European Chemicals Bureau

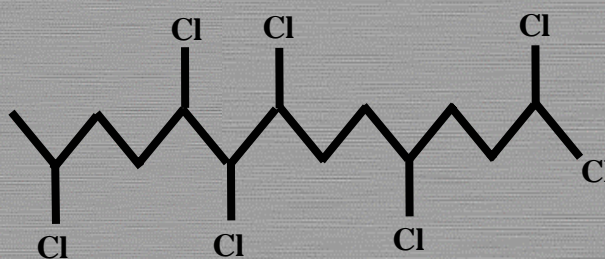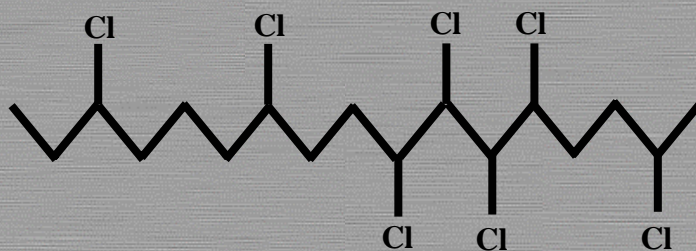# European Union Risk Assessment Report

CAS No: 85535-85-9

EINECS No: 287-477-0

alkanes, C$_{14-17}$, chloro (MCCP) Part I - environment

C$_{14}$H$_{24}$Cl$_6$

C$_{17}$H$_{29}$Cl$_7$

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

EUR 21640 EN

European Union Risk Assessment Report

ALKANES, C$_{14-17}$, CHLORO (MCCP)

Part I – Environment

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RISK ASSESSMENT

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RISK ASSESSMENT

Final Report, 2005

The United Kingdom

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

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Date of Last Literature Search: **2003**
Review of report by MS Technical Experts finalised: **2004**
Final report: **2005**

(The last full literature survey was carried out in 2003 - targeted searches were carried out subsequently.)

Foreword

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

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93[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 t/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 Toxicity, Ecotoxicity and the Environment (CSTEE) 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.

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

Roland Schenkel	**Catherine Day**
Acting Director-General	Director-General
DG Joint Research Centre	DG Environment

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[1] O.J. No L 084, 05/04/1993 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]

0 OVERALL RESULTS OF THE RISK ASSESSMENT

CAS No: 85535-85-9
EINECS No: 287-477-0
IUPAC Name: alkanes, C_{14-17}, chloro

Environment

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.

A low risk to waste water treatment plants and the atmospheric compartment[4] has been identified from both the production and use of medium-chain chlorinated paraffins.

For surface water, this conclusion applies to the assessment of local releases from production, some PVC compounding and/or conversion sites, plastics/rubber compounding, formulation and use of sealants, formulation and use in paints, use in metal cutting/working fluids (except where spent emulsifiable fluid is discharged to waste water), formulation of leather fat liquors, recycling of carbonless copy paper and from regional sources.

For sediment, this conclusion applies to the assessment of local release from production, some use in PVC (compounding in open and closed systems), some uses in plastics/rubber (compounding), formulation and use of sealants, formulation and use in paints, use in emulsifiable metal cutting/working fluids (except where intermittent disposal to drain occurs), formulation of leather fat liquors and from regional sources.

For soil, this conclusion applies to the assessment of local releases from production, PVC plastisol coatings compounding, conversion or combined compounding/conversion sites, PVC extrusion/other compounding sites, PVC extrusion/other conversion sites and PVC extrusion/other combined compounding/conversion sites using open or closed processes, plastics/rubber compounding, conversion and combined compounding/conversion sites, formulation and use of sealants, formulation and use of paints, use in oil-based metal cutting/working fluids, use in emulsifiable metal cutting/working fluids (not intermittent release scenario), formulation of leather fat liquors,, recycling of carbonless copy paper and from regional sources on agricultural land.

For secondary poisoning via the fish food chain, a low risk was identified from formulation and use of sealants, and domestic application of paints. A low risk of secondary poisoning via the earthworm food chain is also indicated for production (sites where no application of sewage sludge onto land occurs), formulation and use in sealants, and domestic application of paints.

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

For surface water, a risk is identified from the following applications:

- Use in the production of PVC in some processes (particularly where compounding or compounding and conversion are carried out in partially open systems).

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[4] Some components of the commercial products have properties that may mean that long-range transport via the atmosphere is a possibility. This issue should be considered further in the appropriate international fora.

- Formulation of metal cutting fluids, and use in emulsifiable metal cutting/working fluids where the spent fluid is discharged to waste water.

- Use in leather fat liquors.

For sediment, a risk is identified from the following applications:

- Use in PVC: plastisol coating – conversion sites or sites carrying out both compounding and conversion.

- Use in PVC: extrusion/other – compounding sites using partially open processes or sites carrying out both compounding and conversion using open, partially open or closed processes.

- Use in PVC: extrusion/other – conversion sites using open, partially open or closed processes.

- Use in plastics/rubber: sites carrying out conversion or both compounding and conversion.

- 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 at sites with intermittent release (disposal) to sewer/drain.

- Use in leather fat liquors: use at sites carrying out processing of hides/leather.

- Use in carbonless copy paper: sites carrying out paper recycling.

For the terrestrial compartment, a risk is identified from:

- Use in PVC: extrusion/other - sites carrying out both compounding and conversion using partially open systems.

- Use in metal cutting/working fluids: formulation sites.

- Use in metal cutting/working fluids: use in emulsifiable fluids at sites with intermittent release (disposal) to sewer/drain.

- Use in leather fat liquors: use at sites carrying out processing of hides/leather.

- Regional assessment of "waste remaining in the environment".

For secondary poisoning, a risk is identified from all uses of medium-chain chlorinated paraffins for the earthworm food chain other than for production (sites where there is no spreading of sewage sludge to land), formulation and use of sealants, and domestic application of paints. The following scenarios also indicate a concern for the fish food chain:

- Production sites.

- Use in the production of PVC - plastisol coating.

- Use in the production of PVC – extrusion/other.

- Use in the production of plastic/rubber.

- Formulation of paints and industrial application of paints.

- Formulation and use in metal cutting/working fluids (all types).

- Formulation and use in leather fat liquors.

- Recycling of carbonless copy paper.

CONTENTS

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

APPENDICES

TABLES

1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

CAS No: 85535-85-9
EINECS No: 287-477-0
IUPAC Name: alkanes, C_{14-17}, chloro
Synonyms: chlorinated paraffin (C_{14-17}); chloroalkanes, C_{14-17}; chloroparaffin; chloroparaffine, C_{14-17}; medium-chain chlorinated paraffins; paraffine clorurate (C_{14-17}); paraffine clorurate a catena media.
Molecular formula $C_xH_{(2x-y+2)}Cl_y$, where x = 14-17 and y = 1-17
Molecular weight: see Section 1.2.1
Structural formula

$C_{14}H_{24}Cl_6$

$C_{17}H_{29}Cl_7$
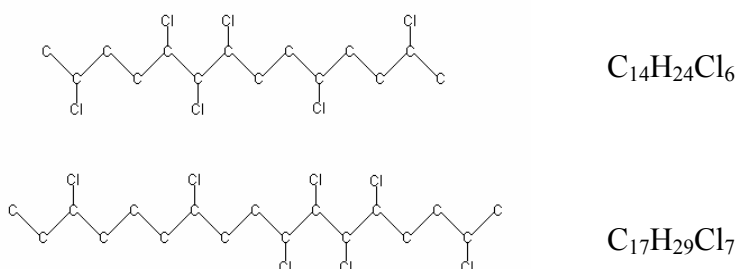
In this assessment the name medium-chain chlorinated paraffin (or MCCP) will be used for the substance, as this is the more common name. The commercially supplied products are usually mixtures of different carbon chain lengths (reflecting the carbon chain length distribution in the parent n-paraffin feedstocks used), and have different degrees of chlorination, although all have a common structure in that no secondary carbon atom carries more than one chlorine atom. Two other groups of chlorinated paraffins are made commercially. These are known as short-chain (typically C_{10-13}) and long-chain (typically $\geq C_{18}$ or C_{20-30}). This assessment is only concerned with the medium-chain (C_{14-17}) chlorinated paraffins, but some information on the other types is included when it is considered to be useful and relevant to the assessment. The short-chain chlorinated paraffins have been assessed previously under Regulation (EEC) 793/93.

It should be noted that around 40 CAS numbers have been used to describe the whole chlorinated paraffin family at one time or another. Some of these are now historical, and others may be in use for the sole purpose of compliance with national or regional chemical inventories. It is possible that some cover the medium-chain chlorinated paraffin group, and those that might are listed in **Table 1.1** (the list is not meant to be exhaustive).

Table 1.1   Substances that might contain medium-chain chlorinated paraffins

Substance	CAS no.	EINECS no.
Alkanes, C_{6-18}, chloro	68920-70-7	272-924-4
Alkanes, C_{10-21}, chloro	84082-38-2	281-985-6
Alkanes, C_{10-26}, chloro	97659-46-6	307-451-5
Alkanes, C_{10-32}, chloro	84776-06-7	283-930-1
Paraffins (petroleum), normal C>10, chloro	97553-43-0	307-202-0
Alkanes, chloro	61788-76-9	263-004-3

Some CAS numbers cover only parts of the alkyl chain length range (e.g. alkanes, C_{10-14}, chloro (CAS no. 85681-73-8, EINECS no. 288-211-6; alkanes, C_{12-14}, chloro, CAS no. 85536-22-7, EINECS no. 287-504-6). Kirk-Othmer (1993) identifies a C_{12-14} feedstock, and Ashford (1994) also lists C_{11-14} and C_{14-18} chlorinated n-paraffins.

This illustrates a problem in using CAS numbers to describe complex substances. From comments made in BUA (1992), it may be that some refer to products derived from feedstocks other than n-paraffins, or are monochlorinated. Such substances might therefore not have suitable properties for the uses considered in this assessment. From the way that n-paraffin fractions are made, the CAS numbers referring to wide ranges of chain length (e.g. 68920-70-7, 84082-38-2, 84776-06-7 and 97659-46-6) may fall into this category.

Only the C_{14-17} feedstock is used in Europe (Ineos Chlor, 2004), but the choice of feedstock might have some subtle consequences. For example, Thomas et al. (2003) indicated that discussions between European and US producers of medium-chain chlorinated paraffins had identified a possible difference in the carbon chain distribution of their products, with the products produced in Europe more likely to have a distribution skewed towards the shorter chain length components compared to a more Gaussian distribution in products in the United States.

