/conversion – C	0.72-1.44	0.072-0.144	14.6	1.46
Use in plastics/ rubber	Compounding	0.30-0.60	0.030-0.060	2.7	0.27
	Conversion	0.48-0.96	0.048-0.096	7.8	0.78
	Compounding/conversion	0.56-1.12	0.056-0.112	10.0	1.00[e]

Table 2 continued

Scenario	Step	Fish[d] (Using measured regional concentrations)		Earthworms – (Using measured regional concentrations)	
		PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC
Use in sealants	Formulation and use	negligible[c]	<1	negligible[c]	<1
Use in paints	Formulation	0.46-0.92	0.046-0.092	7.6	0.76
	Industrial application	0.23-0.64	0.023-0.064	3.3	0.33
	Domestic application	negligible[c]	<1	negligible[c]	<1
Use in metal cutting/working fluids	Formulation	1.60-3.20	0.16-0.32	39.7	3.97
	Use in oil-based fluids (large)	0.76-1.52	0.076-0.152	16.1	1.61
	Use in oil-based fluids (small)	0.72-1.44	0.072-0.144	14.7	1.47
	Use in emulsifiable fluids	0.26-0.52	0.026-0.052	1.7	0.17
	Use in emulsifiable fluids – intermittent release	1.04-2.08	0.104-0.208	129[a]	12.9[a]
Use in leather fat liquors	Formulation	0.38-0.76	0.038-0.076	5.2	0.57
	Use – complete processing of raw hides	1.72-3.44	0.172-0.344	43.0	4.30
	Use – processing of wet blue	6.20-12.4	0.62-1.24	171	17.1
Use in carbonless copy paper	Paper recycling	0.46[b]-0.92[b]	0.046[b]-0.092[b]	8.8[b]	0.88[b]

Note: a) Assumes dilution of sewage sludge at wwtp before application to soil (see EU (2005)).

b) Primary treatment (sludge to landfill) followed by biological waste water treatment (sludge to soil).

c) Process makes no significant contribution to the levels in fish/earthworms.

d) The concentration in fish is estimated taking into account accumulation through the food chain. The range reflects the range for the FAF (1-3).

e) The PECs used for this comparison are taken from EU (2005) and were calculated using EUSES 1. Calculations using EUSES 2.0.3 indicates that these PEC/PNEC ratios are <1 (0.97 and 0.94 respectively).

O = Open systems; PO = Partially open systems; C = Closed systems.

For the earthworm food chain, the original risk assessment concluded that the risk from secondary poisoning was low from production sites (where no sewage sludge is applied to land), formulation and use of sealants, and domestic application of paints. All other uses of medium-chain chlorinated paraffins were found to present a potential risk from secondary poisoning for the earthworm food chain. Again these conclusions were reached using a $PNEC_{oral}$ of 0.17 mg/kg food. Using the new $PNEC_{oral}$ of 10 mg/kg food, several other scenarios now lead to PEC/PNEC <1, but potential risks are still identified for fifteen of the thirty two scenarios considered in the assessment

As discussed in EU (2005) there are some uncertainties over the assessment of bioaccumulation/biomagnification for medium-chain chlorinated paraffins and it should be recognised that there is a general lack of experience in the application of the methods given in the Technical Guidance Document to address these uncertainties. In particular, it should be noted that the Technical Guidance Document only considers relatively simple food chains and higher levels could be predicted using more complex food chain models (for example see EU (2005); although again there would be some uncertainties associated with the modelled results).

It should be noted that medium-chain chlorinated paraffins have a relatively long depuration half-life in laboratory mammals. For example CXR (2005b) found that a steady state concentration in white adipose tissue of rats was reached after approximately 13 weeks continuous exposure to a medium-chain chlorinated paraffin via the diet. The elimination from this tissue was found to be biphasic with an initial half-life of 4 weeks, followed by a much slower elimination. A long half-life in mammalian tissue introduces some uncertainty in the assessment of secondary poisoning when extrapolating from the results of laboratory studies of relatively short duration to estimating PECs and PNECs over the life-time of predatory organisms in the environment (however the assessment factors given in the Technical Guidance Document are intended to address these uncertainties).

As indicated above, the PECs used for this comparison are taken from EU (2005) and were calculated using EUSES 1. EUSES 1 has now been superseded by EUSES 2.0.3. This version of the program has an improved method for calculating concentrations in soil, and if this version of the program is used for the PEC calculations then slightly different PECs are obtained, particularly for soil (and hence earthworms[10]). These small differences are not significant (in terms of the resulting PEC/PNEC ratio) for the majority of the scenarios. However two scenarios (use in PVC – plastisol coating combined compounding/conversion sites and use in plastics/rubber – combined compounding/conversion sites) that give PEC/PNEC ratios of 1 or above using EUSES 1 (PEC/PNEC of 1.04 and 1.00 respectively) would give PEC/PNEC ratios just below 1 using EUSES 2.0.3 (PEC/PNEC ratios of 0.97 and 0.94 respectively). The significance of this in terms of the conclusions is discussed further below.

10 The method for calculating concentrations in worms is also revised in EUSES 2.0.3, to implement the revised method in the second edition of the TGD. This uses a worm-porewater accumulation factor rather than whole soil accumulation factor. Therefore the measured whole soil accumulation factor of 5.6 on a wet weight basis was converted to an equivalent worm-porewater accumulation factor of 5.8×104 l/kg for use in the program.

Result

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

This applies to the assessment of secondary poisoning via the fish food chain from production and all uses of medium-chain chlorinated paraffins except for use in leather processing – processing of wet blue. This also applies to the assessment of secondary poisoning via the earthworm food chain for the following scenarios:

- Production sites (where sewage sludge is not applied to agricultural land).
- Use in PVC – plastisol coating – compounding sites.
- Use in PVC – plastisol coating – conversion sites.
- Use in PVC – extrusion/other – compounding sites using open or closed systems.
- Use in plastics/rubber – compounding sites.
- Use in plastics/rubber – conversion sites.
- Use in sealants – formulation and use.
- Use in paints – formulation sites.
- Use in paints – industrial application and domestic application.
- Use in metal cutting/working fluids – use in emulsifiable fluids.
- Use in leather fat liquors – formulation sites.
- Use in carbonless copy paper – paper recycling.

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

This applies to the following uses for the earthworm food chain:

- Use in PVC – plastisol coating – combined compounding/conversion sites*.
- Use in PVC – extrusion/other – compounding sites using partially open systems.
- Use in PVC – extrusion/other – conversion sites and combined compounding/conversion sites.
- Use in plastics/rubber – combined compounding/conversion sites*.
- Use in metal cutting/working fluids – formulation sites.
- Use in metal cutting/working fluids – use in oil-based fluids at large and small sites.
- Use in metal cutting/working fluids – use in emulsifiable fluids – intermittent release.
- Use in leather fat liquors – processing of raw hides and wet blue.

It should be noted that for the two scenarios for the earthworm food chain marked as * above, the risk identified depends on whether EUSES 1 or EUSES 2.0.3 is used for the calculation. However it should be born in mind that PEC/PNEC ratios >1 were identified for these two scenarios in EU (2005) for the sediment compartment and so risk management is already considered to be necessary for them. Therefore it is recommended that this risk management should also consider the possible risk of secondary poisoning through the earthworm food chain identified here.

In addition, this conclusion also applies to fish food chain for use in leather fat liquors – processing of wet blue. A PEC/PNEC ratio >1 is obtained for this scenario when a FAF of 3 is considered but a PEC/PNEC ratio <1 is obtained when a FAF of 1 is considered. This finding is independent of whether EUSES 1 or EUSES 2.0.3 is used. Although there is, therefore, some uncertainty over whether or not this scenario actually presents a risk of

secondary poisoning via the fish food chain, it should be noted that PEC/PNEC ratios >1 for this scenario have already been identified for surface water, sediment and soil in EU (2005) and so risk management is already considered to be necessary for this use. Therefore it is recommended that this risk management should also consider the possible risk of secondary poisoning through the fish food chain identified here

2 EXPOSURE OF MAN VIA THE ENVIRONMENT

2.1 UPTAKE FROM SOIL INTO ROOT CROPS

This Section revises Section 3.2.4.1 (Bioaccumulation) of EU (2005).

For man exposed via the environment, the default calculations used in the original risk assessment report identified uptake into root crops from soil as potentially a significant route for exposure of man through food. In order to refine the calculations for this source of exposure, a study investigating the actual accumulation of medium-chain chlorinated paraffins in roots of carrot (*Daucus carota*) has been carried out (Thompson *et al.*, 2005).

The substance tested was ^{14}C-labelled 52.5% wt. chlorinated n-pentadecane that was produced as a mixture with unlabelled $C_{14\text{-}17}$, 52.5% wt. chlorinated paraffin.

The soil used in the test consisted of a mixture of 50% sterilised Surrey loam and 50% gravel. The soil was characterised as follows: pebbles (particle size 64-4 mm) – 4.6%, granules (particle size 4-2 mm) – 40.4%, very coarse sand (particle size 2-1 mm) – 5.0%, coarse sand (particle size 1-0.5 mm) - 0.9%, medium sand (particle size 0.5-0.25 mm) – 1.0%, fine sand (particle size 0.25-0.125 mm) – 3.0%, very fine sand (particle size 0.125-0.063 mm) – 3.5% and silt/clay (particle size <0.063 mm) – 41.7%. The soil had an organic carbon content of 2.0% and a pH of 6.6-7.3.

The test substance was added to the soil in a two-stage process. Firstly, a solution of the substance in acetone was added to a sample of dried, powdered, sewage sludge from a treatment plant treating primarily domestic waste water. The acetone was then allowed to evaporate. After this, the spiked dried sewage sludge (175 g) was mixed into the soil (35 kg dry weight) in a 41.5 litre cylindrical container (the container was rotated at approximately 21 revolutions per minute for one hour) in two batches, and the two batches were then combined prior to use. The weight of sewage sludge therefore accounted for 0.5% of the total dry soil. Two nominal exposure concentrations were prepared in this way, 1 mg/kg dry weight and 10 mg/kg dry weight. A control soil was prepared in the same way.

The tests were carried out using rectangular containers (one per treatment) with a volume of 32.8 litres. The depth of soil in the containers was approximately 130 mm. The base of the containers had multiple perforations and the bottom of the container was covered with horticultural capillary matting. The containers were placed on a further layer of capillary matting within individual containment trays. This system was used as it allowed any test substance that was leached from the soil to be retained and drawn back into the soil with the irrigation water. Water (dechlorinated tap water) was provided primarily by sub-irrigation through this matting (the matting was kept wet by daily additions of water), but additional water was provided as necessary as a fine mist to the soil surface. During the test, illumination was provided by an array of 22 fluorescent lights (light intensity ~17,500 Lux at the soil surface) operating on a 16 hours light and 8 hours dark photoperiod. The temperature was maintained at 20±2°C during the study.

The experiment was initially started one day after spiking the soil. The soils were initially planted with 70 seeds per treatment but this series of experiments was terminated 21 days after planting owing to insufficient numbers of viable seedlings in all treatment groups, including the controls. Following termination of this series no further water additions were made to the soil prior to re-seeding the soils.

Two days prior to re-seeding the soils (55 days after the spiked soils were originally prepared) the soils were mixed to full depth. The soils were then re-seeded with 127 seeds per treatment (57 days after the soils were originally prepared), and watering was recommenced. This was taken as day 0 of the growth phase of the study.

Soil samples were analysed for the presence of total radioactivity on day -57 (i.e. immediately after spiking the soil), day -2, day 28 and day 70 of the study. On each sampling occasion, a total of three soil samples (taken from the front, middle and back of the test vessel) were taken for each treatment group, and one soil sample was taken from the control group. Four carrot plants from each treatment group were randomly selected for analysis on day 42, 50, 60 and 70. The roots were washed and dried prior to analysis.

The analytical method used to determine the total ^{14}C-residues in the soil was changed during the study. The samples taken on day -57 were extracted twice with acetone and the acetone extract was analysed for ^{14}C. For day -2, the analytical procedure was modified as other analyses carried out on day -10 and -8 suggested that the acetone extraction procedure was no longer recovering all of the radioactivity in the soil. The modified method involved directly combusting a dried, powdered, sub-sample of soil and determining the amount of $^{14}CO_2$ evolved. In addition, powdered samples were also extracted using an alternative solvent system (two extractions with hexane, followed by two extractions with ethyl acetate and finally two extractions with dichloromethane). For this method the total radioactivity in the combined extracts, and also the residual ^{14}C remaining in the soil after extraction, was determined. Based on this, it was concluded that analysis by direct combustion of the soil was preferable and this method was used for the subsequent time-points.

The total radioactivity in the carrot roots was determined by combustion analysis. As the maximum weight of tissue that could be contained within one combustion cone was ~1 g, multiple cones each containing a sub-sample of the root, were used for the larger roots. Up to day 70, the total root was analysed in this fashion. However, by day 70 the large size of some of the roots precluded such analysis, and so in cases where the total root weight exceeded 10 g sub-samples of the upper, middle and lower portions of the root were taken for analyses.

The results of the experiment are summarised in **Table 3**. The mean concentration found in soil over days -2 to 70 of the study was <0.62 mg/kg dry weight at the lower treatment level and 4.9 mg/kg dry weight at the higher treatment level.

For the experiment at the lower treatment level, both the mean concentrations in the soil and the concentrations in the roots could not be determined reliably (although the level of radioactivity was above the analytical detection limit in some samples, the level in other samples at each time point was below the analytical detection limit). Therefore it was not possible to derive reliable accumulation factors from the data for this treatment level.

For the higher treatment level, the concentration in the roots of the carrots was found to be highest on day 42 and then decreased until the last sampling time (day 70). As the measured concentration in soil was reasonably constant over this period, this suggests that the rate of accumulation of ^{14}C-label from the soil was slower than the rate of growth of the carrots. Another explanation for this is that the rate of uptake from the soil declined as the carrots grew larger resulting from a decrease in the surface area to volume ratio. The mean measured concentration in soil over the day -2 to day 70 period was 4.9 mg/kg dry weight. This value is equivalent to a concentration of 4.34 mg/kg wet weight using the default water content of soil given in the Technical Guidance Document. Using this, and the mean concentration of radiolabel in the roots (given in **0**), the bioaccumulation factor (concentration in root (mg/kg

fresh weight)/concentration in soil (mg/kg wet weight)) can be estimated as 0.088 at day 42, 0.058 at day 50, 0.046 at day 60 and 0.030 at day 70. The mean bioaccumulation factor over days 50-70 was 0.045.

As indicated above, the analytical method was changed part way through the study as the extraction with acetone alone did not appear to recover the expected amount of radiolabel from the soil (i.e. the levels measured by this approach were below the nominal concentration; the actual levels measured by this method were not given other than for day -57). One interpretation of this was that the substance was becoming more tightly bound to the soil with time during the study and so may have had reduced bioavailability to the plants. However, it should be noted that when the analytical method was changed to be based on combustion of the soil, the concentration was found to be relatively constant throughout the experiment (no statistically significantly differences (p=0.05) were found in the levels measured from day -2 to day 70). Since these direct measurements of the total amount of radiolabel present in the soil were also below the nominal concentrations, there is no conclusive evidence for a decline in extractability of the substance from the soil over the course of the experiment.

When considering these data in relation to the assessment of exposure of man via the environment, it should be considered that the weight of the carrot roots at day 42 were only around 1 g and so were well below the size that would be consumed as food. Therefore the mean bioaccumulation factor of 0.045 determined over days 50-70 of the growth period is considered to be most representative for use in the risk assessment.

Table 3 Uptake of medium-chain chlorinated paraffins from soil by carrot roots

Day	Mean concentration in soil (mg/kg dry weight)		Mean concentration in root (mg/kg fresh weight)	
	Treatment 1[a]	Treatment 2[b]	Treatment 1[a]	Treatment 2[b]
-57	1.0	13		
-2	0.95	5.0		
28	• 0.47	5.8		
42			<0.091	0.38
50			<0.042	0.25
60			<0.031	0.20
70	<0.43	3.9	<0.052	0.13

Note: a) Treatment 1 = nominal 1 mg/kg dry weight level in soil.

b) Treatment 2 = nominal 10 mg/kg dry weight level in soil.