In summary, the CAS number that is listed in IUCLID (85535-85-9) is taken to represent the commercial substance used in Europe.

Finally, it is possible that related substances called chloroalkanes are still in production. These are considered in the updated environmental risk assessment of short-chain chlorinated paraffins (Environment Agency, 2004).

1.2   PURITY/IMPURITIES, ADDITIVES

1.2.1   Purity

Table 1.2 shows the theoretical % weight chlorine content of several compounds that can be considered as medium-chain chlorinated paraffins. The amount of chlorine present in the commercial products is usually expressed as a percentage by weight (% wt. Cl), but since the commercial products contain a number of components with different carbon chain lengths, it is not possible to identify exactly which compounds are present in a given product, although **Table 1.2** can be used as a guide. Wherever possible in this report, the actual carbon chain length (or range of chain length) and the degree of chlorination (% wt. Cl) will be given.

Although it is theoretically possible to produce medium-chain chlorinated paraffins with chlorine contents up to 70% wt. Cl, such products are not manufactured commercially. The highest chlorine content of the commercial medium-chain chlorinated paraffins normally available is around 58-60% wt. Cl, although products with chlorine contents of up to 62-63% have recently been developed. The lowest chlorine content of the commercial medium-chain chlorinated paraffins is around 40% wt. Cl, but the largest tonnage of medium-chain chlorinated paraffins have chlorine contents between 45 and 52% wt. Cl (Euro Chlor, 1999).

The purity of the produced chlorinated paraffin is related to the purity of the n-paraffin feedstock. In Western Europe, chlorinated paraffins are made from purified n-paraffin feedstocks containing no more than 1-2% isoparaffins and <100 mg aromatics/kg (the aromatics are removed by treatment of the n-paraffin with sulphuric acid). For some high-stability

applications, n-paraffin fractions with <1% isoparaffins and <10-100 mg aromatics/kg are used (BUA, 1992).

Table 1.2   Theoretical chlorine content of some medium-chain chlorinated paraffins

Formula	Molecular weight	% Cl by weight	Formula	Molecular weight	% Cl by weight	Formula	Molecular weight	% Cl by weight
C$_{14}$H$_{29}$Cl	232.5	15.3	C$_{15}$H$_{24}$Cl$_8$	488.0	58.2	C$_{16}$H$_{18}$Cl$_{16}$	778.0	73.0
C$_{14}$H$_{27}$Cl$_3$	301.5	35.3	C$_{15}$H$_{20}$Cl$_{12}$	626.0	68.1			
C$_{14}$H$_{24}$Cl$_6$	405.0	52.6	C$_{15}$H$_{17}$Cl$_{15}$	729.5	73.0	C$_{17}$H$_{35}$Cl	274.5	12.9
C$_{14}$H$_{21}$Cl$_9$	508.5	62.8				C$_{17}$H$_{32}$Cl$_4$	378.0	37.6
C$_{14}$H$_{18}$Cl$_{12}$	612.0	69.6	C$_{16}$H$_{33}$Cl	260.5	13.6	C$_{17}$H$_{29}$Cl$_7$	481.5	51.6
C$_{14}$H$_{16}$Cl$_{14}$	681.0	73.0	C$_{16}$H$_{30}$Cl$_4$	364.0	39.0	C$_{17}$H$_{26}$Cl$_{10}$	585.0	60.7
			C$_{16}$H$_{27}$Cl$_7$	467.5	53.2	C$_{17}$H$_{23}$Cl$_{13}$	688.5	67.0
C$_{15}$H$_{31}$Cl	246.5	14.4	C$_{16}$H$_{24}$Cl$_{10}$	571.0	62.2	C$_{17}$H$_{21}$Cl$_{15}$	757.5	70.3
C$_{15}$H$_{28}$Cl$_4$	350.0	40.6	C$_{16}$H$_{21}$Cl$_{13}$	674.5	68.4	C$_{17}$H$_{19}$Cl$_{17}$	826.5	73.0

Commercial products are complex mixtures of isomers and standard analytical methods do not permit separation and identification of these. Work by Könnecke and Hahn (1962) provides a basis for estimating the distribution of the chlorine contents present in a given product (although this work was actually carried out with C$_{26}$ chlorinates, it is thought that similar distributions will apply to all chlorinated paraffins). This work gives a prediction of approximately 80% of the isomers present lying within ±10% of the stated average chlorine content and 90% within ±15%. Thus in a medium-chain 50% wt. Cl product, there is likely to be only around 5% of mono- and dichloro isomers present (with a corresponding low percentage of highly chlorinated material) (ICI, 1995).

Any impurities present in the commercial chlorinated paraffins are likely to be related to those present in the n-paraffin feedstock, in which the major non-paraffinic impurity is a small proportion of aromatics (generally in the range 50-100 ppm (mg/kg)). However, there is some evidence that the chlorination reaction does not favour chlorination of aromatics. No specific analytical methods are currently available for the detection of possible impurities present in the commercial products (ICI, 1995).

The levels of chlorinated paraffins of chain lengths other than C$_{14-17}$ present in the current commercial products are <1%. The producers of medium-chain chlorinated paraffins (represented by Euro Chlor) have, since 1991, used paraffin feedstocks in the production process with a C$_{10-13}$ content of <1% (the actual levels are often much lower than this), and a >C$_{18}$ content of <1% (Euro Chlor, 1999).

1.2.2   Additives

It is known that additives/stabilisers such as long-chain epoxidised soya oil or glycidyl ether are added to some chlorinated paraffins to inhibit the release of hydrogen chloride at elevated temperatures. These are used at concentrations of <1% by weight. For some high thermal stability formulations other additives, e.g. organophosphorus compounds, have been reported to be used in conjunction with these (BUA, 1992).

1.2.3   **Physico-chemical properties**

The physico-chemical properties of medium-chain chlorinated paraffins are discussed below and summarised in **Table 1.3**.

Since the products produced contain many components, the physico-chemical properties of the various products can vary, reflecting the different components of the products. Representative values have therefore been selected for the key parameters used for environmental modelling. The effect of the variation of these properties on the risk characterisation is analysed in Appendix H.

1.2.4   **Physical state (at ntp)**

Medium-chain chlorinated paraffins are liquids at room temperature.

1.2.5   **Melting point**

Commercial medium-chain chlorinated paraffins do not have a distinct melting point. Pour points in the range -40°C to -7°C and -45°C to 0°C have been reported for these materials in IUCLID. BUA (1992) reports a similar pour point range of -50°C to 0°C. It has been reported that a medium-chain chlorinated paraffin with a very high chlorine content (62-63% wt. Cl) has a pour point of around 25°C (Euro Chlor, 1999).

Table 1.3   Physico-chemical properties of some medium-chain chlorinated paraffins

Property	Chlorine content (% wt)	Value	Remarks
Physical state (at ntp)	40-63	liquid	
Pour point		-45°C to 25°C	commercial mixtures - no distinct melting point
Boiling point (at ntp)		>200°C	decomposition with release of HCl
Density	41	1.095 g/cm^3 at 20°C	
	56	1.315 g/cm^3 at 20°C	
	40-58	1.1-1.38 g/cm^3 at 25°C	
	56	1.28-1.31 g/cm^3 at 60°C	
Vapour pressure	45	2.27 · 10^{-3} Pa at 40°C	a value of 2.7 · 10^{-4} Pa at 20°C is used in the Environmental Assessment
		0.16 Pa at 80°C	
	52	1.3 · 10^{-4}-2.7 · 10^{-4} Pa at 20°C	
		1.07 · 10^{-3} Pa at 45°C	
		6.0 · 10^{-3} Pa at 60°C	
		0.051 Pa at 80°C	
Water solubility	51	0.005-0.027 mg/l	a value of 0.027 mg/l is used in the Environmental Assessment

Table 1.3 continued overleaf

Table 1.3 continued Physico-chemical properties of some medium-chain chlorinated paraffins

Property	Chlorine content (% wt)	Value	Remarks
Log octanol-water partition coefficient	45	5.52-8.21	measured by a high performance thin layer chromatography method; a value of 7 is used in the Environmental Assessment
	52	5.47-8.01	
Flash point	>40	>210°C	closed cup
Autoflammability		not stated	
Explosivity		not applicable	
Oxidising properties		none	

Ntp   Normal temperature and pressure.

1.2.6   Boiling point

The exact boiling point of medium-chain chlorinated paraffins is unknown as they start to decompose (with liberation of hydrogen chloride) at temperatures of around 200°C. The boiling point can therefore be considered to be >200°C.

1.2.7   Relative density

The density varies with chlorine content of the product. Values reported in IUCLID include 1.095 g/cm^3 for a 41% wt. Cl product and 1.315 g/cm^3 for a 56% wt. Cl product at 20°C, 1.1-1.38 g/cm^3 at 25°C for products with chlorine contents in the range 40-58% wt. Cl and 1.275-1.305 g/cm^3 at 60°C for a 56% wt. Cl product.

Kirk-Othmer (1993) gives the following similar values for the density of C$_{14-17}$ chlorinated paraffins at 25°C: 1.10 g/cm^3 for a 40% wt. Cl product; 1.16 g/cm^3 for a 45% wt. Cl product; 1.25 g/cm^3 for a 52% wt. Cl product; and 1.36 g/cm^3 for a 58% wt. Cl product.

1.2.8   Vapour pressure

A vapour pressure of $2.27 \cdot 10^{-5}$ hPa ($2.27 \cdot 10^{-3}$ Pa) at 40°C has been reported in IUCLID for medium-chain chlorinated paraffins with a chlorine content of 45% wt. Cl. A vapour pressure of 0.16 Pa has been reported for a similar chlorinated paraffin at 80°C (BUA, 1992).

The vapour pressure of a C$_{14-17}$, 52% wt. Cl product has been reported as $1 \cdot 10^{-6}$-$2 \cdot 10^{-6}$ mmHg ($1.3 \cdot 10^{-4}$-$2.7 \cdot 10^{-4}$ Pa) at 20°C by Campbell and McConnell (1980). Vapour pressures for a C$_{14-17}$, 52% wt. Cl product at elevated temperatures have been reported as $1.07 \cdot 10^{-3}$ Pa at 45°C, $6 \cdot 10^{-3}$ Pa at 60°C and 0.051 Pa at 80°C (BUA, 1992).

It has been reported that the volatility of chlorinated paraffins in general decreases with increasing chlorine content (Kirk-Othmer, 1993), and this is borne out by the above figures.

Recently, Drouillard et al. (1998) determined the vapour pressures of a series of short-chain (C$_{10-13}$) chlorinated paraffins at 25°C using a vapour pressure - gas-liquid chromatography technique. They found that vapour pressures of the short-chain chlorinated paraffins decreased with both increasing carbon chain length and degree of chlorination. They derived the following

equation relating vapour pressure (in Pa at 25°C) to the number of carbon and chlorine atoms present in a molecule:

- log (vapour pressure) = -(0.353 · no. of C atoms) - (0.645 · no. of Cl atoms) + 4.462

Using this equation vapour pressures for all possible medium-chain chlorinated paraffin congeners can be estimated. This is shown in Appendix B for all possible combinations of carbon and chlorine numbers. It should be noted that the reliability of this equation for the medium-chain chlorinated paraffins is unknown, however the values estimated for C_{14-17}, ~51-53% Cl chlorinated paraffins are in the region of $5 \cdot 10^{-5}$ Pa for C_{14}, $2 \cdot 10^{-5}$ Pa for C_{15}, $2 \cdot 10^{-6}$ Pa for C_{16} and $9 \cdot 10^{-7}$ Pa for C_{17}, which agrees reasonably well with the measured data above, particularly as the measurements on the commercial mixture will be dominated by the more volatile components (shorter chain length, lower chlorinated components).

For the environmental assessment, the vapour pressure of $2.7 \cdot 10^{-4}$ Pa at 20°C measured by Campbell and McConnell (1980) will be used as a representative value for a commercial product. The vapour pressures of individual isomers are likely to cover a large range of values, being dependent on the carbon chain length and number of chlorine atoms present.

1.2.9 Water solubility

The water solubility of a ^{14}C-labelled chlorinated n-pentadecane (51% wt. Cl) has been determined to be 0.005 mg/l by parent compound measurement and 0.027 mg/l by ^{14}C analysis after 6 months at 20°C. The test substance was prepared by mixing n-pentadecane-8-^{14}C with unlabelled C_{14-17} paraffin prior to chlorination to 51% wt. Cl. Approximately 50 mg of the test substance was weighed out onto a glass microscope slide and this was then placed in 5 litres of water. The test was carried out by stirring the chlorinated paraffin in water for 91 days and then allowing the solution to settle (no stirring) for a further 87 days to ensure that equilibrium was reached. Light was excluded from the test solution. The authors suggested that the discrepancy between the water solubility obtained by the two methods may indicate that some degradation had occurred during the test (Madeley et al., 1983a). However, this discrepancy could also, in part, be due to the different analytical methods used. Given that the substance tested is a complex mixture, the solubility values obtained by the different methods are in reasonable agreement.

Campbell and McConnell (1980) reported the solubility at 16-20°C of a C_{16}, 52% wt. Cl chlorinated paraffin to be 10 µg/l in freshwater and 4 µg/l in seawater, based on radioactivity measurements. Few other details are available about the method used, but the results obtained are comparable with those reported by (Madeley et al., 1983a) above.

A water solubility value of 0.027 mg/l will be used in the assessment. It is likely that the water solubility will vary with both carbon chain length and degree of chlorination.

1.2.10 Partition coefficient

Calculated values for log Kow between 5.5 and >6 are reported in IUCLID for medium-chain chlorinated paraffins.

Log Kow values of 6.95 for $C_{14}H_{26}Cl_4$ (42.2% wt. Cl), 6.37 for $C_{14}H_{23}Cl_7$ (56.5% wt. Cl), 8.54 for $C_{17}H_{32}Cl_4$ (37.5% wt. Cl) and 7.94 for $C_{17}H_{27}Cl_9$ (58.0% wt. Cl) have been calculated using the CLOGP 3.4 computer program (BUA, 1992).

Renberg et al. (1980) determined the octanol-water partition coefficients for medium-chain chlorinated paraffins using a high performance thin layer chromatography (HPTLC) method. The partition coefficients determined (log values) were 5.52-8.21 for a C_{14-17}, 45% wt. Cl product and 5.47-8.01 for a C_{14-17}, 52% wt. Cl product. The range quoted reflects the different HPTLC retention times, and hence octanol-water partition coefficients, of the various components of the commercial products. These measured values are in good agreement with the values estimated above.

Fisk et al. (1998b) determined the octanol-water partition coefficients of two ^{14}C-labelled medium-chain chlorinated paraffins of single carbon chain length (C_{16}). The two substances used were $C_{16}H_{21.7}Cl_{3.3}$, 35% wt. Cl and $C_{16}H_{20.6}Cl_{13.4}$, 69% wt. Cl. The mean log Kow values determined by a HPLC method were reported to be 7.2 for the 35% wt. Cl substance (range of log Kow was 4.7-6.6, 6.6-7.8, 7.8-8.0 and 8.0-8.3 for the four main components of this substance) and 7.4 for the 69% wt. Cl substance (range of log Kow was 6.9-7.8). These are consistent with the other values determined above.

For the environmental assessment, a log Kow value of 7 (approximately the middle of the range of measured values) will be used as a representative value.

1.2.11   Flash point

A flash point of >210°C (closed cup) is reported in IUCLID for a C_{14-17}, >40% wt. Cl product.

1.2.12   Autoflammability

Decomposition starts to occur above 200°C with liberation of hydrogen chloride.

1.2.13   Explosivity

On the basis of chemical structure the substance is not explosive.

1.2.14   Oxidising properties

On the basis of chemical structure the substance has no oxidising properties.

1.2.15   Classification

1.2.16   Current classification

Medium-chain chlorinated paraffins are currently not classified with respect to their effects on human health or the environment.

1.2.17   Proposal of rapporteur

1.2.17.1   Environment

Based on the toxicity seen with daphnids and the lack of biodegradability in standard test systems, the following classification is proposed for environmental effects:

- N – Dangerous for the environment
  R50/53 – Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

This proposal is based on the acute toxicity seen with *Daphnia magna* (48-hour EC50 = 0.0059 mg/l), a high fish bioconcentration factor of 1,087 and the lack of degradation expected in standard ready biodegradation tests. This proposal was agreed at the Environmental Classification and Labelling Expert Meeting in September 2004.

1.2.17.2   Human health

(To be added later)

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

Medium-chain chlorinated paraffins are manufactured at five sites in the EU[5]. The current total production capacity as reported in IUCLID is in the range 45,000-160,000 t/year.

Chlorinated paraffins are manufactured by adding chlorine gas into the starting paraffin in a stirred reactor. Depending on the chain length of the paraffin feedstock, the temperature of the reaction is maintained between 80 and 100°C, with cooling if necessary. Catalysts are not usually needed for the reaction to proceed, but ultraviolet light may be used to aid the reaction. Once the desired degree of chlorination has been reached (as determined by density, viscosity or refractive index measurements), the flow of chlorine gas into the reaction is stopped. Air or nitrogen is then used to purge the reactor of excess chlorine and hydrochloric acid gas and small quantities of a stabiliser (e.g. epoxidised vegetable oil) may be added to the product. The product is then typically filtered and piped to batch storage tanks for filling drums, tankers or bulk storage tanks. The main by-product from the process is hydrogen chloride gas. This is collected by absorption in water and re-used as hydrochloric acid (BUA, 1992).

2.2 USES

The main uses of medium-chain chlorinated paraffins are as secondary plasticisers in polyvinyl chloride (PVC), as extreme pressure additives in metal working fluids, as plasticisers in paints, as additives to adhesives and sealants, in fat liquors used in leather processing and as flame retardant plasticisers in rubbers and other polymeric materials.

Estimates for the amounts of medium-chain chlorinated paraffins used in the various applications within the EU are given in **Table 2.1** (Euro Chlor, 1998).

Figures have been provided for the use of medium-chain chlorinated paraffins in the EU in 1998 (Euro Chlor, 1999). These were provided in a slightly different form to those in **Table 2.1** but indicate that the overall use of medium-chain chlorinated paraffins during 1998 had fallen from the 1997 level to a similar level as in 1994. The reduction in use of medium-chain chlorinated paraffins compared with 1997 was generally spread over all the uses, with the exception of metal cutting working/cutting fluids, which showed a small increase in use, and paints, sealants and adhesives, which remained approximately at the 1997 level. The 1997 consumption figures are used in the environmental assessment to represent a realistic worst case for the amounts used in the various applications.

In a previous assessment of the short-chain (C$_{10-13}$) chlorinated paraffins, risk reduction measures were identified for use in metal cutting/working fluids and leather fat liquors. The medium-chain chlorinated paraffins have similar uses, and can be considered as replacements for the short-chain chlorinated paraffins in some of these applications. Any reduction in use of the short-chain chlorinated paraffins in these areas could lead to an increased use of medium-chain chlorinated paraffins as a replacement. The effect of such substitutions on the amounts of medium-chain chlorinated paraffins likely to be used in the future as a result of risk reduction measures applied to the short-chain chlorinated paraffins is currently unknown, although an

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[5] Entec (2004) indicates that, following on from the recent expansion of the EU, a further production site within the EU exists. This site is not considered in this report.

increasing trend in use in metal working/cutting fluids is evident from **Table 2.1** and information reported in Entec (2004)[6]. Appendix E considers this issue further.

Table 2.1   Use of medium-chain chlorinated paraffins in the EU

Application	Industry category	Use category	Quantity used (t/year) (Percentage of total use given in brackets)			
			1994	1995	1996	1997
PVC[7]	11 (polymers industry)	47 (softeners) or 22 (flame retardant and fire preventing agents)	45,476 (80.2%)	48,640 (82.9%)	49,240 (83.0%)	51,827 (79.4%)
Metal working/ cutting[7]	8 (metal extraction, refining and processing industry	35 (lubricants and additives)	2,611 (4.6%)	2,765 (4.7%)	3,302 (5.6%)	5,953 (9.1%)
Paints, adhesives and sealants[*]	14 (paints, lacquers and varnishes industry) and 15 (others)	47 (softeners) or 22 (flame retardant and fire preventing agents)	3,079 (5.4%)	2,392 (4.1%)	2,638 (4.4%)	3,541 (5.4%)
Rubber/polymers (other than PVC)	11 (polymers industry)	47 (softener) or 22 (flame retardant and fire preventing agents)	2,497 (4.4%)	2,767 (4.7%)	2,324 (3.9%)	2,146 (3.3%)
Leather fat liquors[7]	7 (leather processing industry)	47 (softeners) or 31 (impregnation agents)	1,614 (2.8%)	1,270 (2.2%)	1,172 (2.0%)	1,048 (1.6%)
Carbonless copy paper	12 (pulp, paper and board industry)	48 (solvent)	1,296 (2.3%)	837 (1.4%)	630 (1.1%)	741 (1.1%)
Total			56,673	58,671	59,306	65,256

*   Approximate split is 2/3 used in sealants and 1/3 used in paints (Euro Chlor, 1999).