2.2 APPLICATION OF NEW DATA TO THE CALCULATION OF MAN EXPOSED VIA THE ENVIRONMENT

This Section revises Section 4.1.1.3 (Indirect exposure via the environment) of EU (2005).

The original calculations for exposure of man via the environment were carried out using EUSES 1. This program has now been superseded by EUSES 2.0.3, and this version has been used for the calculations here. This change results in some relatively small (but not significant) changes to some of the underlying concentrations predicted in water, soil and sediment from those reported in EU (2005).

The EUSES program does not use a bioaccumulation related to the soil concentration directly in the calculations. Instead, a plant-water partition coefficient is defined as follows based on the octanol-water partition coefficient.

$$K_{plant\text{-}water} = F_{water(plant)} + (F_{lipid(plant)} \times Kow^{b})$$

where $K_{plant\text{-}water}$ = Partition coefficient between plant tissues and water (m^3/m^3).
$F_{water(plant)}$ = Volume fraction of water in plant tissues (m^3/m^3) – default = 0.65.
$F_{lipid(plant)}$ = Volume fraction of lipid in plant tissues (m^3/m^3) – default = 0.01.
b = Correction for differences between plant lipids and octanol – default = 0.95.

For medium-chain chlorinated paraffins (log Kow = 7), the $K_{plant\text{-}water}$ was estimated as 4.47×10^4 m^3/m^3.

In order to compare the measured accumulation factor with the default estimates used in the published version of the risk assessment, the method given in the Technical Guidance Document for calculation of the concentration in root crops needs to be considered further.

The concentration in plant roots is estimated using the following approach.

$$C_{root} = K_{plant\text{-}water} \times C_{porewater}/RHO_{plant}$$

where C_{root} = Concentration in root tissue of plant (mg/kg fresh weight).
$C_{porewater}$ = Concentration of chemical in soil pore water (mg/m^3).
RHO_{plant} = Bulk density of plant tissue (kg/m^3) – default = 700.

The concentration in pore water can be estimated by the equilibrium partitioning method as follows.

$$C_{soil} = K_{soil\text{-}water} \times C_{porewater}/RHO_{soil}$$

where C_{soil} = Concentration in soil (mg/kg wet weight).
$K_{soil\text{-}water}$ = Soil-water partition coefficient = 1.77×10^4 m^3/m^3 for medium-chain chlorinated paraffins.
RHO_{soil} = Bulk density of wet soil (kg/m^3) – default = 1,700.

Rearranging these equations leads to the following equation.

$$C_{root} = K_{plant\text{-}water}\times RHO_{soil}\times C_{soil}/(RHO_{plant}\times K_{soil\text{-}water})$$

Hence the bioaccumulation factor for root crops (BAF_{root}) can be estimated using the following equation.

$$BAF_{root} = C_{root}/C_{soil} = K_{plant\text{-}water}\times RHO_{soil}/(RHO_{plant}\times K_{soil\text{-}water})$$

Using the default value for $K_{plant\text{-}water}$ estimated above for medium-chain chlorinated paraffins of 4.47×10^4 m^3/m^3, the predicted value for the BAF_{root} is 6.1. Thus the experimentally determined value of 0.045 is around 136 times smaller than the default calculation.

Using the above analysis, an equivalent value for the $K_{plant\text{-}water}$ of 330 m^3/m^3 can be estimated[11] based on the experimental data for carrot roots. This value can be used in the EUSES 2.0.3 program in place of the default value to obtain a more reliable estimate of the resulting concentrations in root crops (and hence other parts of plants such as leaves) and so the likely exposure of man via the environment.

The resulting concentrations in the food chain for human exposure using this value for the $K_{plant\text{-}water}$ are summarised in **Table 4**, and the estimated daily human intakes from environmental sources are summarised in **Table 5**. The calculations used regional concentrations based on measured data of 0.1 µg/l for surface water and 0.088 mg/kg wet wt. for agricultural soil (as used in the environmental parts of the risk assessment). The measured data are taken from representative industrial areas in the United Kingdom and the agricultural soil samples were from sites that were known to receive sewage sludge from treatment plants where chlorinated paraffins were known to be released (further details of these sites are given in EU (2005)).

In the EUSES model, a log Kow value of 7 has been used as being representative for the group as a whole. A fish bioconcentration factor of 1,087 l/kg (see Section 3.1.0.5) has been used in the model to estimate the concentration in wet fish (no biomagnification factor (BMF) has been used in the calculations). For other parts of the food chain, particularly leaf crops, meat and milk, EUSES estimates the concentrations in these using methods that rely on log Kow as no equivalent measured accumulation factors exist for medium-chain chlorinated paraffin. It is not known if these methods would be applicable to medium-chain chlorinated paraffins.

It should also be noted that the change to the K_{plant_water} coefficient value also affects the predicted concentrations in plant leaves and hence meat and milk.

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[11] Estimated from 4.47×104×0.045/6.1. This value represents the value that, when entered into EUSES, results in a BAFroot of 0.045 when defined on a concentration in plant/concentration in wet soil basis.

Table 4 Estimated concentrations in food for human daily intake

Scenario	Step	Estimated concentration in human intake media[b]						
		Wet fish (mg/kg)	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m³)
Production	Site A	0.11	Negligible[a]	negligible[a]	2.6×10^{-5}	negligible[a]	negligible[a]	negligible[a]
	Site B	0.19	Negligible[a]	negligible[a]	4.4×10^{-5}	negligible[a]	negligible[a]	negligible[a]
	Site C	0.26	Negligible[a]	negligible[a]	6.0×10^{-5}	negligible[a]	negligible[a]	negligible[a]
	Site D	0.11	Negligible[a]	negligible[a]	2.5×10^{-5}	negligible[a]	negligible[a]	negligible[a]
Use in PVC – plastisol coating	Compounding - O	0.15	0.024	7.1×10^{-4}	5.0×10^{-5}	0.014	4.3×10^{-3}	negligible[a]
	Conversion – O	0.42	0.15	6.1×10^{-3}	3.2×10^{-4}	0.085	0.027	4.8×10^{-5}
	Compounding/conversion - O	0.46	0.17	6.1×10^{-3}	3.6×10^{-4}	0.092	0.029	4.8×10^{-5}
Use in PVC – extrusion/other	Compounding - O	0.26	0.076	2.3×10^{-3}	1.6×10^{-4}	0.04	0.013	1.8×10^{-5}
	Compounding – PO	0.94	0.40	9.4×10^{-3}	8.4×10^{-4}	0.19	0.059	7.4×10^{-5}
	Compounding – C	0.18	0.037	1.4×10^{-3}	7.9×10^{-5}	0.022	7.1×10^{-3}	1.1×10^{-5}
	Conversion – O	0.57	0.22	8.8×10^{-3}	4.7×10^{-4}	0.13	0.040	7.0×10^{-5}
	Conversion – PO	0.61	0.24	9.4×10^{-4}	5.1×10^{-4}	0.13	0.042	7.4×10^{-5}
	Conversion – C	0.53	0.20	8.1×10^{-3}	4.3×10^{-4}	0.11	0.036	6.4×10^{-5}
	Compounding/conversion – O	0.73	0.30	0.010	6.3×10^{-4}	0.16	0.050	8.2×10^{-5}
	Compounding/conversion - PO	1.4	0.63	0.018	1.3×10^{-3}	0.31	0.099	1.4×10^{-4}
	Compounding/conversion - C	0.60	0.24	8.8×10^{-3}	5.0×10^{-4}	0.13	0.041	7.0×10^{-5}
Use in plastics/rubber	Compounding	0.19	0.040	1.2×10^{-3}	8.6×10^{-5}	0.022	6.9×10^{-3}	9.2×10^{-6}
	Conversion	0.37	0.13	5.2×10^{-3}	2.7×10^{-4}	0.072	0.029	4.1×10^{-5}
	Compounding/conversion	0.44	0.16	5.6×10^{-3}	3.4×10^{-4}	0.087	0.028	4.5×10^{-5}

Table 4 continued

Scenario	Step	Estimated concentration in human intake media[b]						
		Wet fish (mg/kg)	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m³)
Use in sealants	Formulation and use	negligible[a]	Negligible[a]	negligible[a]	negligible[a]	negligible[a]	negligible[a]	negligible[a]
Use in paints	Formulation	0.36	0.12	2.2×10^{-3}	2.6×10^{-4}	0.054	0.017	1.7×10^{-5}
	Industrial application	0.21	0.050	7.1×10^{-4}	1.1×10^{-4}	0.023	7.2×10^{-3}	negligible[a]
	Domestic application	0.11	4.0×10^{-3}	7.1×10^{-4}	2.5×10^{-5}	7.2×10^{-3}	2.3×10^{-3}	negligible[a]
Use in metal cutting/working fluids	Formulation	1.5	0.65	7.3×10^{-4}	1.4×10^{-3}	0.23	0.071	negligible[a]
	Use in oil-based fluids (large)	0.66	0.26	7.2×10^{-4}	5.6×10^{-4}	0.094	0.030	negligible[a]
	Use in oil-based fluids (small)	0.61	0.24	7.2×10^{-4}	5.1×10^{-4}	0.086	0.027	negligible[a]
	Use in emulsifiable fluids	0.15	0.024	7.1×10^{-4}	5.0×10^{-5}	0.014	4.3×10^{-3}	negligible[a]
	Use in emulsifiable fluids – intermittent release	0.94[c]	2.1[c]	7.7×10^{-4} [c]	4.4×10^{-3} [c]	0.70[c]	0.22[c]	negligible[a]
Use in leather fat liquors	Formulation	0.28	0.083	0.011	1.8×10^{-4}	0.089	0.028	8.6×10^{-5}
	Use – complete processing of raw hides	1.6	0.71	7.3×10^{-4}	1.5×10^{-3}	0.24	0.077	negligible[a]
	Use – processing of wet blue	6.1	2.8	7.9×10^{-4}	6.0×10^{-3}	0.95	0.30	negligible[a]
Use in carbonless copy paper	Paper recycling	0.35	0.14	7.1×10^{-4}	3.0×10^{-4}	0.053	0.017	negligible[a]
Regional sources		0.11	4.0×10^{-3}	7.1×10^{-4}	2.5×10^{-5}	7.2×10^{-3}	3.3×10^{-3}	5.6×10^{-6}

Note: a) The process makes no significant contribution to the concentration in food/air.

b) Figures are calculated based on the measured regional water and soil concentrations of 0.1 µg/l and 0.088 mg/kg wet wt. respectively.

c) Assumes dilution of sewage sludge at wwtp before application to soil (see EU, 2005).

O = Open systems; PO = Partially open systems; C = Closed systems.

Table 5 Estimated human daily intake of medium-chain chlorinated paraffins via environmental routes

Scenario	Step	Estimated human daily intake (mg/kg body weight/day)[c]							
		Wet fish	Root crops	Leaf crops	Drinking water	Meat	Milk	Air	Total
Production	Site A	1.8×10^{-4}	-	-	7.5×10^{-7}	-	-	-	1.8×10^{-4}
	Site B	3.1×10^{-4}	-	-	1.3×10^{-6}	-	-	-	3.1×10^{-4}
	Site C	4.3×10^{-4}	-	-	1.7×10^{-6}	-	-	-	4.3×10^{-4}
	Site D	1.8×10^{-4}	-	-	7.1×10^{-7}	-	-	-	1.8×10^{-4}
Use in PVC – plastisol coating	Compounding - O	2.5×10^{-4}	1.3×10^{-4}	1.2×10^{-5}	1.4×10^{-6}	5.9×10^{-5}	3.5×10^{-5}	1.6×10^{-6}	4.9×10^{-4}
	Conversion – O	6.8×10^{-4}	8.2×10^{-4}	1.0×10^{-4}	9.0×10^{-6}	3.7×10^{-4}	2.2×10^{-4}	1.4×10^{-5}	2.2×10^{-3}
	Compounding/conversion - O	7.5×10^{-4}	9.3×10^{-4}	1.0×10^{-4}	1.0×10^{-5}	3.9×10^{-4}	2.3×10^{-4}	1.4×10^{-5}	2.4×10^{-3}
Use in PVC – extrusion/other	Compounding - O	4.3×10^{-4}	4.2×10^{-4}	3.9×10^{-5}	4.6×10^{-6}	1.7×10^{-4}	1.0×10^{-4}	5.2×10^{-6}	1.2×10^{-3}
	Compounding – PO	1.5×10^{-3}	2.2×10^{-3}	1.6×10^{-4}	2.4×10^{-5}	8.0×10^{-4}	4.7×10^{-4}	2.1×10^{-5}	5.2×10^{-3}
	Compounding – C	2.9×10^{-4}	2.1×10^{-4}	2.5×10^{-5}	2.3×10^{-6}	9.6×10^{-5}	5.7×10^{-5}	3.3×10^{-6}	6.8×10^{-4}
	Conversion – O	9.4×10^{-4}	1.2×10^{-3}	1.5×10^{-4}	1.4×10^{-5}	5.4×10^{-4}	3.2×10^{-4}	2.0×10^{-5}	3.2×10^{-3}
	Conversion – PO	1.0×10^{-3}	1.3×10^{-3}	1.6×10^{-4}	1.5×10^{-5}	5.7×10^{-4}	3.4×10^{-4}	2.1×10^{-5}	3.4×10^{-3}
	Conversion – C	8.7×10^{-4}	1.1×10^{-3}	1.4×10^{-4}	1.2×10^{-5}	4.9×10^{-4}	2.9×10^{-4}	1.8×10^{-5}	2.9×10^{-3}
	Compounding/conversion – O	1.2×10^{-3}	1.6×10^{-3}	6.8×10^{-4}	1.8×10^{-5}	6.8×10^{-4}	4.0×10^{-4}	2.4×10^{-5}	4.1×10^{-3}
	Compounding/conversion - PO	2.4×10^{-3}	3.5×10^{-3}	3.1×10^{-4}	3.8×10^{-5}	1.3×10^{-3}	7.9×10^{-4}	4.1×10^{-5}	8.3×10^{-3}
	Compounding/conversion - C	9.9×10^{-4}	1.3×10^{-3}	1.5×10^{-4}	1.4×10^{-5}	5.6×10^{-4}	3.3×10^{-4}	2.0×10^{-5}	3.4×10^{-3}
Use in plastics/rubber	Compounding	3.1×10^{-4}	2.2×10^{-4}	2.0×10^{-5}	2.5×10^{-6}	9.4×10^{-5}	5.5×10^{-5}	2.6×10^{-6}	7.0×10^{-4}
	Conversion	6.0×10^{-4}	6.9×10^{-4}	8.9×10^{-5}	7.6×10^{-6}	3.1×10^{-4}	1.8×10^{-4}	1.2×10^{-5}	1.9×10^{-3}
	Compounding/conversion	7.3×10^{-4}	8.9×10^{-4}	9.7×10^{-5}	9.8×10^{-6}	3.8×10^{-4}	2.2×10^{-4}	1.3×10^{-5}	2.3×10^{-3}

Table 5 continued

Scenario	Step	Estimated human daily intake (mg/kg body weight/day)[c]							
		Wet fish	Root crops	Leaf crops	Drinking water	Meat	Milk	Air	Total
Use in sealants	Formulation and use	-	-	-	-	-	-	-	negligible[b]
Use in paints	Formulation	5.9×10^{-4}	6.7×10^{-4}	3.7×10^{-5}	7.4×10^{-6}	2.3×10^{-4}	1.4×10^{-4}	4.9×10^{-6}	1.7×10^{-3}
	Industrial application	3.4×10^{-4}	2.8×10^{-4}	1.2×10^{-5}	3.0×10^{-6}	9.7×10^{-5}	5.7×10^{-5}	1.6×10^{-6}	7.9×10^{-4}
	Domestic application	1.8×10^{-4}	2.2×10^{-5}	1.2×10^{-5}	7.1×10^{-7}	3.1×10^{-5}	1.8×10^{-5}	1.6×10^{-6}	2.6×10^{-4}
Use in metal cutting/working fluids	Formulation	2.4×10^{-3}	3.6×10^{-3}	1.3×10^{-5}	4.0×10^{-5}	9.7×10^{-4}	5.7×10^{-4}	1.6×10^{-6}	7.6×10^{-3}
	Use in oil-based fluids (large)	1.1×10^{-3}	1.4×10^{-3}	1.2×10^{-5}	1.6×10^{-5}	4.0×10^{-3}	2.4×10^{-4}	1.6×10^{-6}	3.2×10^{-3}
	Use in oil-based fluids (small)	1.0×10^{-3}	1.3×10^{-3}	1.2×10^{-5}	1.5×10^{-5}	3.7×10^{-4}	2.2×10^{-4}	1.6×10^{-6}	2.9×10^{-3}
	Use in emulsifiable fluids	2.5×10^{-4}	1.3×10^{-4}	1.2×10^{-5}	1.4×10^{-6}	5.9×10^{-5}	3.5×10^{-5}	1.6×10^{-6}	4.9×10^{-4}
	Use in emulsifiable fluids – intermittent release[a]	1.5×10^{-3}	0.011	1.3×10^{-5}	1.3×10^{-4}	3.0×10^{-3}	1.8×10^{-3}	1.6×10^{-6}	0.018
Use in leather fat liquors	Formulation	4.5×10^{-4}	4.5×10^{-4}	1.9×10^{-4}	5.0×10^{-6}	3.8×10^{-4}	2.3×10^{-4}	2.5×10^{-5}	1.7×10^{-3}
	Use – complete processing of raw hides	2.6×10^{-3}	3.9×10^{-3}	1.3×10^{-5}	4.3×10^{-5}	1.1×10^{-3}	6.2×10^{-4}	1.6×10^{-6}	8.2×10^{-3}
	Use – processing of wet blue	0.010	0.016	1.4×10^{-5}	1.7×10^{-4}	4.1×10^{-3}	2.4×10^{-3}	1.6×10^{-6}	0.032
Use in carbonless copy paper	Paper recycling	5.8×10^{-4}	7.8×10^{-4}	1.2×10^{-5}	8.6×10^{-6}	2.3×10^{-4}	1.4×10^{-4}	1.6×10^{-6}	1.8×10^{-3}
Regional sources		1.8×10^{-4}	2.2×10^{-5}	1.2×10^{-5}	7.1×10^{-7}	3.1×10^{-5}	1.8×10^{-5}	1.6×10^{-6}	2.6×10^{-4}

Note: a) Intermittent release – likely to occur 2-6 times/year only.

b) Process does not contribute significantly to estimated daily intake.

c) Figures are calculated using a measured regional surface water and soil concentration of 0.1 • g/l and 0.088 mg/kg wet weight respectively.