It is thought that around 50% of the leather fat liquor formulations produced in the EU is exported for use outside the EU (Euro Chlor, 1998).

For use in PVC and other polymers, it is possible that pellets (masterbatch) containing medium-chain chlorinated paraffins could be manufactured outside the EU and then imported into the EU for further processing to give the final product. Similarly, such pellets could be manufactured within the EU and exported for subsequent processing. A similar situation may also exist with finished products containing medium-chain chlorinated paraffins. The actual amounts of medium-chain chlorinated paraffins imported into and exported out of the EU in this way are very difficult to estimate. For the purpose of this assessment it will be assumed that net import into the EU of these products will be small compared with the amount presented in **Table 2.1**.

Some information is available on the amounts of total PVC (flexible and rigid) manufactured and imported into the EU (ECVM, 2000) that is useful in this issue. The total Western European

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[6] Entec (2004) reports figures for the use of medium-chain chlorinated paraffins in 2003 showing that around 60% of the total was used in PVC, around 15% used in metal working/cutting fluids, around 15% used in paints, sealants and adhesives, around 7% in rubber/polymers (other than PVC), around 3% used in leather fat liquors and <<1% used in carbonless copy paper. Overall the total amount of medium-chain chlorinated paraffins used in 2003 was around 82% of the 1997 level. Decreases in use (to the nearest 5%; compared with the 1997 level) had occurred in PVC (ca. 35% reduction) and carbonless copy paper (ca. 90% reduction), with increases in use occurring in metal working/cutting fluids (ca. 35% increase), paints, sealants and adhesives (ca. 135% increase), rubber/polymers (other than PVC) (ca. 65% increase) and leather fat liquors (ca. 35% increase).

[7] Information provided by Euro Chlor indicates that the 2002 EU consumption of medium chain chlorinated paraffins in these applications was around 30,000 t/year in PVC, 8,000 t/year in metal working fluids and 1,550 t/year in leather fat liquors (MCCP User Forum, 2003).

market for PVC was estimated to be 5,594,000 t/year in 1997, compared to the total amount of PVC produced in Western Europe of 5,528,000 t/year in the same year. This gives a net import of PVC into the EU of around 66,000 t/year, or 1.2% of the total produced. This indicates that the net import of medium-chain chlorinated paraffins into the EU in PVC or masterbatch is likely to be small compared to the amounts produced in the EU presented in **Table 2.1**.

In Sweden, the use of all chlorinated paraffins in metal working fluid has been reduced by 80% overall (a 95% reduction in water-oil emulsions (i.e. 160 t in 1986 and 8.5 t in 1993) and a 75% reduction in straight oil based cutting fluids (i.e. 520 t in 1986 and 130 t in 1993) between 1986 and 1993, and is expected to reduce further (Stenhammar and Björndal, 1994). More than 80% of the chlorinated paraffins used in emulsion cutting fluids and at least 20% of the chlorinated paraffins used in straight oil applications were reported to be C_{10-13} chlorinated paraffins (the remainder would include the C_{14-17} chlorinated paraffins).

Further information on the use of medium-chain chlorinated paraffins has been obtained from the Danish product register. In the register, 28 t/year of medium-chain chlorinated paraffins were reported in a total of 42 products. The product types identified included fillers/sealants (typically 10-20% chlorinated paraffin content), cutting fluids, process regulators (e.g. hardeners) and paints, lacquers and varnishes (typically 1-5% chlorinated paraffin content). Most products contained medium-chain chlorinated paraffin in the range 10-20% by weight of the formulation.

Information has been provided on the breakdown of use of medium-chain chlorinated paraffins by country (Euro Chlor, 1999). This information is considered confidential but did indicate that the main user countries are Italy and the United Kingdom, with use in the United Kingdom accounting for just over 25% of the total EU use. The use pattern in the main user countries was broadly in line with that outlined in **Table 2.1**.

2.2.1   Use as a plasticiser

2.2.1.1   PVC

Medium-chain chlorinated paraffins are used as secondary plasticisers mainly in PVC. The primary plasticisers used are generally phthalates or phosphate esters (Kirk-Othmer, 1993). The phosphate esters are normally used only when flame retardant benefits are needed (Euro Chlor, 1999). The medium-chain chlorinated paraffins may also be used in some other plastics, but here the major function is likely to be as a flame retardant rather than as a plasticiser (see Section 2.2.2.2).

Primary plasticisers in PVC are used to increase the elongation properties and softness of the polymer. Secondary plasticisers, when used in combination with primary plasticisers, cause an enhancement of the plasticising effects and so are also known as extenders. The majority of secondary plasticisers used in PVC applications are medium-chain chlorinated paraffins with chlorine contents around 45% wt. Cl or 50-52% wt. Cl, with only very small amounts (<1% of total sales) of medium-chain chlorinated paraffins with higher (e.g. 56-58% wt. Cl) or lower (e.g. ~40% wt. Cl) chlorine contents being used in PVC (Euro Chlor, 1999).

There are two main types of PVC produced e.g. suspension and paste-forming (emulsion) PVC, and the methods for incorporation of plasticisers in the two types are different. World-wide approximately 70% of PVC resin is suspension, with 20% emulsion and small amounts of bulk (9% of total resin production; produces irregular particles with little or no impurities) and

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solution (1% of total resin production; used to make specialised resins for metal coatings, record manufacture, powder coatings and surface coatings) (Rubin, 1990).

Polymers of suspension PVC (also known as pearl, bead or granular) are produced by suspending vinyl chloride monomer in water and carrying out the polymerisation using a monomer-soluble initiator. This results in the PVC particles formed having a relatively large particle size (e.g. 100-150 μm). These particles are highly porous and so can absorb large amounts of plasticiser. The PVC particles are typically processed using a dry-blend cycle. In this cycle, all the polymer formulation ingredients, including plasticisers, are heated to around 70-110°C and mixed to form a dry powder product. This can be either stored or further processed immediately. Processing of the dry powder can take the form of extrusion, injection moulding or calendering. The powder can also be extruded and chipped to form pellets of PVC compound which can subsequently be further processed to give the final product. Many producers of PVC products purchase PVC compound as it is easy to store and similarly many companies exist that produce PVC compound (Kirk-Othmer, 1996).

Paste-forming (plastisol) PVC polymers are produced as a paste or plastisol rather than a dry powder (a plastisol is a suspension of a solid in a liquid in which it does not dissolve, but does form an homogenous mixture at elevated temperatures; the term organosol is used for a plastisol that contains more than 10 parts of a solvent per 100 parts of resin (Rubin, 1990)). Microsuspension polymerisation or emulsion polymerisation is usually used to form the PVC for these applications. Both these processes result in the formation of PVC particles with a much smaller particle size than produced by suspension polymerisation processes. The small particle size means that the initial product has low porosity and so formulation with additives (e.g. plasticisers) is not possible using a dry-blending cycle, and instead a paste is formed. This paste or plastisol can then be spread, coated, rotationally cast or sprayed onto the desired item, or may be semi-gelled for storage (i.e. heat is applied to convert it into a semi-solid form). A wide range of plasticisers are used in these applications as the choice affects the viscosity of the plastisol, which is important in the further processing steps, and it is common for 2 or 3 different plasticisers to be used in a single formulation to achieve the desired final properties (Kirk-Othmer, 1996).

During the formation of finished products, the PVC formulation may be exposed to temperatures of 180°C for up to several minutes. In some processes, for example sheet and film production by calendering or spread coating there is the potential for volatilisation of the plasticiser as the hot plastic is exposed to the surrounding air. Processes involving injection moulding and extrusion are carried out in closed equipment and so little exposure of the hot product to air occurs and so the potential for volatilisation of the plasticiser is reduced. In some facilities filtering or incineration of the exhaust gas is used to reduce the air emissions from the process. It has been reported that concentrations of primary plasticiser (e.g. di-(2-ethylhexyl) phthalate (DEHP)) are typically 500 mg/m^3 in air extracted from spread coating ovens, which can be reduced to <20 mg/m^3 by the use of filtration equipment, with exhaust air incineration reducing the emission to practically zero (Kirk-Othmer, 1996). It has been reported (Kirk-Othmer, 1996) that the use of filters and/or incinerators in calendering and spread coating plants has been steadily increasing in recent years. Figures for 1990 are shown in **Table 2.2**. The figures refer to the percentage of the total phthalate plasticiser processed in each application. Of the processes listed in **Table 2.2**, medium-chain chlorinated paraffins are used mainly in spread coating (e.g. for wall coverings and PVC 'leather cloth') and calendered flooring.

Table 2.2   Exhaust air treatment in Western Europe by process in 1990 (Kirk-Othmer, 1996)

Process	Amount of phthalate plasticiser used in process (t/year)	Percentage of phthalate use undergoing exhaust air treatment	
		Filter treatment	Incineration
Spread coating	192,000	53%	22%
Slush, dip and rotational moulding	17,000	26%	6%
Automotive underseal	67,000		100%
Calendered sheet and film	138,000	23%	25%
Calendered flooring	31,000	15%	56%

The majority of flexible PVC is thought to be used in applications such as flooring, wall covering, upholstery, and sheaths for wire and cable.

The properties and compatibility of the chlorinated paraffin with both PVC and the primary plasticiser vary with both the carbon chain length and the degree of chlorination. Generally, as the chain length of the chlorinated paraffin is increased, its volatility decreases and so the potential for migration from the finished PVC is reduced. At the same time, however, the compatibility with PVC and the primary plasticiser is reduced. On the other hand, the compatibility of chlorinated paraffins with PVC and the primary plasticiser increases with increasing chlorination, and so the potential for migration is reduced, but the flexibility of the final product is also reduced. As a result of these properties, medium-chain chlorinated paraffins with varying degrees of chlorination are used in most applications (BUA, 1992).