O = Open systems; PO = Partially open systems; C = Closed systems.

3 PBT ASSESSMENT

No assessment of the properties of medium-chain chlorinated paraffins against the PBT-criteria was carried out in the original risk assessment. An assessment of the properties of medium-chain chlorinated paraffins against the criteria for a persistent, bioaccumulative and toxic substance is given below. The information used is taken from the existing published environmental risk assessment for medium-chain chlorinated paraffins (EU, 2005), along with the February 2006 draft version[12] of the human health assessment and new information from the literature.

The assessment of medium-chain chlorinated paraffins against the PBT-criteria is not straight forward as medium-chain chlorinated paraffins are complex substances, containing components with different carbon chain lengths and different numbers of (and positions of) chlorine atoms per molecule. The actual properties of individual components will differ. Much of the data available for medium-chain chlorinated paraffins has been obtained for the commercial products, although some data are also available for a limited number of medium-chain chlorinated paraffins with a single carbon chain length. Therefore it is not possible to conclude on precisely which components of medium-chain chlorinated paraffins meet and which do not meet the PBT criteria; instead, more general conclusions are given.

3.1 PERSISTENCE

A substance is considered to be persistent (P) or very persistent (vP) if it has a half-life of >60 days in marine water or >180 days in marine sediment. In addition a substance is also considered to be persistent if it has a half-life of >40 days in freshwater or >120 days in freshwater sediment.

The available degradation data for medium-chain chlorinated paraffins are summarised in Section 3.1.1.4 of the published risk assessment report (EU, 2005).

No standard ready or inherent biodegradation tests have been carried out for medium-chain chlorinated paraffins, and no results from simulation tests are available. However tests have been carried out investigating the biological oxygen demand (BOD) after five days or up to twenty five days. In one series of experiments (Hoechst AG, 1976 and 1977), the degradation seen after five days (as expressed as a BOD/COD[13] ratio) was <1.6% for a C_{14-17}, 41% wt. Cl substance and 1.4% for a C_{14-17}, 49% wt. Cl substance.

Another series of experiments investigated the BOD using both non-acclimated and acclimated inocula (Madeley and Birtley, 1980). Using the non-acclimated inocula, the degradation seen after twenty five days (as expressed as a BOD/ThOD[14] ratio) was between 0% and 15% for four C_{14-17} chlorinated paraffins with chlorine contents ranging between 40% wt. and 58% wt. Using the acclimated inocula, the degradation seen was between 0% and 32%. In this study the medium-chain chlorinated paraffins with lower chlorine contents (e.g. 40% wt. and 45% wt.) generally showed more degradation than the medium-chain chlorinated paraffins with higher chlorine contents (e.g. 52% wt. and 58% wt.).

Based on these BOD experiments, it is concluded that medium-chain chlorinated paraffins are unlikely to be readily or inherently biodegradable in standard test systems, but there is

12 Document version R331_0602_hh.
13 COD = Chemical oxygen demand.
14 ThOD = Theoretical oxygen demand.

evidence that medium-chain chlorinated paraffins may undergo some degradation, particularly those with lower chlorine contents.

In addition to these data, data are also available on the degradation of medium-chain chlorinated paraffins in isolated bacterial cultures (Omori *et al.*, 1987). Dechlorination of medium-chain chlorinated paraffins was seen in some bacterial strains in cometabolic systems. However, the conditions used in these tests make it difficult to extrapolate the results to the environment.

Relatively short half-lives of 12 days and 58 days have been reported in aerobic sediment for two medium-chain length chlorinated paraffins (^{14}C-labelled $C_{16}H_{31}Cl_3$ and $C_{16}H_{21}Cl_{13}$ respectively) at 11.6°C (Fisk *et al.*, 1998b). These data were determined as part of a study investigating the accumulation of medium-chain chlorinated paraffins in oligochaetes (*Lumbriculus variegatus*). However, it should be noted that the degradation reported in this study was based on the difference between toluene-extractable ^{14}C-measurements (taken to represent unchanged chlorinated paraffins) and total ^{14}C-measurements in the sediment. Therefore half-lives quoted depend crucially on the assumption that the non-extractable ^{14}C represented degraded chlorinated paraffins and this may not have been the case.

Also relevant to the discussion here are the biodegradation simulation studies that have recently been completed by Thompson and Noble (2007) for the related $C_{10\text{-}13}$ chlorinated paraffins (short-chain chlorinated paraffins) and the results from this study are summarised below (full details are given in ECB (2007)).

The test was carried out using freshwater and marine sediments under both aerobic and anaerobic conditions. Two ^{14}C-labelled substances were tested, a C_{10}, 65% wt. Cl substance and a C_{13}, 65% wt. Cl substance. The tests determined the amounts of mineralisation products (e.g. $^{14}CO_2$ and $^{14}CH_4$) evolved over a 98-day incubation period. Under aerobic conditions the mineralisation half-life was determined to be around 1,340 days for the C_{10}, 65% wt. Cl substance in freshwater sediment, 335 days for the C_{10}, 65% wt. Cl substance in marine sediment, 1,790 days for the C_{13}, 65% wt. Cl substance in freshwater sediment and 680 days for the C_{13}, 65% wt. Cl substance in marine sediment. In the experiments under anaerobic conditions no significant formation of ^{14}C-labelled methane was observed and only a limited amount of ^{14}C-labelled CO_2 was formed (≤1.3 % of the applied amount).

Read-across of these data to medium-chain chlorinated paraffins is not straight forward in that the short-chain chlorinated paraffin tested had a high chlorine content (65% by weight). The available evidence suggests that the rate of biodegradation of medium-chain chlorinated paraffins may increase with decreasing chlorine content, but there is also some evidence that the rate of degradation may decrease with increasing carbon chain length (for example in the above simulation study, a slightly longer mineralisation half-life was obtained for the C_{13} chlorinated paraffin than the C_{10} chlorinated paraffin but, owing to the relatively slow rates of degradation seen, it is not clear how significant this difference is). Thus it is difficult to draw firm conclusions from the recent study on short-chain chlorinated paraffins to the likely environmental half-life of medium-chain chlorinated paraffins which typically have chlorine contents of 45 and 52% by weight. However, the mineralisation half-lives found for short-chain chlorinated paraffins are sufficiently long that it is considered likely that medium-chain chlorinated paraffins would also be considered persistent within such test systems.

Overall it is considered that medium-chain chlorinated paraffins are not readily or inherently biodegradable, and therefore meet the screening criteria for P or vP. There is evidence that

some microorganisms may be capable of degrading medium-chain chlorinated paraffins in the environment in acclimated or cometabolic systems, but it is not possible to estimate a likely environmental degradation half-life from these data. It should also be considered that the potential for biodegradation appears to decrease with increasing chlorine content, which implies that the more highly chlorinated medium-chain paraffins may be expected to be more persistent than the less chlorinated medium-chain paraffins. In this respect it is worth noting that the most common types of medium-chain chlorinated paraffins in commercial use have chlorine contents of between around 45% wt. Cl and 52% wt. Cl. Of these the 52% wt. Cl products would be expected to be more persistent than the 45% wt. product.

In accordance with the testing strategy in the Technical Guidance, a simulation test for biodegradability would be required to determine the actual half-life in the marine environment, as the next step. Such a test could take a considerable amount of time (up to a year or more) to perform for such a poorly soluble complex substance (since radiolabelled components are probably needed) and may not even then be sufficient to show definitively that medium-chain chlorinated paraffins are not persistent.

3.2 BIOACCUMULATION

A substance is considered to be bioaccumulative (B) if it has a bioconcentration factor (BCF) >2,000 l/kg or very bioaccumulative (vB) if it has a BCF >5,000 l/kg. The available information on uptake and accumulation is summarised in Section 3.1.1.5 of the published risk assessment report (EU, 2005).

The highest measured BCF value for (freshwater) fish with medium-chain chlorinated paraffins is 1,087 l/kg (Thompson *et al.*, 2000) determined in a flow-through study. The substance tested in this study was a ^{14}C-labelled C_{15}-chlorinated paraffin with a chlorine content of around 51% wt., that was mixed with an unlabelled C_{14-17}, 51% wt. Cl substance. The BCF value was based on ^{14}C measurements (and so may represent accumulation of metabolites as well as the C_{15}-chlorinated paraffin) and the value was determined using the uptake and depuration kinetics[15]. There are several other fish bioconcentration factors (many of questionable reliability) below this value. In the risk assessment report (EU, 2005) this value was taken to be representative for the commercially supplied substance for the assessment of secondary poisoning.

Based on the available BCF data for fish, medium-chain chlorinated paraffins do not meet the criteria for B or vB. However the highest reliable BCF value for fish for medium-chain chlorinated paraffin was obtained using a substance with a C_{15}-chain length and a chlorine content of 51% wt. Medium-chain chlorinated paraffins are complex substances and so contain a range of components with different carbon chain lengths (C_{14}-, C_{15}-, C_{16}- and C_{17}-) and chlorine contents. Little information is available on the variation of BCF with carbon chain length. For short-chain chlorinated paraffins, the highest BCF value for fish was determined to be 7,816 l/kg using a radiolabelled C_{11}, 58% wt. Cl substance (EU, 2000).

[15] The depuration kinetics used in this determination were not growth corrected. It is not normal to growth correct the depuration rate constant from a BCF study (such a correction is not mentioned in the OECD 305 test guideline) but it has been suggested that it is appropriate to do this correction when interpreting the results of feeding studies with fish. No growth data were given in the Thompson et al. (2000) study but if a growth rate constant of 0.013 day-1 (a typical value from the Fisk et al. (1996, 1998a and 2000) series of feeding studies for the same species) is assumed, the growth corrected kinetic BCF from the Thompson et al. (2000) study would be around 1,530 l/kg, with a growth-corrected depuration half-life of around 22 days.

There are also other data that should be considered in relation to the bioaccumulation potential. These are discussed below.

Other accumulation data

BCF values in the range 339-2,856 l/kg have been determined for a marine mollusc (*Mytilus edulis*) (Madeley and Thompson, 1983). The interpretation of the results of these studies is, however, not straight forward as there is a possibility that at least some of the exposure of the organisms resulted from direct ingestion of undissolved substance or the substance adsorbed to food particles. Therefore, although these data appear to indicate a BCF of >2,000 l/kg it may not be appropriate to compare these values directly with the criteria for a bioaccumulative or very bioaccumulative substance, and so no firm conclusions can be drawn.

Another BCF study with *Mytilus edulis* has recently come to light (Renberg *et al.,* 1986; this study was not considered in EU, 2005). The substance tested in this study was a ^{14}C-labelled C_{16}-chlorinated paraffin with a chlorine content of 34% (the average formula was given as $C_{16}H_{30.7}Cl_{3.3}$). The radiolabel was in the 1-position of the carbon chain but no information on the purity of the radiolabelled substance was given (the paper indicates that the purity was checked but gives no further details). The test system used was a continuous-flow system. The test substance, along with a control substance (2,4',5-trichlorobiphenyl) was delivered to the exposure vessel as a solution in acetone. The nominal exposure concentration was 0.13 • g/l for the C_{16}-chlorinated paraffin and 5.0 • g/l for 2,4',5-trichlorobiphenyl. The mussels used in the test had a mean length of 3.0 cm and a mean wet weight of 0.5 g and were allowed to attach to glass plates for approximately one week prior to the start of the test. The exposure consisted of a 28 day uptake phase (depuration was not studied), and two mussels were sampled on each of day 1, 3, 7, 14, 21 and 28 of the study. The concentration in water was also determined at the same time as in the mussels.

During the study, the measured concentration of the chlorinated paraffin in water was between 0.080 • g/l and 0.172 • g/l. The mean measured concentration was not given in the paper, but it can be calculated as 0.11 • g/l (± standard deviation of 0.04 • g/l) from the data reported. The concentration of the chlorinated paraffin in the mussel was found to reach a relatively constant value of between 540 and 705 • g/kg wet weight after 14 days exposure and the authors concluded that the BCF for the C_{16} chlorinated paraffin was 6,920 l/kg based on the steady state concentration of radioactivity in the mussel (it is not entirely clear how this value is derived but it is close to the mean value obtained based on the actual concentrations of radioactivity measured in fish and water on days 14, 21 and 28 of the study). In addition, the data were analysed statistically and this lead to a similar BCF of 7,090 l/kg with a standard error of 1,100 l/kg and confidence limits[16] of 4,620-9,570 l/kg. The BCF for the 2,4',5-trichlorobenzene control substance was around 13,800 l/kg.

It should be noted that the chlorine content of the substance tested in the Renberg *et al.* (1986) study was around 35% by weight. This is lower than that of the main medium-chain chlorinated paraffin products that are in commercial use (for example EU (2005) indicates that the lowest chlorine content of a medium-chain chlorinated paraffin in commercial production is around 40% by weight, with the largest tonnage being medium-chain chlorinated paraffins with between 45% by weight and 52% by weight) and so the results may not be directly applicable for the main commercial products. However, medium-chain chlorinated paraffins are complex substances, containing components with various

[16] The actual confidence level was not given. The values probably refer to the 90% or 95% confidence limits.

combinations of carbon chain length and chlorine content and this is considered further below.

A number of feeding studies have been carried out with medium-chain chlorinated paraffins in fish (for example Fisk *et al.* (1996), Fisk *et al.* (1998a) and Fisk *et al.* (2000)). These show that uptake into fish from food occurs, and that the concentration in the fish can exceed the concentration in the food, when expressed on a growth corrected lipid weight basis. The potential for uptake from food appears to reduce with increasing chlorine content.

BMFs (defined as the growth corrected concentration in fish on a lipid weight basis/the concentration in food on a lipid weight basis) in the range 1-3 were determined for several medium-chain chlorinated paraffins of specific carbon chain lengths. As discussed in the original risk assessment there is some uncertainty over the relevant basis on which to express these BMFs. It should also be noted that the majority of the food uptake studies are based on ^{14}C-measurements, and there is some evidence that substantial metabolism may have been occurring in the organisms. This means that although radioactivity was found in the organisms, the concentrations found do not necessarily represent those of the parent compound. In terms of the assessment of bioaccumulation, no criteria are given in the TGD for BMFs in relation to B or vB.