For soft PVC products that require a high flexibility at normal and low temperatures, medium-chain chlorinated paraffins with chlorine contents around 40-45% wt. Cl are used as secondary plasticiser. Examples of applications for this type of PVC include coatings, some types of flooring, garden hose and shoe compounds. The secondary plasticiser is added at 10-15% by weight of the total plastic (BUA, 1992; Euro Chlor, 1999).

Medium-chain chlorinated paraffins with higher degrees of chlorination (typically around 50-52% wt. Cl) are more compatible with PVC and have a lower volatility than lower chlorinated analogues. They are used as secondary plasticisers in calendered flooring, cable sheathing and insulation and in general purpose PVC compounds. In heavily filled products, such as some types of calendered flooring, they can be used as the sole plasticiser at levels of around 10% in the finished product (Euro Chlor, 1999).

The more highly chlorinated medium-chain paraffins (e.g. 56-58% wt. Cl) are less volatile still and are used for softening plastics that are subject to higher temperatures during processing (BUA, 1992).

2.2.1.2   Paints and varnishes

Medium-chain chlorinated paraffins, with chlorine contents around 50-60% wt. Cl are used as plasticisers in some paints, varnishes and other coatings. The main areas of application appear to be in corrosion or weather resistant coatings/paints for steel constructions, ships, industrial flooring, containers, swimming pools, facades and road markings (BUA, 1992).

The medium-chain chlorinated paraffins can be used as plasticisers in paints based on many resins, but are most commonly used in chlorinated rubber or vinyl copolymer-based paints. The

chlorinated rubber-based paints are used in aggressive marine and industrial environments whereas the vinyl copolymer-based paints are used principally for the protection of exterior masonry.

A survey of the use of chlorinated paraffins in paints and coatings in the United Kingdom has been carried out (BCF, 1999). A total of 141 companies were contacted and initial responses were obtained from 106 of these. Of the companies responding, 22 (~21%) indicated that they used medium-chain chlorinated paraffins or other chlorinated paraffins. More detailed information on the use of chlorinated paraffins was obtained from 12 (~55%) of the 22 companies. The chlorine content of the chlorinated paraffins used range from around 40% wt. Cl to 70% wt. Cl (with the 70% wt. Cl substances being long-chain length ($\geq C_{18}$ products)). The types of paint/coating and the typical chlorinated paraffin contents are shown in **Table 2.3**.

Euro Chlor (1999) reported that the typical level of a medium-chain chlorinated paraffin in the formulated paint would be 4-15% by weight. After drying (evaporation of solvent) the medium-chain chlorinated paraffin content of the coating would be around 5-20% by weight.

In tonnage terms, the amount of chlorinated paraffins used in the United Kingdom in paints/coatings appears to be small; with a total of up to around 34 t/year being identified in the BCF survey (it is not possible to extrapolate this figure to give the total United Kingdom or EU usage). Further, it was found that paints containing chlorinated paraffins make up only a very small proportion of the total paint manufactured at a site (typically <1-2% of the total, up to 5% in some cases). The total number of sites in the United Kingdom manufacturing paints and coatings containing medium-chain chlorinated paraffins is estimated at around 30 (BCF, 1999).

Table 2.3   Chlorinated paraffin content of paints (BCF, 1999)

Coating type	Chlorinated paraffin content (% by weight)
Organic solvent borne chlorinated rubber primers and topcoats	1-5
Organic solvent borne chlorinated rubber systems for swimming pools/fishponds	5-20
Organic solvent borne zinc rich (epoxy) primers	2-5
Organic solvent borne acrylic container coatings	2-10
Organic solvent borne chemical and water resistant coatings	5-20
Organic solvent borne vacuum metallising lacquers	1-5
Organic solvent borne flame retardant coating for wood	1-5
Organic solvent borne intumescent coating for structural steel	20-30
Organic solvent borne floor paints	5-10
Organic solvent borne water-proofing coatings for walls	5

The BCF (1999) survey also tried to identify the number of sites where coatings containing medium-chain chlorinated paraffins might be used in the United Kingdom, but this did not prove to be possible. The major users of the paints are professional painters and specialist applicators, but some DIY paints containing medium-chain chlorinated paraffins may be used by the general public. In the United Kingdom, it was estimated that there would be around 40,000 users of coatings containing medium-chain chlorinated paraffins for water proofing of walls, with around 1,000-1,500 users of paints and coatings for other uses.

2.2.1.3 Adhesives/sealants

Chlorinated paraffins, including medium-chain ones, are used as plasticisers/flame retardants in adhesives and sealants. Examples include polysulphide, polyurethane, acrylic and butyl sealants used in building and construction and in sealants for double and triple glazed windows. The chlorinated paraffins are typically added at amounts of 10-14% wt. of the final sealant but could be added at amounts up to 20% wt. of the final sealant in exceptional cases. The medium-chain chlorinated paraffins used in these applications generally have a chlorine content of 50-58% wt. Cl (BUA, 1992; Euro Chlor, 1999).

The difference between an adhesive and sealant can be fairly blurred in that some sealants are used as adhesives and *vice versa*. Generally, sealants are considered to be materials that are installed into a gap or joint to prevent water, wind, dirt or other contaminants from passing through the joint or crack. Adhesives, on the other hand, are used to transfer loads and are typically designed with much higher tensile and shear strength than sealants (Palmer and Klosowski, 1997). The main use of medium-chain chlorinated paraffins in this area is in sealants.

2.2.2 Use as a flame retardant plasticiser

Chlorinated paraffins are used as flame retardant additives in some applications. However, when used primarily as a flame retardant, chlorinated paraffins with high chlorine content (e.g. 70% wt. Cl) are used. As medium-chain chlorinated paraffins are not produced with these high chlorine contents, they are not considered primarily as flame retardants. However, some applications make use of both their plasticising and flame retardant properties.

2.2.2.1 Rubber

Medium-chain chlorinated paraffins are used as softener (or process oil) additives with flame retardant properties for rubber. The chlorinated paraffins used generally have high chlorine content and are present at up to 15% wt. of the total rubber. The rubber is used in conveyor belts and also in building and automotive applications (BUA, 1992).

2.2.2.2 Plastics

As well as acting as (secondary) plasticisers in PVC and plastics, chlorinated paraffins also act as flame retardants in these materials. When used as a plasticiser, the chlorinated paraffin with moderate chlorine contents (e.g. >50% wt. Cl) will reduce to some extent the flammability of the final product, but when used specifically as a flame retardant, chlorinated paraffins with a high degree of chlorination (e.g. >C_{20} 70-72% wt. Cl) are used, along with a synergist e.g. antimony trioxide. When used as a flame retardant additive, up to around 5% wt. for PVC and up to 15% wt. for polystyrene and unsaturated polyester resins of the chlorinated paraffin may be added (BUA, 1992; Euro Chlor, 1999).

There are no medium-chain chlorinated paraffins available with 70-72% wt. Cl. contents and so they are not considered as specific flame retardant additives in plastics. The medium-chain chlorinated paraffins are generally used as flame retardant plasticisers (Euro Chlor, 1999).

2.2.2.3 Adhesives/sealants

Medium-chain chlorinated paraffins are used as flame retardant additives in some sealants. They also act as plasticisers and so have a dual function and no distinction is made between the two functions in this report as the amount (and types) of chlorinated paraffin used in a given sealant is similar regardless of whether the primary function is as a plasticiser or as a flame retardant (chlorinated paraffins with higher chlorine contents may be more effective as flame retardants).

2.2.3 Extreme pressure additive (Metal cutting/working fluids)

Medium-chain chlorinated paraffins are used in a wide variety of cooling and lubricating fluids used during metal cutting, grinding and forming operations. The two main types of lubricants used are water-based emulsions, whose function is mainly cooling, and oil-based lubricants. The medium-chain chlorinated paraffins used generally have a chlorine content of between 40 and 55% wt. Cl. The amount of chlorinated paraffin present in a given fluid depends on the final application (BUA, 1992).

For oil-based fluids the chlorinated paraffin content of the fluid ranges from about 5% wt. for light machining to up to 70% wt. for heavy drawing processes (metal forming fluids) (BUA, 1992).

The market for metal forming fluids in the United Kingdom is around 500 t/year. These contain up to 70% by weight of chlorinated paraffin, but the average content is around 50% by weight. (Euro Chlor, 1998). The chlorinated paraffin used in these applications is likely to be short-chain (C_{10-13}), for which no suitable alternative appears to be currently available.

The amount of chlorinated paraffin present in the water-based cooling lubricant concentrate is up to 4% as chlorine (i.e. up to around 8% as chlorinated paraffin). This is diluted with water to give a 3-5% aqueous emulsion that is used in grinding, rough machining and sawing applications (BUA, 1992). Thus the concentration of chlorinated paraffin in the final water-based fluid is around 0.2-0.4% wt.

2.2.4 Fat liquors (for leather)

Medium-chain chlorinated paraffins are used in fat liquors for leather. They are used in conjunction with sulphated or sulphonated oils (Kirk-Othmer, 1993), chlorosulphonated paraffins, natural fats and oils (Euro Chlor, 1998). Typically, medium-chain chlorinated paraffins with a relatively low chlorine content (e.g. 40% wt. Cl) are used in these applications.

In general the chlorinated paraffins are used in leathers for the top end of the quality range and give the following advantages (Euro Chlor, 1998):

> High light-fastness
> Strong binding to the leather compared to other additives (low migration)
> Dry feel surface finish with excellent suppleness.

The formulation of leather fat liquors is by a simple mixing process using an enclosed system at ambient temperature. The main components of the fat liquor are water, natural fats (e.g. fish oils), surfactants and the chlorinated paraffin. The chlorinated paraffin accounts for about 10% (range 5-15%) by weight of the formulated fat liquor.