As well as laboratory feeding data, some limited field data are available on the bioaccumulation potential in aquatic organisms, for example Muir *et al.* (2002). These data showed no indications of biomagnification in three lake trout-fish food chains but did appear to show BMFs>1 for medium-chain chlorinated paraffins in an invertebrate-fish food chain. Furthermore there were some indications from the data that although biomagnification did not appear to be occurring, the actual bioaccumulation seen in fish may be higher than would be expected by bioconcentration processes alone (although it should be noted that there is considerable uncertainty in these data). In addition to this the Swedish Environmental Protection Agency (1998) found no evidence for biomagnification in the herring to seal food chain for chlorinated paraffins based on the results of Jansson *et al.* (1993) (the levels found in herring were higher than in seals).

Overall, these data provide some evidence that uptake from food may increase the actual accumulation of medium-chain chlorinated paraffins over that expected purely from bioconcentration processes alone. This does not necessarily mean that biomagnification of the substance (here the term is meant to represent increasing concentrations with increasing trophic levels) is occurring[17], rather that the level of the substance found in any one organism within a food chain has significant contributions from both food ingestion and direct uptake from water.

One possible way of considering this is to define the overall concentration likely in a species exposed via both water and food as follows (see EU, 2005 for further details).

$$PEC_{oral,\ predator} = PEC_{water} \times BCF_{fish} \times (1 + BMF_{fish})$$

where BCF_{fish} = the fish BCF value.
BMF_{fish} = the fish biomagnification factor derived from laboratory feeding studies.

17 In this scheme, biomagnification would be evidenced by comparison of the PECoral for different trophic levels.

The overall bioaccumulation factor (BAF) can then be defined as $BCF_{fish} \times (1 + BMF_{fish})$. Thus it can be seen that the BMF can make a significant contribution to the total accumulation in an aquatic organism when it is below 1 (for example a BMF of 0.5 would imply that the actual concentration in fish would be 1.5 times higher than would be expected based on bioconcentration processes alone).

In relation to the assessment against the B-criterion, it is relevant to consider that when the BMF is around 1 the overall BAF for medium-chain chlorinated paraffins would be >2,000 l/kg. However, as the B-criterion is written in terms of BCF values, this on its own is not considered sufficient to consider the substance as meeting the B-criterion.

In addition to data for aquatic organisms, experiments have show that medium-chain chlorinated paraffins can be taken up by worms from soil (Thompson *et al.*, 2001). The BCF for earthworm (the concentration in earthworm on a wet weight basis/concentration in soil on a wet weight basis) was estimated from the data to be 5.6 for the standard soil assumed in the TGD. Again, no criteria are given in the TGD for such BCFs in relation to B or vB.

Further considerations in relation to the possible variation of the BCF with carbon chain-length and chlorine content

Based on the available BCF values, and the data reported from the available feeding studies with medium-chain chlorinated paraffins (see above and EU (2005)) and short-chain chlorinated paraffins (see EU (2000) and the updated environmental risk assessment report[18]), it appears that the bioaccumulation potential of chlorinated paraffins may possibly decrease with increasing carbon chain-length and increasing chlorine content. The consequence of this is that it is possible that the BCF value for some components of medium-chain chlorinated paraffins (for example those with a C_{14}-carbon chain) may be higher than found experimentally with the C_{15}-substance. This is a relevant consideration for medium-chain chlorinated paraffins has Industry has confirmed that the commercial products have a significant C_{14} content. Therefore, although the currently available BCF data indicate that medium-chain chlorinated paraffins do not meet the criteria for B or vB, it is not possible to be certain that this is the case for all of the major components of the technical products.

The currently available fish BCF for medium-chain chlorinated paraffins of 1,087 l/kg was generated using a ^{14}C-labelled C_{15}-substance with a chlorine content of 51% by weight, and this value is considered to be representative of the main components of one of the main commercial products currently in production (and hence it was used as a representative value for the assessment of secondary poisoning in EU (2005)). However, for the PBT assessment it is also relevant to consider that medium-chain chlorinated paraffins are complex substances and so there may be components of the commercial products that may have BCFs higher or lower than this "typical" value. In order to investigate this possibility further, a series of predictions of the fish BCF were carried out for a number of hypothetical medium-chain chlorinated paraffin structures. The approach taken is outlined below.

- Firstly, log Kow values were estimated from the chemical structure for a range of chlorinated paraffins using the USEPA EPIWIN (version 3.12) software using SMILES notation as input. The structures chosen represented carbon chain lengths from C_{10} up to C_{18}, for three (approximately) constant chlorine contents of around 45%, 52% and 60% by weight (the chlorine contents were chosen to represent the main medium-chain chlorinated paraffins in commercial production).

[18] Updated Risk Assessment of Alkanes, C10-13, Chloro. Final Draft Report R010_0508, August 2005.

- These log Kow values were then used to estimate the fish BCF using the QSAR equations given in the Technical Guidance Document.
    - For log Kow up to 6, log BCF_{fish} = 0.85×log Kow – 0.70
    - For log Kow >6, log BCF_{fish} = -0.20×$(\log Kow)^2$ + 2.74×log Kow – 4.72.
- The predicted BCF values were then compared with the available BCF values for short-chain chlorinated paraffins (BCF of 7,816 l/kg for a C_{11}, ~58% by weight substance; see EU, 2000) and medium-chain chlorinated paraffins (BCF of 1,087 l/kg for a C_{15}, ~51% by weight substance; see EU, 2005). This showed that the predictions were higher than the measured values in both cases.
- The predicted BCF values were then "normalised" to the available value for medium-chain chlorinated paraffins as follows.
    - Normalised BCF = Predicted BCF×1087/7186, where 7,186 represents the predicted BCF for a C_{15}, ~52% wt. Cl substance.

The results from this analysis are summarised in **Table 6** and displayed graphically in **Figure 1**.

As can be seen, normalising the data to the actual BCF for medium-chain chlorinated paraffins leads to a reasonably accurate prediction of the available BCF for short-chain chlorinated paraffins (a predicted value of ca 6,700-6,900 is obtained for a C_{11}, 52-60% wt. Cl substance, compared with the experimental value of 7,816 l/kg for a C_{11}, 58% wt. Cl substance). The predictions indicate that at lower carbon chain lengths (up to around C_{13}), the BCF is expected to increase with increasing carbon chain length for a constant chlorine content. At longer carbon chain lengths (C_{14} and above) the reverse trend is apparent. The variation with chlorine content is predicted to depend on the carbon chain length. For C_{10} there is a predicted increase in the BCF with increasing chlorine content. For C_{11} and C_{12}, the chlorine content is predicted to have little effect on the BCF. At higher chain lengths (C_{13} and above) the BCF is predicted to decrease with increasing chlorine content. An important finding in relation to the PBT assessment of medium-chain chlorinated paraffins is that the fish BCF is predicted to be >2,000 l/kg for the C_{14}, ~45% wt. Cl and C_{14}, ~52% wt. Cl example structures. This suggests that at least some components of the commercially supplied chlorinated paraffins could have BCF values sufficiently high to meet the B-criterion.

It is recognised that there are many uncertainties inherent in this approach as it depends firstly on the prediction of log Kow values and then prediction of BCF values from these predicted log Kow values. However, the normalisation procedure has been used to try to take into account any systematic errors inherent in the prediction of log Kow and/or BCF. It should also be recognised that the approach taken here uses the TGD methodology for predicting the BCF. There are other methods available for predicting BCF values and it is possible that a different predicted trend in the variation of BCF with carbon chain length would be obtained using alternative methods.

In order to try to address some of these uncertainties, a further analysis using different methods of predicting both the log Kow values and the BCF values was undertaken (see Appendix A). Both the above equations from the TGD and the BCFWINv2.15 program (part of the USEPA EPIWIN (version 3.12) software) were used to estimate the BCF value. The log Kow values used were either those predicted using EPIWIN or were predicted using the method of Sijm and Sinnige (1995).

The BCFWIN predictions using the log Kow values predicted using the Sijm and Sinnige (1995) method were in good agreement with the available data for medium chain chlorinated paraffins (e.g. the predicted value for a C_{15}, 51/52% wt. Cl substance was 998 l/kg compared with the measured value of 1,087 l/kg). Using this method, the highest BCFs predicted for any component of medium chain chlorinated paraffins with chlorine contents of 52% or below was 1,537 l/kg, estimated for a C_{14}, 52% wt. Cl substance and a C_{15}, 45% wt. Cl substance. These values are below the cut-off for a B-substance. However, this method estimates BCFs above 2,000 l/kg for C_{14}- and C_{15}- substances with chlorine contents of around 60%.

When the TGD method for predicting BCFs is considered using the log Kow values estimated by the method of Sijm and Sinnige (1995), the method consistently overpredicts the known BCFs for both medium- and short-chain chlorinated paraffins. Scaling the predicted BCF to the known BCF for medium chain chlorinated paraffin (as above) leads to an underestimation of the known BCF for short-chain chlorinated paraffins (estimated value approximately 1,157 l/kg compared with the measured value of 7,816 l/kg). Using this approach the highest predicted BCF for a component of a medium-chain chlorinated paraffin is around 1,157 l/kg for a $C_{14,}$ 45% wt. Cl substance.

Overall, it can be concluded that there are considerable uncertainties in the estimated BCFs for medium-chain chlorinated paraffin components. Both the EPIWIN and TGD methods lead to predicted BCFs for some medium-chain chlorinated paraffins >2,000 l/kg but the two methods are not consistent in terms of the chlorine contents at which these high BCFs would occur. The BCFWIN method predicts that the C_{14} and C_{15} components of the medium-chain chlorinated paraffins with relatively high chlorine contents (around 60%) may have BCFs above 2,000 l/kg whereas the TGD method predicts that the C_{14} components with relatively low chlorine contents (around 52% or below) may have BCFs above 2,000 l/kg. The main difference between the two methods relates to the structural correction factors applied in the BCFWIN method for structures with eight or more $–CH_2$- groups in the carbon chain. The applicability of these correction factors to medium-chain chlorinated paraffins is unclear, but the application of these factors leads to some apparent discrepancies in the predicted BCFs that cannot be easily reconciled in mechanistic terms (for example high BCFs are predicted using this method for C_{12}- and C_{14}- substances with chlorine contents around 60% by weight, but not a C_{13}- substance with a similar chlorine content; see Appendix A for details).

Given the uncertainties over the applicability of EPIWIN methodology across the range of carbon chain lengths and chlorine contents considered, it is considered that the “best-fit” to the available experimental data for both medium- and short-chain chlorinated paraffins as shown in the analysis carried out in 0 must also be considered as a plausible estimation. These predictions appear to be reasonably consistent with the (limited) available BCF data and so, at this stage, it cannot be ruled out that the actual BCF values of some components of the commercially supplied medium-chain chlorinated paraffins could be >2,000 l/kg.

It should also be noted that the analysis depends on the log Kow value used. It could be considered to determine a reliable log Kow value for the components of the medium-chain chlorinated paraffins of interest as a first stage. However, it should be noted that the method of Sijm and Sinnige (1995) is derived from measured data on short-chain chlorinated paraffins and so is likely to give a reasonable estimate of the actual log Kow for medium-chain chlorinated paraffins. Importantly, even if a measured log Kow values were available for some of the components of medium-chain chlorinated paraffins, there would still be a problem in determining exactly what these meant in terms of BCFs (i.e. there would still be

considerable uncertainty in estimating a reliable BCF for the components), and it is likely that this uncertainty could only be addressed by experimental determination of the BCF. Therefore, although of interest, a reliable determination of the log Kow value for the components medium-chain chlorinated paraffins would be unlikely to fully address whether some components have actual BCF values >2,000 l/kg.

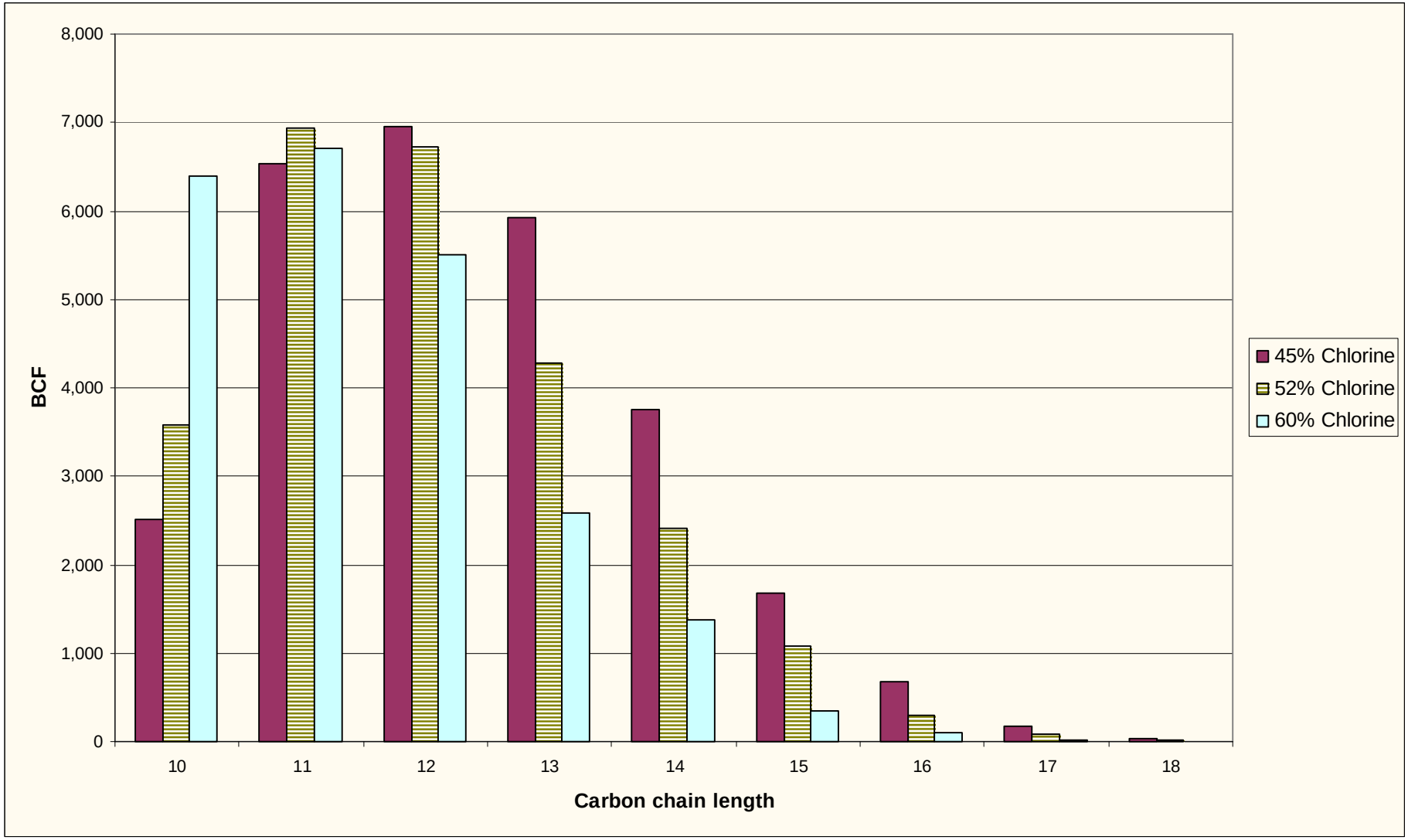
Table 6 Estimated log Kow and BCF for a series of hypothetical chlorinated paraffin structures