The fat liquor is applied to the leather as a diluted solution. The fat liquoring step is the last stage of leather preparation. The amount of fat liquor used in this step is around 7-12%, based on the shaved weight of the leather to be treated (i.e. around 70-120 g of fat liquor/kg of leather). Since the fat liquor typically contains around 10% (range 5-15%) chlorinated paraffin, the amount of chlorinated paraffin used in this step is around 7-12 g chlorinated paraffin/kg leather (range 3.5-18 g chlorinated paraffin/kg leather). The process itself takes place in enclosed rotating drums at temperatures in the region of 40-60°C, with each batch taking around 1-4 hours depending on the end-product being produced. The pH of the reaction is carefully controlled throughout the process by the addition of formic acid to the emulsion (pH is changed from around 5.5 at the start to 3.6 at the end of the process). The pH is used to affect the nature of the leather surface, the rate of absorption of the fat liquor and the stability of the emulsion. The high binding efficiency of the leather for the chlorinated paraffin means that the relative composition of the additives in the fat liquor solution changes with time during the process. It is believed that not more than 2% of the original amount of chlorinated paraffin is present in the spent fat liquor solution at the end of the process (Industry estimate based on experience of the process (Euro Chlor, 1998)).

2.2.5   Carbonless copy paper

Another use that has been reported for chlorinated paraffins in general is as a solvent used in carbonless copy paper (BUA, 1992). The European consumption of carbonless copy paper was around 710,000 t/year in 1996, but was predicted to fall to around 660,000 t/year by 1998. Only a small proportion of this paper will contain medium-chain chlorinated paraffins. The most common applications for carbonless copy paper include delivery dockets, credit card slips and business forms

Carbonless copy paper consists of at least 2 sheets of paper. It is produced by coating the back side of the top piece of paper with gelatine (or synthetic polymer) capsules containing a colour former in a solvent. Medium-chain chlorinated paraffins can be used as the solvent in some applications. Binders, such as modified starch, polyvinyl alcohols, acrylates or carboxylated styrene-butadiene rubber latices, are used to attach the gelatine capsules to the paper. The upper surface of the bottom sheet is coated with reactive montmorillonite clay. For copy paper with three or more sheets, the middle sheets would be coated with the reactive clay on the upper surface and the gelatine capsules on the lower surface. Writing pressure results in breakage of the gelatine capsule which releases the colour former. This then reacts with the clay to form the colour on the surface of the lower sheet.

The majority of European manufacturers of carbonless copy paper are members of the Association of European Manufacturers of Carbonless Paper (AEMCP). Around 1992, all members of the AEMCP agreed to stop using chlorinated paraffins in the production of carbonless copy paper, and this agreement still remains in force today. Members of the AEMCP account for around 95% of the carbonless copy paper that is used in Europe.

Based on the figures reported, the amount of carbonless copy paper containing medium-chain chlorinated paraffins in the EU is at most 5% of the 660,000 t/year i.e. 33,000 t/year. This assumes that the 5% of companies not covered by the AEMCP agreement use medium-chain chlorinated paraffins in all the carbonless copy paper that they produce, which would appear to be unlikely.

2.3 EXISTING CONTROL MEASURES

A number of uses of medium-chain chlorinated paraffins will be covered under the Integrated Pollution Prevention and Control Directive (Directive 1996/61/EC). This will include (depending on the size of operation) production of medium-chain chlorinated paraffins, metal working (only large companies in the ferrous and non-ferrous metals sectors), some PVC and plastics compounding/conversion sites and leather processing sites (larger sites only) (Entec, 2004).

In Germany, chlorinated paraffin-containing wastes, e.g. metal working fluids with >2 g halogen/kg and halogen-containing plasticisers, are classified as potentially hazardous waste and are incinerated (BUA, 1992).

In Norway, medium-chain chlorinated paraffins are included in the national 'List of Priority Substances' for which emissions are to be substantially reduced by 2010 at the latest (Entec, 2004).

Within the UK, the MCCPs User Forum was formed in 2001. The Forum is made up of users and suppliers of medium-chain chlorinated paraffins and it aims to encourage best practice in the use of medium-chain chlorinated paraffins. The MCCPs User Forum has developed a targeted plan to reduce risk to the UK environment from medium-chain chlorinated paraffins, focusing on areas where advances can be made quickly, rather than seeking to be completely comprehensive. Specific activities that have been carried out include the following (Entec, 2004):

- A commitment to work towards an overall 25% reduction in emissions by December 2003, based on the estimate of emissions at that time.

- A voluntary agreement to operate best practice by companies using more than 50% of the medium-chain chlorinated paraffin tonnage in the PVC industry.

- A commitment by formulators of metal working fluids to operate to, and encourage, best practice.

- The agreement of the leather industry to adopt best practice should medium-chain chlorinated paraffins be used in leather treatment chemicals (they are not currently used in the United Kingdom).

- The development of a good practice guide by the only identified UK formulator of elastomers using medium-chain chlorinated paraffins.

- In addition, the MCCP User Forum believes that the paints industry and sealants and adhesive industry have demonstrated their commitment to operate to best practice.

2.4 NATURAL SOURCES

It is impossible to say categorically that naturally occurring chlorinated paraffins do not exist. A large number of organohalogen compounds are known to be produced naturally in the environment (especially in the marine environment, where there is an abundance of chlorine and bromine), and a comprehensive review of these has been published (Gribble, 1996). This study reported around 2,570 naturally occurring organohalogen compounds (detected up to mid-1994). A number of naturally occurring compounds with straight carbon chains in the C_{14} to C_{20} range were identified in this study, but none were paraffinic, and all contained one or more functional groups such as acid (COOH) or ester (COOR) groups, and none contained more than one halogen atom. Therefore although there is a possibility of natural formation, there is currently no

evidence of any significant natural source of the medium chain chlorinated paraffins currently in commercial production.

2.5   MEDIUM-CHAIN CHLORINATED PARAFFINS PRESENT AS IMPURITIES IN OTHER PRODUCTS

It has recently been reported that some long-chain chlorinated paraffins based on a C_{18-20} carbon chain length may contain a substantial proportion of C_{17} chlorinated paraffins, with only very small amounts of chlorinated paraffins of shorter chain lengths (Environment Agency, 2001). The typical levels reported were 17% C_{17} and <1% C_{16}, although the range of the C_{17} impurity was given as 10-20%. The amounts of chlorinated paraffins with carbon chain lengths of C_{15} or lower present in the C_{18-20} liquid products would be negligibly small.

These substances are used in PVC applications, paints and leather fat liquors. Regional releases from this source are considered further in Section 3.1.1.3. At a local level, the emissions to the environment of the C_{16-17} impurities present in certain types of long-chain chlorinated paraffins are related to the use of the long-chain chlorinated paraffin and so are considered in the risk assessment of that substance (Environment Agency, 2001).

3 ENVIRONMENT

3.1 EXPOSURE ASSESSMENT

3.1.1 General discussion

In this assessment, releases to the environment are considered in various scenarios. The background to these is explained more fully in the Technical Guidance Document (TGD, Chapter 3, EC, 2003). The local environment is considered to be the environment near to a site of release (e.g. a production, formulation or processing site). The regional environment is taken to represent a highly industrialised area (the size is 200 km, with 20 million inhabitants) and it is assumed that 10% of the total EU production and use takes place in this area. The continental environment is the size of the EU and is generally used to obtain "background" concentrations of the substance.

In the following Sections, releases to the environment have been estimated using both the default emission factors given in Appendix 1 of the Technical Guidance Document and industry-specific information where available. The industry-specific information is used in preference to derive the PECs later in this report. The PECs have been calculated using the EUSES program, which implements the methods given in the Technical Guidance Document.

3.1.1.1 Releases from production

3.1.1.1.1 Default release estimate

Default release estimates for production can be obtained using the emission factors contained in Appendix I of the Technical Guidance document. These are carried out for a typical production site, assuming a production of around 10,000-20,000 t/year.

The default emissions factors (Table A1.1 of Appendix I of the TGD: Main Category 1c; vapour pressure <1 Pa) are 0 to air and 0.003 (0.3%) to waste water. The number of days of release can be estimated as 300 (Table B1.1 of Appendix I of the TGD).

Therefore, using these figures, the default release estimates for the (10,000-20,000 t/year) production site are:

> 0 kg/day to air
> 100-200 kg/day to waste water (over 300 days)

3.1.1.1.2 Industry-specific release information

There are currently five production sites for medium-chain chlorinated paraffins in the EU[8]. Site specific release information has been received for four of these sites. The detailed information is contained in a confidential Annex and will be used to derive PECs for these sites. The estimated releases to water from the sites are as follows:

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[8] Entec (2004) indicates that a further production site is now operating within the EU as a result of the recent enlargement of the EU. This site is not considered further in this assessment.

- Site A: 65 kg/year in effluent to waste water treatment plant
- Site B: 19 kg/year to surface water after treatment
- Site C: 18 kg/year to surface water after effluent treatment
- Site D: 3 g/year to surface water after effluent treatment

A further site in the EU is understood to have started production recently. Qualitative information has been received from this site indicating that the releases to surface water/waste water from the production process will be similar to those found at the other sites.

Releases to air from the production process are thought to be negligible due to the low vapour pressure of the substance.

For regional releases, normally 10% of the total production is assumed to occur within a region. However, in the case of medium-chain chlorinated paraffins, there are only five production sites, and so as a worst case approach the highest known release figure from a single plant will be assumed to occur in the region. Therefore, the regional release from production will be assumed to be 65 kg/year to waste water.

3.1.1.1.3   Transportation losses

In theory chemicals can be released to the environment during loading of transport containers at productions site and unloading containers at the sites where the substance is used. These losses can take the form of spillages (to waste water) or volatilisation losses. Medium-chain chlorinated paraffins have a low vapour pressure and so any losses to the atmosphere should be negligible from loading or emptying containers. Losses to waste water could occur but these are considered as part of the general losses from production sites or use (formulation sites) and are already included in the release estimates reported in Sections 3.1.1.1.2 and 3.1.1.2 and so are not considered separately here.

3.1.1.2   Release from use

3.1.1.2.1   Release from use in PVC

Around 51,800 t/year of medium-chain chlorinated paraffins were used as (secondary) plasticisers in PVC in 1997. They are usually added at 10-15 parts per hundred resin (phr), although some of the more highly chlorinated substances (e.g. >52% wt. Cl) are more compatible with the PVC and can be used at concentrations of around 25 phr in e.g. a cable compound. Taking into account the other additives present in the PVC such as primary plasticiser, filler, stabiliser, lubricant etc., these loadings on a resin basis equate to a medium-chain chlorinated paraffin content of around 6-10% by weight based on the PVC compound for the typical 10-15 phr loading and 15% by weight based on the PVC compound for the higher 25 phr loading. For some applications higher loadings of medium-chain chlorinated paraffins on a resin basis may be used, for example where a C_{14-17}, 52% wt. Cl is used as sole plasticiser in a flooring composition, the rate of addition may be around 40-45 phr. However, in such cases the amounts of other additives, particularly fillers are also high (e.g. filler content may be as high as 300 or 400 phr) and this loading equates to a medium-chlorinated paraffin content of around 8-10% based on the final compound weight (Euro Chlor, 1999).

Medium-chain length chlorinated paraffins are not used as flame retardant additives in their own right but as secondary plasticisers with flame retardant properties, often in conjunction with other plasticisers such as phosphate esters (Euro Chlor, 1999).

From the above discussion it can be seen that a medium-chain chlorinated paraffin content of 10-15% by weight of the PVC compound/product is a reasonable worst case value, with a lower limit of around 6% by weight of the PVC. The higher medium-chain chlorinated paraffin contents of 15% by weight of the PVC are usually found in extrusion compounds, with lower levels being used in PVC for coating processes (Euro Chlor, 1999).

Default release estimation

Appendix 1 of the Technical Guidance Document gives default release estimates for substances used in the polymers industry. The release factors for plasticisers (Use Category 47) during the polymer processing step for thermoplastics are 0.01 (1%) to air (boiling point <400°C/unknown) and 0.001 (0.1%) to waste water (Table A.3.11 of Appendix I of the TGD).

Assuming around 51,800 t/year of medium-chain chlorinated paraffins are used in PVC in the EU at 10-15% by weight, then the amount of PVC containing them produced in the EU is 345,333-518,000 t/year (medium-chain chlorinated paraffin content of 6% by weight would give a higher total of 863,300 t/year of PVC). According to the Technical Guidance Document, 10% of this i.e. 34,500-51,800 t/year would be produced in a region. Using Table B3.9 of Appendix 1 of the Technical Guidance Document, the amount of PVC containing medium-chain chlorinated paraffins produced on a site would be 5% of this i.e. 1,725-2,590 t/year over 300 days. The amount of medium-chain chlorinated paraffin used to produce this plastic on a site would be 259 t/year.

Based on the above figures, the following default release estimates can be calculated:

- Local release: 259 kg/year or 0.86 kg/day to waste water
  2,590 kg/year or 8.6 kg/day to air

- Regional release: 5,180 kg/year to waste water
  51,800 kg/year to air

- Total EU release: 51,800 kg/year to waste water
  518,000 kg/year to air

Industry-specific release information

The Use Category Document on plastics additives (UCD, 1998) considers the possible release of additives from use in PVC. Around 220,000 t/year of flexible PVC is produced in the United Kingdom in closed, partially open and open systems, depending on the processing method used to produce the final product. Thus possible releases of medium-chain chlorinated paraffins from many different processes have to be considered. According to UCD (1998) the worst case amounts of flexible PVC processed at a site are 744 t/year for a site using open processing systems, 3,990 t/year for a site using partially open processing systems and 341 t/year for a site using closed processing systems. These are based on the known production volume of flexible PVC in the United Kingdom, along with information on the number and size distribution of production sites. It is thought that these figures will also be representative of the situation throughout the EU.

In the following calculations it will be assumed that all the flexible PVC produced at a site contains the medium-chain chlorinated paraffin at either 10% by weight (for coating processes)

or 15% by weight (for extrusion and other processes). These represent the situations where the chlorinated paraffin acts as a secondary plasticiser, which is the major use of medium-chain chlorinated paraffins in this area.

The amounts of medium-chain chlorinated paraffins estimated to be used on a polymer processing site are shown in **Table 3.1**.

Table 3.1   Estimated amounts of medium-chain chlorinated paraffins used at flexible PVC processing sites

Type of processing	Amount of PVC processed	Amount of medium-chain chlorinated paraffin used per site	
		10% MCCP in resins (coating process)	15% MCCP in resins (extrusion/other process)
Open system	744 t/year	74.4 t/year	112 t/year
Partially open system	3,990 t/year	[399 t/year]a	599 t/year
Closed system	341 t/year	[34.1 t/year]a	51 t/year

a)   Coating processes are usually carried out in open systems as defined in UCD (1998).

Raw materials handling (formulation – step 1)

Medium-chain chlorinated paraffins are liquids of low vapour pressure. Losses to the atmosphere are likely to be negligible when the substance is handled at ambient temperature. The liquid plasticisers are usually transported and handled in bulk, using enclosed storage systems and so a minimal loss by spillage can occur. The worst case release figure for loss through spillage is estimated at 0.01% (UCD, 1998).

Using this figure, the release to the environment from sites using the various processing types is (note: coating operations are usually carried out only in open processing systems as defined in UCD (1998)):

- Open processing: coating   7.4 kg/year (0.025 kg/day)
                              extrusion/other   11.2 kg/year (0.037 kg/day)
- Partially open processing: extrusion/other   59.9 kg/year (0.20 kg/day)
- Closed processing: extrusion/other   5.1 kg/year (0.017 kg/day)

The total usage of medium-chain chlorinated paraffins in the EU in this application is assumed to be 51,800 t. The EU-wide release from raw materials handling can therefore be estimated at 5.18 t/year. According to the Technical Guidance Document, the regional release will be 10% of this figure, around 518 kg/year.

As these release figures refer to spillage, the releases can be assumed to enter the waste water stream as a worst case approach.

Compounding (formulation – step 2)

There are two general methods used for compounding PVC: dry blending and plastisol blending (UCD, 1998; see Section 2.2.1.1).

Dry blending is used to prepare blends for extrusion, injection moulding and sometimes calendering (Banbury blending is also occasionally used to prepare blends for calendering, but the emissions from this processes are similar to those associated with dry blending (UCD, 1998)). Dry blending accounts for the compounding of around 65-70% of all plasticisers used in PVC. Dry blending involves mixing the PVC powder/granules with the plasticiser using a high

speed rotating agitator which heats the material by friction (maximum temperature reached is 100-120°C). The plasticiser is completely absorbed by the PVC in the process, and the only source of release to air is from the hot material. The loss to air of a plasticiser such as di-(2-ethylhexyl) phthalate (DEHP) from the process is estimated to be a maximum of 0.01%. However, some medium-chain chlorinated paraffins used in PVC are slightly more volatile than DEHP (e.g. vapour pressure of DEHP is around $2.2 \cdot 10^{-5}$ Pa at 20°C, compared with around $2.7 \cdot 10^{-4}$ Pa for medium-chain chlorinated paraffin with a 52% wt. Cl content). In this situation, it is suggested that the release to air could be around 5 times higher (UCD, 1998).

Information is available from Industry comparing the loss (volatility) of medium-chain chlorinated paraffins with that of DEHP from PVC (Euro Chlor, 1999). This is summarised below:

a) weight loss on heating plasticiser alone

	Weight loss after 4 hours heating at 150°C	Weight loss after 4 hours heating at 180°C
DEHP	0.3%	1.9%
C_{14-17}, 45% wt. Cl	0.7%	2.8%
C_{14-17}, 52% wt. Cl	0.5%	1.4%
C_{14-17}, 58% wt. Cl	0.3%	0.8%

b) weight loss from PVC

		Ageing loss from PVC compounds (BS 2782 methods 465A and B, 1979)
56 parts DEHP: 0 parts C_{14-17},	45% wt. Cl	0.55%
50 parts DEHP: 10 parts C_{14-17},	45% wt. Cl	0.85%
43 parts DEHP: 20 parts C_{14-17},	45% wt. Cl	1.0%
36 parts DEHP: 30 parts C_{14-17},	45% wt. Cl	1.15%
51 parts DEHP: 10 parts C_{14-17},	52% wt. Cl	0.6%
43 parts DEHP: 20 parts C_{14-17},	52% wt. Cl	0.7%
37 parts DEHP: 30 parts C_{14-17},	52% wt. Cl	0.85%

From these data, although not directly comparable to the losses expected from dry blending of PVC, it can be seen that the C_{14-17}, 45% wt. Cl substance appears to be around 3 times more volatile than DEHP and the C_{14-17}, 52% wt. Cl substance appears to be around 1.4 times more volatile than DEHP from PVC (see Appendix G for further details of these calculations). The C_{14-17}, 58% wt. Cl substance is of similar or slightly lower volatility to DEHP. When the data for heating of the plasticiser alone are considered, it appears that the 45% wt. Cl substance is around twice as volatile as DEHP. However, the relative volatility of the two plasticisers from PVC will depend to some extent on their compatibility (or solubility) in the PVC, as well as their vapour pressure. As discussed in Section 2.2.1.1, the compatibility of the chlorinated paraffin with both PVC and the primary plasticiser varies with both the carbon chain length and degree of chlorination. Therefore a factor of 3 rather than a factor of 5 as suggested in UCD (1998) appears to represent a reasonable worst case in order to take into account the slightly higher volatility of the 45% wt. Cl substance compared to DEHP. This value will be used as a basis for the local PEC calculations as a worst case. For the 52% wt. Cl substance, a factor of 1.4 appears to be reasonable in order to take into account its slightly higher volatility compared to DEHP. This will be taken into account in the estimation of regional releases. The effect of the lower volatility of the 52% wt. Cl product on the local releases is considered further in Appendix G.

Based on these data, and the information reported in UCD (1998), the worst case release factor for a 45% wt. Cl medium-chain chlorinated paraffins from the dry blending process will be taken as 0.03% to air (the equivalent emission factor for a 52% wt. Cl substance will be 0.014%).

Approximately 30-35% of all plasticiser use in PVC is in plastisol applications. Plastisol blending takes place in stirred vessels at ambient temperature. Cooling is used to remove any heat generated by friction. The releases to the air from this process are thought to be negligible due to the lower temperatures involved. Losses due to raw materials handling in this process are covered in the previous Section.

The estimated worst case emissions of a 45% wt. Cl medium-chain chlorinated paraffin to the air from the dry blending process are shown below:

Open processing:	extrusion/other	33.6 kg/year (0.11 kg/day)
Partially open processing:	extrusion/other	180 kg/year (0.60 kg/day)
Closed processing:	extrusion/other	15.3 kg/year (0.051 kg/day)

The releases to air from plastisol blending for coating processes are negligible.