Formula	Molecular weight (g/mol)	Chlorine content (% by weight)		SMILES notation used for estimating log Kow	Log Kow estimate (EPIWIN v3.12)	Predicted BCF - TGD method (l/kg)	Predicted BCF scaled to known BCF for MCCPs (l/kg)
		Actual	Group for plot				
$C_{10}H_{19}Cl_3$	245.5	43.4	45.0	CC(Cl)CC(Cl)CCC(Cl)CCC	5.79	16,653	2,519
$C_{11}H_{20}Cl_4$	294.0	48.3	45.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	6.47	43,214	6,537
$C_{12}H_{22}Cl_4$	308.0	46.1	45.0	CC(Cl)CC(Cl)CC(Cl)CCCC(Cl)CC	6.96	45,928	6,947
$C_{13}H_{24}Cl_4$	322.0	44.1	45.0	CC(Cl)CC(Cl)CC(Cl)CCCCC(Cl)CC	7.45	39,129	5,919
$C_{14}H_{26}Cl_4$	336.0	42.3	45.0	C(Cl)CCCCC(Cl)CCCC(Cl)CC(Cl)CC	8.01	24,853	3,759
$C_{15}H_{27}Cl_5$	384.5	46.2	45.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CCCC(Cl)CC	8.61	11,091	1,678
$C_{16}H_{29}Cl_5$	398.5	44.5	45.0	CC(Cl)CC(Cl)CCC(Cl)CCC(Cl)CCC(Cl)CCC	9.10	4,487	679
$C_{17}H_{31}Cl_5$	412.5	43.0	45.0	C(Cl)CC(Cl)CC(Cl)CCCC(Cl)CCCC(Cl)CCCC	9.67	1,186	179
$C_{18}H_{32}Cl_6$	461.0	46.2	45.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CCC(Cl)CCC(Cl)CCC	10.26	218	33
$C_{10}H_{18}Cl_4$	280.0	50.7	52.0	CC(Cl)CC(Cl)C(Cl)CC(Cl)CCC	5.97	23,686	3,583
$C_{11}H_{19}Cl_5$	328.5	54.0	52.0	C(Cl)CC(Cl)CCC(Cl)CC(Cl)CC(Cl)C	6.72	45,827	6,932
$C_{12}H_{21}Cl_5$	342.5	51.8	52.0	CC(Cl)C(Cl)CC(Cl)CCC(Cl)CCC(Cl)C	7.14	44,430	6,721
$C_{13}H_{22}Cl_6$	391.0	54.5	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)C	7.88	28,335	4,286
$C_{14}H_{24}Cl_6$	405.0	52.6	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CC	8.37	15,937	2,411
$C_{15}H_{26}Cl_6$	419.0	50.8	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CCC	8.86	7,186	1,087
$C_{16}H_{27}Cl_7$	467.5	53.2	52.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CCC(Cl)C(Cl)C	9.46	2,005	303
$C_{17}H_{29}Cl_7$	481.5	51.6	52.0	CC(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CC(Cl)CC	9.95	553	84
$C_{18}H_{31}Cl_7$	495.5	50.2	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CCCC(Cl)CCC	10.52	93	14
$C_{10}H_{16}Cl_6$	349.0	61.0	60.0	CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)	6.41	42,245	6,390

Table 6 continued

$C_{11}H_{17}Cl_7$	397.5	62.5	60.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)	7.15	44,310	6,703
$C_{12}H_{19}Cl_7$	411.5	60.4	60.0	C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)CC	7.57	36,376	5,503
$C_{13}H_{20}Cl_8$	460.0	61.7	60.0	C(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)	8.32	17,073	2,583
$C_{14}H_{22}Cl_8$	474.0	59.9	60.0	C(Cl)CC(Cl)C(Cl)C(Cl)CC(Cl)CCC(Cl)CC(Cl)C(Cl)C	8.73	9,070	1,372
$C_{15}H_{23}Cl_9$	522.5	61.1	60.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)C(Cl)CC(Cl)CC(Cl)C	9.41	2,258	342
$C_{16}H_{25}Cl_9$	536.5	59.6	60.0	C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C	9.89	655	99
$C_{17}H_{26}Cl_{10}$	585.0	60.7	60.0	C(Cl)CC(Cl)C(Cl)C(Cl)C(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CC	10.57	79	12
$C_{18}H_{27}Cl_{11}$	633.5	61.6	60.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)CC(Cl)C(Cl)C(Cl)CC(Cl)C(Cl)C	11.24	6	1

Figure 1 Plot of predicted BCF against carbon number of a series of hypothetical chlorinated paraffin structures



Monitoring data

There are only limited monitoring data for medium-chain chlorinated paraffins for biota. The data are presented in EU (2005) and a brief summary of the available data is given in **Table 7** for convenience. The interpretation of these data is complicated by the fact that many of the studies have measured total chlorinated paraffins or C_{10-20} chlorinated paraffins and may not relate directly to the levels of medium-chain chlorinated paraffins present. However, medium-chain chlorinated paraffins have been reported to be present in marine fish and marine mammals (top predators such as porpoise and fin whale) amongst others (e.g. see Greenpeace (1995) in Section 3.1.5.2 of the published risk assessment (EU, 2005)). These limited data provide some further supporting evidence that medium-chain chlorinated paraffins are taken up by organisms in the environment. However, given that the substance has a fish BCF of 1,087 l/kg, the fact that medium-chain chlorinated paraffins are found in organisms in the environment is not in itself surprising, nor is it on its own sufficient to determine that the substance is bioaccumulative within the meaning of the PBT assessment.

Table 7 Summary of available monitoring data for medium-chain chlorinated paraffins in biota

Reference	Summary of findings	
	Results	**Comments**
CEFAS (1999)	Medium-chain chlorinated paraffins possibly present in freshwater fish and benthos near to sources (and also at a control site). Range of concentrations <0.1-5.2 mg/kg wet wt. Also possibly detected in earthworms at <0.1-1.7 mg/kg wet wt. from locations where sewage sludge containing medium-chain chlorinated paraffins was applied to soil	The actual identity of the residues was difficult to assign and it was not clear what types of chlorinated paraffins were present.
Campbell and McConnell (1980).	C_{10-20} chlorinated paraffins found in marine fish, mussels, predatory freshwater fish, seals, seabirds' eggs, seabirds' livers, human food stuffs (dairy products, vegetable oils and derivatives, fruit and vegetables) and also sheep (close to a source of release).	The levels refer to C_{10-20} chlorinated paraffins and it is not possible to distinguish the contribution from medium-chain chlorinated paraffins.
Greenpeace (1995)	Medium-chain chlorinated paraffins detected in mackerel (46 • g/kg lipid), fish oil (herring; 12 • g/kg lipid), margarine (28 • g/kg lipid), porpoise (3-7 • g/kg lipid), fin whale (144 • g/kg lipid), pork (11 • g/kg lipid), cows milk (16 • g/kg lipid) and mothers' milk (7 • g/kg lipid).	The analytical method determined the levels of C_{10-24} chlorinated paraffins. The C_{14-17} chlorinated paraffins were found to account for 6-29% of the total.
Thomas and Jones (2002)	Medium-chain chlorinated paraffins detected in one out of 22 samples of human breast milk at 61 • g/kg lipid. Also detected in a sample of cows milk at 63 ug/kg lipid and butter samples at 8.8-52 • g/kg lipid.	The analytical detection limit was relatively high (in the range 16-740 • g/kg lipid depending on the sample size).
Thomas *et al.* (2003)	Medium-chain chlorinated paraffins detected in twenty five samples of human breast milk at 6.2-320 • g/kg lipid. The median and 95th percentile levels were 21 and 127.5 • g/kg lipid respectively.	

Table 7 continued

Environment Agency Japan (1991).	Chlorinated paraffins not detected in 108 samples of fish from Japan.	The type of chlorinated paraffin analysed for was not specified. The detection limit was relatively high (0.5 mg/kg wet wt.).
Murray *et al.* (1987)	Medium-chain chlorinated paraffins detected in mussels downstream of a chlorinated paraffin manufacturing site at 170 • g/kg. Not detected in mussels upstream.	
Jansson *et al.* (1993)	Chlorinated paraffins of unspecified chain length detected in fish (570-1,600 • g/kg lipid), seal (130-280 • g/kg lipid), rabbit muscle (2,900 • g/kg lipid), reindeer suet (140 • g/kg lipid) and osprey muscle (530 • g/kg lipid).	The chain length of the chlorinated paraffins was not specified. The chlorinated paraffins had between 6 and 16 chlorine atoms per molecule.
Tomy *et al.* (1998)	Reports that medium-chain chlorinated paraffins were not detected in zebra muscle downstream of a chlorinated paraffin manufacturing site.	The detection limit was relatively high (3.5 mg/kg)
Bennie *et al.* (2000)	Medium-chain chlorinated paraffins detected in beluga whale blubber (fifteen females at 1.78-79 mg/kg wet wt. and ten males at 15.8-80 mg/kg wet wt.), beluga whale liver (three females at 0.55-20.9 mg/kg wet wt. and three males at 2.74-5.82 mg/kg wet wt.), carp (three individuals at 0.276-0.563 mg/kg wet wt.) and rainbow trout (ten individuals at 0.257-4.39 mg/kg wet wt.).	The authors indicated that the method used (involving low resolution mass spectrometry) may be more subject to interferences from other organohalogen compounds than some of the methods used in other analyses, therefore the results are uncertain.
Muir *et al.* (2002)	Samples from Lake Ontario a collected in 2001.The mean total levels of C_{14-17} chlorinated paraffins found in the various samples were 109 • g/kg wet weight (2,198 • g/kg lipid) in two samples of smelt, 108 • g/kg wet weight (~2,218 • g/kg lipid) in two samples of slimy sculpin, 35 • g/kg wet weight (1,285 • g/kg lipid) in two samples of alewife, 15 • g/kg wet weight (112 • g/kg lipid) in six samples of lake trout and 12 • g/kg wet weight (426 • g/kg lipid) in one sample of Dipoereia.	The levels of individual components were also reported. The concentration of the $C_{14}H_{25}Cl_5$ component was highest in Lake Trout (up to 1.32 • g/kg wet weight) which accounted for around 3% of the total medium-chain chlorinated paraffins present. In the same sample, $C_{14}H_{24}Cl_6$ accounted for around 9% of the total. The most abundant component in this species was $C_{14}H_{22}Cl_8$. In the other fish, the most abundant component was $C_{15}H_{24}Cl_8$. It should be noted however, that a lack of analytical standards, and the many possible congeners of chlorinated paraffins, makes analysis of specific components problematical and the exact assignment of the components found should be treated with caution.

Metabolism and toxico-kinetic data

A number of studies are available investigating the distribution and depuration of medium-chain chlorinated paraffins following exposure. These are summarised in EU (2005) for fish, birds and oligochaetes and in the human health risk assessment[12] for laboratory mammals. The available depuration half-life data are summarised in **Table 8**.

As can be seen from the available data, the elimination of medium-chain chlorinated paraffins from all the species studied is relatively slow.

Mammalian studies using radiolabelled medium-chain chlorinated paraffin (summarised in the human health assessment) have shown that absorption following oral exposure is significant (probably at least 50% of the administered dose; however the concentration

reached in the organism is generally lower than that in food). Following absorption in mammals there is an initial preferential distribution of the radiolabel to tissues of high metabolic turnover/cellular proliferation. Subsequently there is a re-distribution of radiolabel to fatty tissues where half-lives of up to 8 weeks have been determined for abdominal fat. Of special interest to this assessment is the recent study by CXR (2005b) that found that a steady state concentration in white adipose tissue was reached after approximately 13 weeks exposure via the diet. The elimination from this tissue was found to be biphasic with an initial half-life of 4 weeks followed by a much slower elimination.

Table 8 Reported depuration half-lives for medium-chain chlorinated paraffins

Organism	Chlorinated paraffin	Depuration half-life	Reference
Fish			
Bleak	C_{14-17}, 50 wt. Cl	Little reduction in body concentration over 7 days.	Bengtsson *et al.* (1979)
Rainbow trout	C_{14}, 42% wt. Cl	39 days (growth corrected).	Fisk *et al.* (1998a)
	C_{14}, 48% wt. Cl	46-53 days (growth corrected).	Fisk *et al.* (1998a)
	C_{14}, 53% wt. Cl	29-43 days (growth corrected).	Fisk *et al.* (1998a)
	C_{14}, 55.7% wt. Cl	41-58 days (growth corrected)	Fisk *et al.* (2000)
	C_{15}, 51% wt. Cl	15-17 days[15].	Thompson *et al.* (2000)
	C_{16}, 35% wt. Cl	37-50 days (growth corrected).	Fisk *et al.* (1996)
	C_{16}, 69% wt. Cl	58-77 days (growth corrected).	Fisk *et al.* (1996)
Oligochaete			
Lumbriculus variegatus	C_{16}, 35% wt. Cl	33 days.	Fisk *et al.* (1998b)
	C_{16}, 69% wt. Cl	30 days.	Fisk *et al.* (1998b)
Mammals			
Rat	C_{14-17}, 52% wt. Cl	8 weeks (abdominal fat).	Birtley *et al.* (1980)
	C_{15}, 52% wt. Cl	2-5 days (liver, kidneys) 2 weeks (white adipose)	CXR, 2005a
	C_{14-17}, 52% wt. Cl	Biphasic depuration from white adipose tissue. Initial half-life 4 weeks followed by much slower elimination.	CXR, 2005b

For fish, elimination half-lives of up to 77 days (11 weeks) have been determined for medium-chain chlorinated paraffins. Similarly half-lives of up to 33 days (~5 weeks) have been determined in oligochaetes.

The long elimination half-life means that significant concentrations of the substance may remain within an organism for several months, possibly years, after cessation of emissions. Although this in itself is not sufficient in determining whether or not medium-chain chlorinated paraffins meet the B-criterion, a long elimination half-life is a characteristic of bioaccumulative substances.

Other considerations

A further consideration is that studies carried out to investigate the mechanism of the internal haemorrhages that have been seen to develop post-natally in rat pups have demonstrated that oral doses of medium-chain chlorinated paraffins in the parent can lead to exposure of young via breast milk. These studies are discussed in detail in the human health risk assessment. Although this issue is related mainly to the T-criterion (these effects lead to a classification of R64 for medium-chain chlorinated paraffins) it is also relevant to consider them here as monitoring data are also available to show that medium-chain chlorinated paraffins have been found at low levels in humans. Therefore exposure of humans via a relevant route has been demonstrated in the general population. The effects on pups exposed through breast milk are, however, addressed in the standard risk assessment for secondary poisoning and so are not sufficient on their own to consider the substance as meeting the B-criterion.

Overall conclusion in relation to bioaccumulation

Overall, the conclusions for medium-chain chlorinated paraffins in relation to the B or vB criteria are not unambiguous. The currently available BCF data in fish for medium-chain chlorinated paraffins are well below the cut-off for B, but there is evidence that uptake from food as well as water is important in the overall accumulation potential for medium-chain chlorinated paraffins. When the accumulation seen in feeding studies is taken into account, this could lead to an overall bioaccumulation factor (BAF) >2,000 l/kg for some medium-chain chlorinated paraffins. In addition to aquatic organisms, uptake into terrestrial species (e.g. earthworms) has also been demonstrated.

It should be noted that many of the laboratory studies available are based on ^{14}C-measurements using radiolabelled medium-chain chlorinated paraffins, and some of these studies indicate that metabolism is occurring in the organisms. Thus, although radioactivity was found to be taken up into the organism, the concentrations (and hence degree of accumulation) found in the organism do not necessarily represent those of the parent compound.

In addition to this a number of other factors need to be considered in relation to the overall bioaccumulation potential for medium-chain chlorinated paraffins. These are summarised below.

- Medium-chain chlorinated paraffins are complex substances. The bioaccumulation potential of individual components of the substance would be expected to vary with both carbon chain length and chlorine content. It is therefore possible that at least some of the components present within a technical product could have a fish BCF value higher than has currently been measured. In particular, based on predictions of the fish BCF, the C_{14} 45% wt. Cl and C_{14} 52% wt. Cl components of the commercial products may have fish BCFs >2,000 l/kg, however there is a large uncertainty in this.
- Although very limited, the available monitoring data have show medium-chain chlorinated paraffins to be present in marine fish and marine mammals (top predators such as porpoise and fin whale).
- Medium-chain chlorinated paraffins (or metabolites of medium-chain chlorinated paraffins) have been demonstrated to have relatively long elimination half-lives in a number of species including fish, oligochaetes and laboratory mammals.
- Medium-chain chlorinated paraffins have been demonstrated to cause effects in young rats exposed via breast milk, and have been determined to be present (at low levels) in breast milk in the general population (it should be noted that this is addressed in the

human health risk assessment where it was concluded that no risk currently exists from this source for humans). However, it is therefore possible that medium-chain chlorinated paraffins may also be present in mothers' milk of mammals in the wild.

Therefore, although the definitive criteria for both a bioaccumulative substance or a very bioaccumulative substance are not met, when the whole data set is considered it can tentatively be concluded that the actual bioaccumulation potential of medium-chain chlorinated paraffins could be higher than expected based on the available fish BCF data alone, and so they (or some components of the technical products) could be considered as potentially bioaccumulative in relation to the PBT assessment. It should, however, be noted that the available database is relatively limited and considerable uncertainty exists over the actual bioaccumulation potential. Further work is needed in order to provide a more solid conclusion for this endpoint.

It should also be taken into account that uptake via the food is already accounted for in the assessment of secondary poisoning for the fish food chain, and this does not lead to the identification of risks from production and most uses of medium-chain chlorinated paraffins (only one scenario results in a possible risk for the fish food chain). Risks are, however, identified for several uses of medium-chain chlorinated paraffins for the earthworm food chain.

3.3 TOXICITY

The available ecotoxicity data for medium-chain chlorinated paraffins are summarised in the published risk assessment report (EU, 2005). The available mammalian toxicity data is reviewed in the February 2006 draft version of the human health assessment.

A substance is considered to be toxic if it has a chronic NOEC <0.01 mg/l. The most reliable NOEC for short-chain chlorinated paraffins is 0.01 mg/l for *Daphnia magna* from a 21 day study using a C_{14-17}, 52% wt. chlorinated paraffin. This value sits right on the cut-off for the toxicity criterion. As discussed in EU (2005) there are a number of other data for *Daphnia magna* close to (and in one case just below) this value, and effects have been seen with Daphnia at concentrations <0.01 mg/l in an acute study (i.e. a 48h-EC_{50} of 0.0059 mg/l was determined). Taken together it is considered that the substance meets the T-criterion based on its aquatic toxicity.

In addition, medium-chain chlorinated paraffins have been proposed to be classified as R64 – May cause harm to breast-fed babies. According to the TGD, substances classified as R64 should be considered to fulfil the toxicity criterion where the assignment of the R-phrase is as a result of one or two generation studies in animals which indicate the presence of adverse effects on the offspring due to transfer in the milk. For medium-chain chlorinated paraffins R64 is being proposed on the basis of effects seen post-natally in rat pups (internal haemorrhaging and death) that were thought to result, at least in part, from transfer of medium-chain chlorinated paraffins or metabolites through breast milk.

Overall, based on the NOEC of 0.01 mg/l found in *Daphnia*, medium-chain chlorinated paraffins can be considered to be toxic (T). This would be supported by the classification as R64 if this is agreed.

The available toxicity data for medium-chain chlorinated paraffins have generally been obtained using commercial products. There is little information on how the toxicity of medium-chain chlorinated paraffins varies with both chlorine content and carbon chain length. This is an important consideration for the PBT assessment of medium-chain chlorinated paraffins as the assessment for the B-criteria (Section 3.2) indicates that the C_{14} components with chlorine contents in the range 45-52% by weight may have BCFs in fish >2,000 l/kg. Therefore it needs to be considered if these components of the commercial products can be considered to meet the T-criteria themselves. In this respect, it is informative to consider the available aquatic toxicity data for both short-chain (i.e. $C_{10\text{-}13}$) chlorinated paraffins and medium-chain chlorinated paraffins. The most relevant data are the 21-day NOEC values for *Daphnia magna* of 0.010 mg/l for medium-chain chlorinated paraffins obtained in a test using a $C_{14\text{-}17}$, 52% wt. Cl chlorinated paraffin (EU, 2005), and 0.005 mg/l for short-chain chlorinated paraffins obtained in a test using a $C_{10\text{-}13}$, 58% wt. Cl chlorinated paraffins (EU, 2000). Although there are some differences in the chlorine contents between the medium-chain and short-chain chlorinated paraffins tested in these studies, it can be seen that as both $C_{14\text{-}17}$, 52% wt. Cl products and $C_{10\text{-}13}$, 58% wt. Cl products meet the criterion for T, it is highly likely that the C_{14}-components with chlorine contents up to 52% by weight will also meet the T-criterion. Therefore the C_{14}-components of the commercial medium-chain chlorinated paraffin products can be considered to be toxic (T).

3.4 OTHER CONSIDERATIONS

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a global treaty to protect human health and the environment. The screening criteria for consideration of a chemical as a POP are given in Annex D of the convention text. One of the screening criteria used in relation to bioaccumulation within the Convention is a bioaccumulation factor >5,000 l/kg and it is unlikely that medium-chain chlorinated paraffins would meet this criterion based on the available data.

With regards to the screening criteria for long range transport, the published risk assessment (EU, 2005) concluded that the potential for long-range transport for medium-chain chlorinated paraffins is probably less than that for the related short-chain chlorinated paraffins, but that it also needed to be considered that medium-chain chlorinated paraffins are complex, multi-component substances, with the components exhibiting a range of physico-chemical properties. Some of the components of the commercial products may, therefore, have properties that may mean that long-range transport via the atmosphere is a possibility (for example see Environment Canada (2004)). It should also be noted that data are generally lacking on the occurrence (or not) of medium-chain chlorinated paraffins in the Arctic in particular, and remote regions in general, and therefore there is little or no direct evidence that long-range transport is actually occurring for medium-chain chlorinated paraffins.

Overall, based on the currently available data set it is considered unlikely that medium-chain chlorinated paraffins would meet the Stockholm Convention screening criteria, although some long range transport via the atmosphere cannot be totally ruled out.

3.5 POTENTIAL SOURCES AND PATHWAYS TO THE MARINE ENVIRONMENT

As well as the local sources of release associated with production and direct use, medium-chain chlorinated paraffins can also be emitted to air (due to volatilisation) and water (due to leaching) from products over extended periods of time (i.e. over the lifetime of the product). The estimation of all of these releases is described in the original risk assessment, and they are subject to uncertainties. Although it is not possible to quantify how much of these releases will enter the marine environment, it is considered that both the local emissions and diffuse emissions provide potential pathways into the marine environment. For example, leaching losses could eventually end up in surface water that enters the marine environment and the substance present in the atmosphere could be transported to marine environments and subsequently rained out to marine water

4 SUMMARY OF OVERALL CHANGES TO THE CONCLUSIONS FOR MEDIUM-CHAIN CHLORINATED PARAFFINS

This update considers three main aspects of the environmental risk assessment for medium-chain chlorinated paraffins that was published in 2005.

4.1 SECONDARY POISONING

A revised $PNEC_{oral}$ of 10 mg/kg food has been derived using new data on the toxicity of medium-chain chlorinated paraffins that have become available since the original environmental risk assessment was published. This has significantly affected the conclusions drawn for secondary poisoning via both the fish and earthworm food chains.

For the fish food chain, the original risk assessment concluded that production and all uses other than formulation and use of sealants, and domestic application of paints, presented a potential risk from secondary poisoning. These conclusions were based on a $PNEC_{oral}$ of 0.17 mg/kg food. Using the new $PNEC_{oral}$ of 10 mg/kg food, all scenarios considered in the risk assessment, with the exception of use in leather fat liquors – processing of wet blue, lead to a PEC/PNEC <1, and hence it is now concluded that the risks of secondary poisoning from production and most uses of medium-chain chlorinated paraffins are low for the fish food chain.

For the earthworm food chain, the original risk assessment concluded that the risk from secondary poisoning was low from production sites (where no sewage sludge is applied to land), formulation and use of sealants, and domestic application of paints. All other uses of medium-chain chlorinated paraffins were found to present a potential risk from secondary poisoning for the earthworm food chain. Again these conclusions were reached using a $PNEC_{oral}$ of 0.17 mg/kg food. Using the new $PNEC_{oral}$ of 10 mg/kg food, several other scenarios now lead to PEC/PNEC <1, but potential risks are still identified for fifteen of the thirty two scenarios considered in the assessment.

Result

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

This applies to the assessment of secondary poisoning via the fish food chain from production and all uses of medium-chain chlorinated paraffins except for use in leather fat liquors – processing of wet blue. This also applies to the assessment of secondary poisoning via the earthworm food chain for the following scenarios:

- Production sites (where sewage sludge is not applied to agricultural land).
- Use in PVC – plastisol coating – compounding sites.
- Use in PVC – plastisol coating – conversion sites.
- Use in PVC – extrusion/other – compounding sites using open or closed systems.
- Use in plastics/rubber – compounding sites.
- Use in plastics/rubber – conversion sites.
- Use in sealants – formulation and use.
- Use in paints – formulation sites.

- Use in paints – industrial application and domestic application.
- Use in metal cutting/working fluids – use in emulsifiable fluids.
- Use in leather fat liquors – formulation sites.
- Use in carbonless copy paper – paper recycling.

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

This applies to the following uses for the earthworm food chain:

- Use in PVC – plastisol coating – combined compounding/conversion sites*.
- Use in PVC – extrusion/other – compounding sites using partially open systems.
- Use in PVC – extrusion/other – conversion sites and combined compounding/conversion sites.
- Use in plastics/rubber – combined compounding/conversion sites*.
- Use in metal cutting/working fluids – formulation sites.
- Use in metal cutting/working fluids – use in oil-based fluids at large and small sites.
- Use in metal cutting/working fluids – use in emulsifiable fluids – intermittent release.
- Use in leather fat liquors – processing of raw hides and wet blue.

It should be noted that for the two scenarios for the earthworm food chain marked as * above, the risk identified depends on whether EUSES 1 or EUSES 2.0.3 is used for the calculation. However it should be born in mind that PEC/PNEC ratios >1 were identified for these two scenarios in EU (2005) for the sediment compartment and so risk management is already considered to be necessary for them. Therefore it is recommended that this risk management should also consider the possible risk of secondary poisoning through the earthworm food chain identified here.

In addition, this conclusion also applies to fish food chain for use in leather fat liquors – processing of wet blue. A PEC/PNEC ratio >1 is obtained for this scenario when a BMF of 3 is considered but a PEC/PNEC ratio <1 is obtained when a BMF of 1 is considered. This finding is independent of whether EUSES 1 or EUSES 2.0.3 is used. Although there is, therefore, some uncertainty over whether or not this scenario actually presents a risk of secondary poisoning via the fish food chain, it should be noted that PEC/PNEC ratios >1 for this scenario have already been identified for surface water, sediment and soil in EU (2005) and so risk management is already considered to be necessary for this use. Therefore it is recommended that this risk management should also consider the possible risk of secondary poisoning through the fish food chain identified here.

4.2 MAN EXPOSED VIA THE ENVIRONMENT

A new study investigating the uptake into carrot roots from soil is available. This showed that the uptake of medium-chain chlorinated paraffins into root crops is substantially lower than is predicted using the default methods in the Technical Guidance Document. This new value has been used to revise the calculations for man exposed via environmental routes and has resulted in substantially lower estimates for the daily human exposure via environmental routes. These data have been discussed by human health experts at TCNES and a conclusion ii) was agreed.

Result

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

4.3 PBT ASSESSMENT

It is concluded that the substance meets the T-criterion and meets the screening criterion for P or vP. However there are no data from simulation tests that can be used to unambiguously confirm that the substance is a P or vP substance. With regards to the B-criterion, the highest BCF available for a medium-chain chlorinated paraffin in fish is 1,087 l/kg and so, on this basis, the substance does not meet the specific criteria for either B or vB laid down in the Technical Guidance Document. However, there are a number of other factors that need to be considered in this respect and the balance of evidence is that the substance meets the screening criteria for bioaccumulation. In particular, uptake via food appears to be important for medium-chain chlorinated paraffins (possibly resulting in higher concentrations in organisms than may be expected based on the BCF alone), and, based on modelling and extrapolation, it is also possible that the actual BCF for some components of the technical medium-chain chlorinated paraffin products could be >2,000 l/kg (these same components are also considered to meet the T-criterion and the screening criterion for P or vP).

Overall, although medium-chain chlorinated paraffins are not shown to meet the specific criteria for a PBT substance, there are other data available to suggest that medium-chain chlorinated paraffins (or components of medium-chain chlorinated paraffins) may have the properties of a PBT substance. There are uncertainties over both the persistence and bioaccumulation potential for medium-chain chlorinated paraffins in particular, and the available database of reliable laboratory studies and field monitoring data is fairly limited. Therefore further information is needed in order to confirm whether or not the substance should be considered as a PBT substance or not.

Result

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

A simulation test for biodegradability could be performed to determine the half-life in the marine environment in order to confirm whether or not the substance meets the actual criteria for persistence. However it is considered that such a test would be technically very difficult to carry out, and may not even then be sufficient to show definitively that medium-chain chlorinated paraffins are not persistent. Such a test has recently been completed for the related short-chain chlorinated paraffins. This test confirmed that short-chain chlorinated paraffins are persistent, but read-across of these results to medium-chain chlorinated paraffins is not straight forward as the chlorine content of the short-chain chlorinated paraffins tested was much higher (around 65% by weight) than typically found in the commercial medium-chain chlorinated paraffins (typically around 45-52% by weight) and there is some evidence that the rate of biodegradation of medium-chain chlorinated paraffins may increase with decreasing chlorine content. However, the mineralisation half-lives found with short-chain chlorinated paraffins were sufficiently long (around1,630-1,790 days in freshwater sediment and 335-680 days in marine sediment) that it is considered likely that medium-chain chlorinated paraffins would also be persistent within the meaning of the PBT assessment and that it is unlikely that further testing with medium-chain chlorinated paraffins themselves would change this interpretation.

The assessment of this substance against the B- or vB criteria is not straight forward. The available evidence suggests that some components of the technical products meet the screening criteria for B. It should be noted that the available database is relatively limited and extrapolation and modelling have been used in order to assess the likely bioaccumulation potential of some components. Therefore uncertainty exists over the actual bioaccumulation potential. Further work is needed order to provide a more solid conclusion for this endpoint. As there are a number of issues that need to be considered, a tiered approach is recommended. This should include the following.

1. Further information to assess the bioaccumulation potential of relevant components of medium-chain chlorinated paraffins, e.g. a further fish bioconcentration study using a C_{14}-chain length chlorinated paraffin of low-moderate chlorine content (e.g. 45% wt. Cl and/or 52% wt. Cl). The available evidence suggests that the accumulation potential of medium-chain chlorinated paraffins probably decreases with increasing carbon chain length and degree of chlorination (although some predictions indicate an opposite trend with chlorine content). The available fish BCF of 1,087 l/kg for medium-chain chlorinated paraffins was determined with a C_{15}, 51% wt. Cl substance and so it is possible that the fish BCF for a C_{14} chlorinated paraffin may be higher than this value. Estimates suggest that a BCF of >2,000 l/kg could be expected for a C_{14}, 45% wt. Cl and C_{14}, 52% wt. Cl substance.

The need for further information should then be reviewed based on the outcome of this testing. It must be recognised that the bioaccumulation potential of medium-chain chlorinated paraffins may remain uncertain even after the above testing. In such circumstances it may be necessary to consider the need to generate further data. These data could include the following:

2. A further fish feeding study to obtain a reliable BMF value. However, it should be noted that there is, as yet, no agreed methodology for carrying out such a study, and no agreed way to take account of the results of such a study in the risk assessment. Several fish feeding studies are already available for medium-chain chlorinated paraffins, and the problems with interpreting these data are outlined in EU (2005). It is thought that any new fish feeding study would be subject to similar problems and uncertainties until an agreed method for carrying out and interpreting such studies is available.
3. Monitoring of biota. The available monitoring data for medium-chain chlorinated paraffins in biota are generally limited. Medium-chain chlorinated paraffins are complex substances and this provides serious challenges for the analysis of the substances in environmental media (the problems with the analysis are discussed in EU (2005)). Many of the methods used in the past did not unambiguously determine medium-chain chlorinated paraffins (e.g. interference from short-chain chlorinated paraffins in particular could have occurred in many of these studies), but more recent studies have confirmed that medium-chain chlorinated paraffins are present in human breast milk, cows milk, and in some cases marine fish and marine mammals. The number of reliable data available, particularly for fish and marine mammals, is currently very limited and so it could be considered to carry out further monitoring of such organisms to verify whether or not medium-chain chlorinated paraffins show a wide-spread occurrence in such biota, and possibly provide some information on the trends in these levels. This would provide useful information in relation to the conclusions on bioaccumulation potential for the PBT assessment, and also possibly

the long-range transport potential. However, it should be stressed that the analysis of medium-chain chlorinated paraffins is not straight forward in such samples.

When considering the need for further testing it should be born in mind that the substance has already been detected in marine biota (including marine mammals), although the number of reliable monitoring studies is very limited. The trends in levels are unknown, and they may be due (in part at least) to a local source or uses that take place in other regions, or uses that are now better controlled in the EU. It is therefore possible that levels may decrease if the current level of emission does not increase. However, the possibility of long range transport can not totally be excluded. Whilst it is not possible to say whether or not on a scientific basis there is a current or future risk to the environment, in light of:

- data indicating presence in marine biota;
- the apparent persistence of the substance (i.e. absence of significant degradation in laboratory screening tests);
- the time it would take to gather the information; and
- the fact that it could be difficult to reduce exposure if the additional information confirmed a risk;

consideration could be given at a policy level to the need to investigate precautionary risk management options now in the absence of measured environmental half-life data and confirmatory bioaccumulation data, to reduce the inputs to water (and soil from the application of sewage sludge), including from "waste remaining in the environment".

In this respect it should also be taken into account that an assessment of secondary poisoning for medium-chain chlorinated paraffins has already been carried out, and this leads to the identification of risks from several uses of medium-chain chlorinated paraffins for the earthworm food chain, but possible risks are identified only for one scenario for the fish food chain. A key consideration is therefore whether or not there is any added concern for medium-chain chlorinated paraffins over and above that already identified based on a PEC/PNEC approach[19], given that the PEC/PNEC approach already considers that uptake into aquatic organisms may occur from both exposure via water and via food. Such considerations could include uncertainties around the BCF values for all components of the technical products, and also the very long apparent depuration half-life that has been found recently in mammalian systems. These may introduce uncertainties into the risk assessment of secondary poisoning when extrapolating from the results of laboratory tests to PECs and PNECs related to exposure over an organism's lifetime

[19] It should also be born in mind that the original risk assessment also identified risks to sediment from many uses of medium-chain chlorinated paraffins (and risks to surface water and soil were also identified from some scenarios) and any risk reduction measures implemented as a result of these conclusions for water, sediment and soil will also have an impact on the amount of medium-chain chlorinated paraffins that would be released to environment in the future.

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APPENDIX A OTHER METHODS FOR ESTIMATING THE BCF

A key part of the PBT assessment of medium-chain chlorinated paraffins is whether or not certain components of the commercial products could have fish BCF values above 2,000 l/kg. Estimations for this are given in the main part of the PBT assessment, but it needs to be recognised that there are considerable uncertainties in the estimation methods used (both in terms of prediction of the log Kow value and prediction of the BCF value). This Appendix considers other ways of estimating the BCF for medium chain chlorinated paraffins, and investigates the effects of the uncertainty in the log Kow value on the predictions. This latter point is a relevant consideration in terms of the overall testing strategy in order to determine whether it would be useful to determine a reliable log Kow value for certain components of the medium-chain chlorinated paraffin products in order to allow more reliable estimates of the BCF to be made as a first stage.

Other methods for estimating the BCF

The USEPA BCFWINv2.15 program[20] uses the following equations to estimate the fish BCF value from log Kow.

For log Kow in the range 1.0 to 7.0

$$\log BCF = 0.77 \times \log Kow - 0.70 + \text{structural correction factor}$$

For log Kow >7.0

$$\log BCF = -1.37 \times \log Kow + 14.4 + \text{structural correction factor}$$

For log Kow >9

$$\log BCF = 0.50$$

The following structural correction factors are applied for substances with alkyl chains containing 8 or more $–CH_2-$ groups.

Structural correction factor	-1.00 (for log Kow of 4-6)
	-1.5 (for log Kow of 6-10)

The BCFs estimated using this method are shown in Table A1. The BCFs estimated using the TGD methodology are also shown for comparison. Both the estimates obtained directly from the methods, and those obtained by normalising the predicted BCF to the known BCF of 1,087 l/kg for a C_{15}, 51% wt. Cl substance are shown.

[20] BCFWINv2.15 is available as part of the USEPA EPIWINv3.12 suite. The estimation methodology is described in Meylan et al. (1999).

Table A1 Estimated log Kow and BCF for a series of hypothetical chlorinated paraffin structures

Formula	Molecular weight (g/mol)	Chlorine content (% by weight)		SMILES notation used for estimating log Kow	Log Kow estimate (EPIWIN v3.12)	Predicted BCF (l/kg)		Predicted BCF scaled to known BCF for MCCPs (l/kg)	
		Actual	Group			BCFWINv2.15	TGD method	BCFWINv2.15	TGD method
$C_{10}H_{19}Cl_3$	245.5	43.4	45.0	CC(Cl)CC(Cl)CCC(Cl)CCC	5.79	5,772	16,653	1,045,694	2,519
$C_{11}H_{20}Cl_4$	294.0	48.3	45.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	6.47	18,990	43,214	3,440,355	6,537
$C_{12}H_{22}Cl_4$	308.0	46.1	45.0	CC(Cl)CC(Cl)CC(Cl)CCCC(Cl)CC	6.96	45,350	45,928	8,215,908	6,947
$C_{13}H_{24}Cl_4$	322.0	44.1	45.0	CC(Cl)CC(Cl)CC(Cl)CCCCC(Cl)CC	7.45	497	39,129	90,040	5,919
$C_{14}H_{26}Cl_4$	336.0	42.3	45.0	C(Cl)CCCCC(Cl)CCCC(Cl)CC(Cl)CC	8.01	84	24,853	15,218	3,759
$C_{15}H_{27}Cl_5$	384.5	46.2	45.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CCCC(Cl)CC	8.61	13	11,091	2,355	1,678
$C_{16}H_{29}Cl_5$	398.5	44.5	45.0	CC(Cl)CC(Cl)CCC(Cl)CCC(Cl)CCC(Cl)CCC	9.10	3	4,487	544	679
$C_{17}H_{31}Cl_5$	412.5	43.0	45.0	C(Cl)CC(Cl)CC(Cl)CCCC(Cl)CCCC(Cl)CCCC	9.67	3	1,186	544	179
$C_{18}H_{32}Cl_6$	461.0	46.2	45.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CCC(Cl)CCC(Cl)CCC	10.26	3	218	544	33
$C_{10}H_{18}Cl_4$	280.0	50.7	52.0	CC(Cl)CC(Cl)C(Cl)CC(Cl)CCC	5.97	7,949	23,686	1,440,094	3,583
$C_{11}H_{19}Cl_5$	328.5	54.0	52.0	C(Cl)CC(Cl)CCC(Cl)CC(Cl)CC(Cl)C	6.72	29,790	45,827	5,396,955	6,932
$C_{12}H_{21}Cl_5$	342.5	51.8	52.0	CC(Cl)C(Cl)CC(Cl)CCC(Cl)CCC(Cl)C	7.14	41,900	44,430	7,590,883	6,721
$C_{13}H_{22}Cl_6$	391.0	54.5	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)C	7.88	126	28,335	22,827	4,286
$C_{14}H_{24}Cl_6$	405.0	52.6	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CC	8.37	27	15,937	4,892	2,411
$C_{15}H_{26}Cl_6$	419.0	50.8	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CCC	8.86	6	7,186	1,087	1,087
$C_{16}H_{27}Cl_7$	467.5	53.2	52.0	CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CCC(	9.46	3	2,005	544	303

Formula	Molecular weight (g/mol)	Chlorine content (% by weight)		SMILES notation used for estimating log Kow	Log Kow estimate (EPIWIN v3.12)	Predicted BCF (l/kg)		Predicted BCF scaled to known BCF for MCCPs (l/kg)	
		Actual	Group			BCFWINv2.15	TGD method	BCFWINv2.15	TGD method
				Cl)C(Cl)C					
$C_{17}H_{29}Cl_7$	481.5	51.6	52.0	CC(Cl)CC(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(Cl)CC(Cl)CC	9.95	3	553	544	84
$C_{18}H_{31}Cl_7$	495.5	50.2	52.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CCCC(Cl)CCC	10.52	3	93	544	14
$C_{10}H_{16}Cl_6$	349.0	61.0	60.0	CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)	6.41	17,170	42,245	3,110,632	6,390
$C_{11}H_{17}Cl_7$	397.5	62.5	60.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)	7.15	39,720	44,310	7,195,940	6,703
$C_{12}H_{19}Cl_7$	411.5	60.4	60.0	C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)CC	7.57	10,640	36,376	1,927,613	5,503
$C_{13}H_{20}Cl_8$	460.0	61.7	60.0	C(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)	8.32	32	17,073	5,797	2,583
$C_{14}H_{22}Cl_8$	474.0	59.9	60.0	C(Cl)CC(Cl)C(Cl)C(Cl)CC(Cl)CCC(Cl)CC(Cl)C(Cl)C	8.73	272	9,070	49,277	1,372
$C_{15}H_{23}Cl_9$	522.5	61.1	60.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(Cl)C(Cl)CC(Cl)CC(Cl)C	9.41	33	2,258	5,979	342
$C_{16}H_{25}Cl_9$	536.5	59.6	60.0	C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C	9.89	3	655	544	99
$C_{17}H_{26}Cl_{10}$	585.0	60.7	60.0	C(Cl)CC(Cl)C(Cl)C(Cl)C(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)CC	10.57	3	79	544	12
$C_{18}H_{27}Cl_{11}$	633.5	61.6	60.0	C(Cl)CC(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)CC(Cl)C(Cl)C(Cl)CC(Cl)C(Cl)C	11.24	3	6	544	1

Effect of log Kow on the predicted BCF

The predicted BCFs in Table A1 were all obtained using values of the log Kow estimated by the EPIWIN program. As the methods used to predict the BCF depend on the log Kow value, any errors and uncertainty in the log Kow value will be translated into errors/uncertainty in the predicted BCF. In the assessment against the B-criterion in the main report, some of this uncertainty was addressed by normalising the predicted BCFs to the known BCF for a C_{15}, 51% wt. Cl substance.

As well as predicted values, some experimental data are available on the log Kow for chlorinated paraffins. The experimental data available for specific chain-lengths and chlorine contents has been collated by Tomy *et al.* (1998) and the data are summarised in Table A2.

Table A2 Reported depuration half-lives for medium-chain chlorinated paraffins

Substance	Chlorine content	Log Kow	Reference
$C_{10}H_{19}Cl_3$	43%	5.85[a]	Sijm and Sinnige (1995)
$C_{10}H_{18}Cl_4$	50%	5.93[a]	Sijm and Sinnige (1995)
$C_{10}H_{17}Cl_5$	56%	6.04-6.20[a]	Sijm and Sinnige (1995)
$C_{11}H_{20}Cl_4$	48%	5.93[a]	Sijm and Sinnige (1995)
$C_{11}H_{19}Cl_5$	54%	6.20-6.40[a]	Sijm and Sinnige (1995)
$C_{11}H_{18}Cl_6$	58%	6.40[a]	Sijm and Sinnige (1995)
$C_{12}H_{20}Cl_6$	56%	6.40-6.77[a]	Sijm and Sinnige (1995)
		6.2[b]	Fisk *et al.* (1998)
$C_{12}H_{19}Cl_7$	59%	7.00[a]	Sijm and Sinnige (1995)
$C_{12}H_{18}Cl_8$	63%	7.00[a]	Sijm and Sinnige (1995)
$C_{12}H_{16}Cl_{10}$	69%	6.6[b]	Fisk *et al.* (1998)
$C_{13}H_{23}Cl_5$	49%	6.61[a]	Sijm and Sinnige (1995)
$C_{13}H_{22}Cl_6$	53%	6.77-7.00[a]	Sijm and Sinnige (1995)
$C_{13}H_{21}Cl_7$	58%	7.14[a]	Sijm and Sinnige (1995)
$C_{16}H_{31}Cl_3$	32%	7.2[b]	Fisk *et al.* (1998)
$C_{16}H_{21}Cl_{13}$	69%	7.4[b]	Fisk *et al.* (1998)

Note: a) Values determined using a "slow-stirring" method.
b) Values determined using an HPLC method.

Based on their own data, Sijm and Sinnige (1995) developed the following relationship relating log Kow to the total number of chlorine and carbon atoms (N_{tot}).

$$\log Kow = -0.386 + 0.60 \times N_{tot} - 0.0113 \times N_{tot}^2 \qquad r^2 = 0.992$$

Using this equation, the log Kow values for the example structures considered in Table A1 can be estimated. The resulting log Kow values are shown in Table A3, along with the BCFs predicted using these log Kow values. It should be noted that the equation derived by Sijm and Sinnige (1995) was derived using data for C_{10} to C_{13} chlorinated paraffins and so the reliability of the method for medium-chain chlorinated paraffins is not clear.

Table A3 Estimated log Kow and BCF for a series of hypothetical chlorinated paraffin structures

Formula	Molecular weight (g/mol)	Chlorine content (% by weight)		Log Kow estimate (Sijm and Sinnige (1995) method)	Predicted BCF (l/kg)		Predicted BCF scaled to known BCF for MCCPs (l/kg)	
		Actual	Group		BCFWINv2.15	TGD method	BCFWINv2.15	TGD method
$C_{10}H_{19}Cl_3$	245.5	43.4	45.0	5.50	3,428	9,520	3,771	240
$C_{11}H_{20}Cl_4$	294.0	48.3	45.0	6.07	9,417	34,937	10,361	879
$C_{12}H_{22}Cl_4$	308.0	46.1	45.0	6.32	14,670	40,604	16,140	1,022
$C_{13}H_{24}Cl_4$	322.0	44.1	45.0	6.55	697	44,289	767	1,114
$C_{14}H_{26}Cl_4$	336.0	42.3	45.0	6.75	994	45,984	1,094	1,157
$C_{15}H_{27}Cl_5$	384.5	46.2	45.0	7.09	1,537	44,936	1,691	1,131
$C_{16}H_{29}Cl_5$	398.5	44.5	45.0	7.23	988	43,203	1,087	1,087
$C_{17}H_{31}Cl_5$	412.5	43.0	45.0	7.34	699	41,261	769	1,038
$C_{18}H_{32}Cl_6$	461.0	46.2	45.0	7.51	409	37,900	450	954
$C_{10}H_{18}Cl_4$	280.0	50.7	52.0	5.80	5,834	16,956	6,419	427
$C_{11}H_{19}Cl_5$	328.5	54.0	52.0	6.32	14,670	40,604	16,140	1,022
$C_{12}H_{21}Cl_5$	342.5	51.8	52.0	6.55	22,050	44,289	24,259	1,114
$C_{13}H_{22}Cl_6$	391.0	54.5	52.0	6.93	1,368	46,033	1,505	1,158
$C_{14}H_{24}Cl_6$	405.0	52.6	52.0	7.09	1,537	44,936	1,691	1,131
$C_{15}H_{26}Cl_6$	419.0	50.8	52.0	7.23	988	43,203	1,087	1,087
$C_{16}H_{27}Cl_7$	467.5	53.2	52.0	7.44	510	39,423	561	992
$C_{17}H_{29}Cl_7$	481.5	51.6	52.0	7.51	409	37,900	450	954
$C_{18}H_{31}Cl_7$	495.5	50.2	52.0	7.55	360	36,820	396	926

Table A3 continued

$C_{10}H_{16}Cl_6$	349.0	61.0	60.0	6.32	14,670	40,604	16,140	1,022
$C_{11}H_{17}Cl_7$	397.5	62.5	60.0	6.75	31,440	45,984	34,590	1,157
$C_{12}H_{19}Cl_7$	411.5	60.4	60.0	6.93	43,260	46,033	47,595	1,158
$C_{13}H_{20}Cl_8$	460.0	61.7	60.0	7.23	988	43,203	1,087	1,087
$C_{14}H_{22}Cl_8$	474.0	59.9	60.0	7.34	22,090	41,261	24,303	1,038
$C_{15}H_{23}Cl_9$	522.5	61.1	60.0	7.51	12,920	37,900	14,215	954
$C_{16}H_{25}Cl_9$	536.5	59.6	60.0	7.55	360	36,820	396	926
$C_{17}H_{26}Cl_{10}$	585.0	60.7	60.0	7.58	328	36,224	361	911
$C_{18}H_{27}Cl_{11}$	633.5	61.6	60.0	7.51	409	37,774	450	950

Discussion of the BCF estimates

As can be seen from Table A1 and Table A3, when the BCFWIN method is used, the predicted BCF is broadly similar to that obtained using the TGD methodology for substances with a log Kow up to 7 and with less than eight $–CH_2-$ groups in the alkyl chain. This corresponds to chlorinated paraffins with chain lengths mainly in the C_{10}-C_{12} range. For longer chain lengths, the predictions using the BCFWIN are generally much lower than those obtained using the TGD method.

These differences in the predictions between the BCFWIN method and the TGD method are particularly important when considering the predictions for medium-chain chlorinated paraffins. This difference probably relates to the fact that the BCFWIN method applies a structural correction factor of either -1 or -1.5 log units to the predicted log BCF for structures where there are eight or more $–CH_2-$ groups (it should be noted that such corrections are applied regardless of whether the eight or more $–CH_2-$ units are consecutive, or whether there are just eight or more $–CH_2-$ groups anywhere in the carbon chain). Such a correction is not applied in the TGD method. Therefore it is important to consider whether such a correction is applicable to the medium-chain chlorinated paraffins.

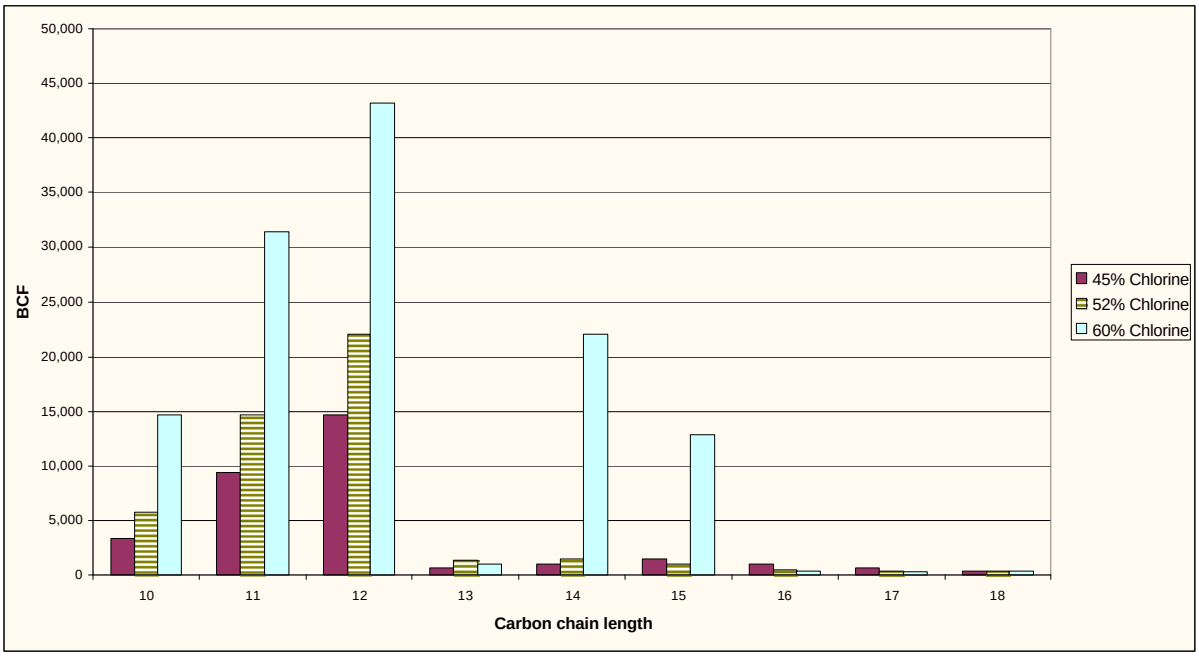
There are two data points available with which to compare the various estimates for the BCF. These are the measured BCFs of 1,087 l/kg for a C_{15}, 51% Cl wt. substance and 7,816 l/kg for a C_{11}, 58% wt. Cl substance. The various estimates for these two substances (approximated to $C_{15}H_{26}Cl_6$ (~50.8% wt. Cl) and $C_{11}H_{26}Cl_6$ (~58.6% wt. Cl; data not shown in the Tables) are summarised below for the two methods of estimating the log Kow value used .

	$C_{15}H_{26}Cl_6$	**$C_{11}H_{26}Cl_6$**
Measured BCF	1,087 l/kg	7,816 l/kg
Estimated TGD method/EPIWIN log Kow	7,186 l/kg	46,132 l/kg
Estimated TGD method/Sijm & Sinnige log Kow	43,203 l/kg	44,310 l/kg
Estimated BCFWIN/EPIWIN log Kow	6 l/kg	41,020 l/kg
Estimated BCFWIN/Sijm & Sinnige log Kow	985 l/kg	21,997 l/kg

Based on these data it appears that the combination of the BCFWIN method with a log Kow estimated using the Sijm and Sinnige (1995) method provides the best estimates of the BCF for both the short-chain chlorianted paraffin (BCF is overestimated by a factor of 2.8) and the medium-chain chlorinated paraffin (BCF is underestimated by a factor of 1.1).

However, if a broader view of the estimates obtained by this method is taken, the reliability of the predictions obtained using BCFWIN becomes more questionable. Figure A1 shows a plot of the predicted BCFs obtained using this method for a range of carbon chain lengths and chlorine contents (based on the information reported in Table A3).

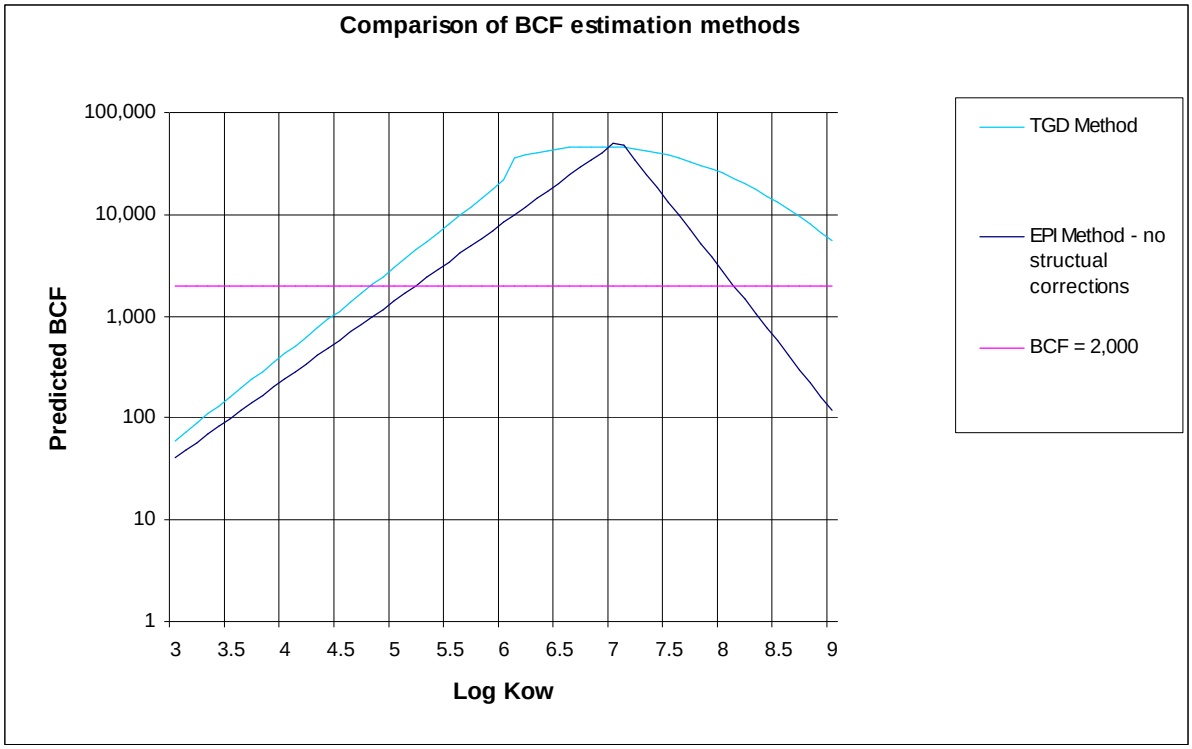
Figure A1 Estimated BCF values obtained using BCFWIN and log Kow values estimated according to Sijm and Sinnige (1995).



From this plot it can be noted that the predictions for short-chain chlorinated paraffins generally show an increasing trend with increasing carbon chain length up to C_{12} but then show a marked decrease at C_{13}. The predicted BCFs then remain relatively low (below the 2,000 l/kg cutoff) except for C_{14} and C_{15} substances with higher chlorine contents. This plot reflects the correction factors that are applied in the BCFWIN method. However, in reality it is difficult to envisage a mechanistic process by which such a pattern of accumulation would occur. For example, if a relatively high BCF is predicted for both a C_{12} and C_{14}, 60% wt. Cl substance, it is difficult to envisage why a similarly high level of accumulation would not be predicted for a C_{13} substance of similar chlorine content. Therefore the applicability of these corrections to chlorinated paraffins can therefore be questioned.

The importance of these correction factors to the predicted BCFs can be further seen by comparing the predictions that would be obtained using BCFWIN if these corrections were not applied with the predictions from the TGD method. This is shown in Figure A2. This plot clearly shows that the underlying predictive equations used in the BCFWIN and TGD method are similar and that the differences in the predictions result mainly from the correction factors applied in the BCFWIN method.

Figure A2 Comparison of the predicted BCFs that would be obtained using BCFWIN if the structural corrections were not applied with the predicted BCF using the TGD method



The structural correction factors in BCFWIN were determined empirically from the available training set and no attempt was made to rationalise these on a mechanistic basis. The training set used to derive the BCFWIN method contained a number of long-chain n-alkanes amongst other substances. One possible explanation for the correction factors derived may be related to potential for metabolism. If the potential for metabolism of chlorinated paraffins is much lower than the corresponding n-alkane, then it is possible that the structural correction factors derived may not be appropriate for chlorinated paraffins.

It should also be noted that the corrections applied in BCFWIN method are not always transparent. For example, the substance $C_{13}H_{20}Cl_8$ will, at face value, have less than eight $–CH_2-$ groups) however the estimates obtained using BCFWIN appear to apply the structural correction to the predicted BCFs for this substance using the structure given in Table A1[21].

In conclusion, although the BCFWIN estimates obtained using log Kow values estimated using the Sijm and Sinnige (1995) method (Table A3) appear to give good estimates of the known BCF values for a short- and a medium-chain chlorinated paraffins, there are some uncertainties associated with the correction factors used in these estimates which throw some doubt on the BCF estimated for other chlorinated paraffins, particularly those with lower chlorine contents. It should, however, be noted that this method does still predict that some C_{14} and C_{15} substances with relatively high chlorine contents would have predicted BCFs in excess of the 2,000 l/kg cut-off for a B-substance. Examples are shown below.

Substance	**Log Kow (Sijm & Sinnige method)**	**Predicted BCF (BCFWIN)**

[21] The structural correction factors are given in Meylan et al. (1999). This indicates that they are applied when there are 8 or more –CH2- groups in the molecule. It is not always clear from the BCFWIN output when these factors have been applied but it appears in some case that they may have been applied when there only 7 –CH2- groups in the molecule and that a terminal chloroalkyl group (CH2Cl-) appears to be counted as a –CH2- group for some calculations.

$C_{14}H_{22}Cl_8$ (60% wt. Cl)	7.34	22,090 l/kg
$C_{15}H_{23}Cl_9$ (60% wt. Cl)	7.51	12,920 l/kg

When the estimated BCFs using the TGD method are considered (Table A1), it is apparent that the method overestimates the actual BCF when the log Kow values estimated using the EPIWIN program are considered. However this overestimate appears to relatively constant (the actual BCF for the C_{11}, 58% wt. Cl substance is overestimated by a factor of 5.7 and the actual BCF for the C_{15}, 51% wt. Cl substance is overestimated by a factor of around 6.6). Thus, when the available predicted BCFs are normalised to the known measured BCF for a C_{15}, 51% wt. Cl substance, it can be seen that TGD method can then predict the known BCF for the C_{11}, 58% wt. Cl substance (predicted value of ca 6,700-6,900 l/kg is obtained for a C_{11}, 52-60% wt. Cl substance compared with the experimental value of 7,816 l/kg for a C_{11}, 58% wt. Cl substance).

When the TGD method for predicting BCFs is considered (Table A3) using the log Kow values estimated by the method of Sijm and Sinnige (1995), the method again overpredicts the known BCFs for both medium- and short-chain chlorinated paraffins. However in this case, scaling the predicted BCF to the known BCF for medium chain chlorinated paraffin leads to an underestimation of the known BCF for short-chain chlorinated paraffins (estimated value approximately 1,157 l/kg compared with the measured value of 7,816 l/kg).

Based on the scaled/normalised estimates obtained using the TGD method with the log Kow values estimated by EPIWIN, BCFs >2,000 l/kg are predicted for C_{14} chlorinated with low to moderate chlorine contents. Examples are given below (values from Table A1).

Substance	**Log Kow (EPIWIN method)**	**Predicted BCF (TGD method)**
$C_{14}H_{26}Cl_4$ (42% wt. Cl)	8.01	3,759 l/kg
$C_{14}H_{24}Cl_6$ (53% wt. Cl)	8.37	2,411 l/kg

Overall, it can be concluded that there are considerable uncertainties in the estimated BCFs for medium-chain chlorinated paraffins. Two main methods have been explored, taking into account possible variability in the key physico-chemical property (log Kow). Both methods lead to predicted BCFs for some medium-chain chlorinated paraffins >2,000 l/kg but the two methods are not consistent in terms of the chlorine contents at which these high BCFs would occur. The BCFWIN method predicts that the C_{14} and C_{15} components of the medium-chain chlorinated paraffins with relatively high chlorine contents (around 567% or above) may have BCFs above 2,000 l/kg whereas the TGD method predicts that the C_{14} components with relatively low chlorine contents (around 52% or below) may have BCFs above 2,000 l/kg.

As noted above, the BCFWIN estimates depend crucially on the correction factors that are applied to molecules with eight or more $–CH_2-$ groups in the carbon chain. The applicability of these corrections to chlorinated paraffins is unclear.

The estimates obtained using the TGD method depend crucially on the log Kow value used. The conclusions drawn above are based on the estimates obtained using the log Kow value estimated using the EPIWIN method. However, it should be noted that no BCF values >2,000 l/kg would be obtained using log Kow values estimated using the Sijm and Sinnige (1995) method, and scaling the resulting BCF to the known BCF for a C_{15}, 51% wt. Cl substance. However, in this latter case the method does not predict well (underpredicts) the actual BCF for a C_{11}, 58% chlorinated paraffin.

The limited amount of experimental data with which to compare the predicted BCFs makes it difficult to draw firm conclusions as to which predictive method is the most reliable. However, the uncertainties over the applicability of the structural corrections applied in the EPIWIN method to

medium-chain chlorinated paraffins (as illustrated in Figure A1) means that these predictions are considered overall less reliable, particularly in their ability to predict trends in the BCF with changes in carbon uchain length and chlorine content, than those obtained using the TGD method.

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Abstract

An environmental risk assessment of alkanes, C_{14-17}, chloro (medium-chain chlorinated paraffins or MCCPs) produced in accordance with Council Regulation (EEC) 793/93 was published in December 2005. This report provides the updated risk assessment dealing with new data and the consequences of the new data for the conclusions in the original report. The report has been prepared by the United Kingdom in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

This report considers the secondary poisoning assessment and the exposure of man via the environment based on new information. This update includes also the PBT assessment which was not addressed in the original report for medium-chain chlorinated paraffins.

The updated environmental risk assessment concludes that risks are identified for the earthworm food chain due to various uses of MCCPs. Risks are not identified any longer for the fish food chain, with the exception of the use in leather fat liquors. The exposure of man via environmental routes has been revised with new information. It is now concluded that there is no longer concern for this route of human exposure. The PBT assessment concludes that further information is needed in order to confirm whether or not the substance should be considered as a PBT substance or not. A testing strategy is discussed in the report.

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