The total usage of medium-chain chlorinated paraffins in the EU in this application is 51,800 t. Of this, 52% wt. Cl products (emission factor 0.014% to air) are thought to make up around 2/3 of the total, with the remainder being more volatile (e.g. 45% wt. Cl) products (emission factor 0.03%). If it is assumed that the split of this use between dry blending and plastisol blending is the same as for plasticisers in general, then up to 70% of this could be used in the dry blending process. Thus the EU-wide release from compounding can be estimated at 7.01 t/year (3.38 t/year of 52% wt. Cl product and 3.63 t/year of 45% wt. Cl product). According to the Technical Guidance Document, the regional release will be 10% of this figure, around 0.70 t/year. These releases are initially to the air.

Conversion (processing)

This Section considers the releases from several processing methods. The release estimates assume that some fume reduction equipment is used. Such equipment is generally found at large sites (using >250 t of plasticiser/year). The equipment is less common at smaller plants (using <250 t of plasticiser/year) and the releases for some processes could be around 10 times higher at plants where fume reduction equipment is not present (UCD, 1998). The 250 t plasticiser limit is considered to be a reasonable criterion to distinguish between large plants and smaller plants. This figure refers to the total plasticiser use in the flexible PVC (medium-chain chlorinated paraffins are usually used with other plasticisers). According to the UCD (1998), the typical total plasticiser level in flexible PVC is 30-50%. Thus 250 t/year plasticiser is equivalent to a production of around 500-830 t/year of flexible PVC. As can be seen from the figures derived in **Table 3.1**, the size of the open system site and partially open system site can be taken to represent large sites, where fume reduction equipment is used, whereas the closed system site use falls into the size of site where fume reduction equipment may not always be used. This will be taken into account in the release estimates derived for closed systems. The following Sections describe the possible losses to the environment (atmosphere) from the various processes. The resulting release estimates for the worst case sites, region and the total EU are shown in **Table 3.2**.

Calendering (open system)

A reasonable worst case emission of plasticiser (e.g. DEHP) from a calendering process is around 0.05% to air. For a more volatile plasticiser such as a 45% wt. Cl medium-chain

chlorinated paraffin, it is suggested that the emission factor is increased by a factor of around 3 (see Compounding Section). Thus, the air emission factor for a 45% wt. Cl medium-chain chlorinated paraffin is around 0.15% (the equivalent emission factor for a 52% wt. Cl product would be 0.07%). This assumes emission reduction equipment is used (UCD, 1998).

Extrusion (partially open or closed system)

The major types of flexible PVC products produced by extrusion are wire, cable and hoses, and blow moulded film. For wire, cable and hose production, there is no emission/exposure from the extruder itself. The main source of release is likely when the hot material leaves the die. As the surface area and exposure (of the hot plastic to air) time is lower than for calendering processes, a release factor of 0.01% to air is estimated for a typical plasticiser (e.g. DEHP). Again, for a 45% wt. Cl medium-chain chlorinated paraffin, the emission factor to air will be around 3 times this value (0.03%), to take into account its higher volatility (see Compounding Section) (the equivalent factor for a 52% wt. Cl product would be 0.014%). This figure assumes emission reduction equipment is used. For applications where this equipment is not generally used, the emission factor for a 45% wt. Cl medium-chain chlorinated paraffin could be around 10 times this value (i.e. 0.3%) (the equivalent factor for a 52% wt. Cl product would be 0.14%).

Injection moulding (closed system)

Injection moulding can be considered to be comparable to extrusion except that both the moulding and cooling phases of the process take place in closed systems. Therefore, losses should be lower than for extrusion. However, as a worst case UCD (1998) recommends a release factor of 0.01% for a general plasticiser (e.g. DEHP). Again, for a more volatile plasticiser such as a 45% wt. Cl medium-chain chlorinated paraffin the release factor would be 0.03% for site with emission reduction equipment and 0.3% for sites with no emission reduction equipment (the equivalent factors for a 52% wt. Cl product would be 0.014% and 0.14% respectively).

Plastisol spread-coating (open system)

Spread coating products include articles such as cushioned flooring, wall coverings, tarpaulins etc. These products are gelled in tunnel ovens heated with hot air at about 180°C. The release figure for a typical plasticiser for the process is thought to be around 1% to air within the oven (not all of this will reach the external environment), based on both calculation and laboratory experiments (UCD, 1998). This figure refers to the air leaving the equipment. Not all of this reaches the environment since condensation takes place in cooler pipes, ducts and stacks. Air treatment is thought to be relatively commonplace within the industry (75% of activity in 1989; approaching 100% in 1998 (UCD, 1998)). The two types of air treatment used are air filtration (removes 95% of the plasticiser in the air) and incineration. Thus the overall emission factors for a typical plasticiser such as DEHP is between 0-0.05% to air for the vast majority of sites with air emission treatment and 0.5% to air from a plant with no air treatment. Again, these figures refer to a plasticiser like DEHP. For a more volatile plasticiser such as a 45% wt. Cl medium-chain chlorinated paraffin (see Compounding Section), the emission factors could be around 3 times higher, i.e. 0-0.15% to air assuming air emission treatment and 1.5% to air assuming no air emission treatment [the equivalent factor for a 52% wt. Cl product would be 0.07% assuming air emission treatment and 0.7% assuming no air emission treatment].

Other plastisol processes

Other processing methods for plastisol PVC include car underbody coating and sealing, rotational coating, dipping and slush moulding. Of these, car underbody coating and sealing is the most important in terms of volume, but it is thought that medium-chain chlorinated paraffins are not used in this application. In these processes, the coatings are dried in long air-heated tunnel ovens at temperatures of 130-160°C. The ovens in this industry have integrated air incinerators since the same process is used to simultaneously dry paint coats (UCD, 1998). Therefore, the releases of medium-chain chlorinated paraffins from this process, if they are used, should be near zero.

The other possible plastisol processing steps are all small volume applications. The releases from dip coating and slush moulding are likely to be similar to those from spread coating and so will not be considered separately in the release estimation. Rotational moulding takes place in closed moulds and so the loss of plasticiser to the atmosphere from this process will be low.

Summary of worst case release estimates from PVC conversion (processing)

The estimated worst case releases of medium-chain chlorinated paraffins to air from plastic processing obtained for various sites using the information reported above are shown in **Table 3.2**. As can be seen from the emission estimates, the actual estimated releases from the various sites are very similar. This is because although the overall emission factors at large sites may be lower than small sites, due to use of emission controls on air releases, this is counteracted to some extent by the higher amounts of plastics processed at such sites. The emissions have been estimated based on a 45% wt. Cl product as a worst case. The emissions for a 52% wt. Cl product would be expected to be lower than these figures due to the lower volatility. Appendix G considers the releases from sites using this type of product.

For the regional release estimate, the relative proportions of the two main plasticiser types (e.g. ≤45% wt. Cl products and ≥52% wt. Cl products) have to be taken into account as emission factors have been derived for both types of product. Of the total plasticiser use in PVC, 52% wt. Cl products make up around 2/3 of the total, the remainder being more volatile (e.g. 45% wt. Cl) products.

The actual breakdown of the use of medium-chain chlorinated paraffins between the various processes is not known. However, UCD (1998) gives the following breakdown of the production of flexible PVC: 25% in closed systems; 49% in partially open systems and 26% in open systems. If the same approximate breakdown applies to the medium-chain chlorinated paraffins then a worst case release figure of 204.3 t/year to air for the polymer processing step can be estimated for the EU (assuming a release of 1.5% from open systems and 0.3% from partially open and closed systems for the 45% wt. Cl product and a release of 0.7% from open systems and 0.14% from partially open and closed systems for the 52% wt. Cl product, and an EU consumption of medium-chain chlorinated paraffins of 51,800 t/year). The regional release will be 10% of this figure, 20.4 t/year. These figures assume that no air emission control is applied. The estimated emissions would be a factor of 10 lower if this was taken into account. The actual overall proportion of the industry with such controls is currently unknown, but the use of such equipment is relatively common place, particularly at large sites, and is becoming increasingly common at other sites.

According to the Use Category Document (UCD, 1998), the releases to air are as hot gases. For substances with low vapour pressures such as medium-chain chlorinated paraffins the possibility of condensation as the gas cools needs to be considered. This may lead to some of the releases

initially to air entering other waste streams such as water. The Use Category Document gives no guidance as to the fraction of the air release that could eventually end up in waste water. As a worst case approach it could be assumed that 50% of the release to air would eventually reach waste water. In the absence of other information, this assumption will be used later in the PEC calculations.

Industry has recently carried out workplace monitoring for medium-chain chlorinated paraffins at four PVC processing (conversion) plants in the EU (MCCP User Forum, 2003). The plants represented 21.7% of the total United Kingdom use in this area and used a variety of emission treatment methods (e.g. thermal oxidisers or vapour recovery) prior to release into the atmosphere. The emissions to air from the process vents were found to be zero at one plant (using 900 t/year of medium-chain chlorinated paraffins) equipped with a thermal oxidiser, and were assumed to be the same at another similar plant (using 300 t/year of medium-chain chlorinated paraffins). The emission to air from two other sites (using a total of 820 t/year of medium chain chlorinated paraffin) was determined to be a total of 6.4 kg/year.

To put these measured emission data into context, the estimated total emission to air during conversion (injection moulding or extrusion; assuming emission control) using the UCD (1998) methodology for a site using 820 t/year of medium chain chlorinated paraffin would be around 246 kg/year for a 45% wt. Cl substance and 115 kg/year for a 52% wt Cl substance. This indicates that the methods presented in UCD (1998) may overestimate the actual emissions from plastic processing in general, particularly at well-controlled sites. However, the monitoring study only considered air emissions from a limited number of processing sites in the United Kingdom and so it is difficult to extrapolate these results to the 'realistic worst case' representative of the whole of the EU. Therefore the emissions estimated in **Table 3.2** will be considered in the PEC calculations.

Table 3.2 Estimated worst case emissions of medium-chain chlorinated paraffins to air from processing sites[d]

Process	Type of system	Release factor to air		Amount of MCCP used/site	Release of MCCP/site[b]	
		Air emission control	No air emission control	(t/year)	Air emission control	No air emission control[c]
Calendering	Open	0.15%	1.5%	112	168 kg/year (0.56 kg/day)	
Extrusion	Partially open	0.03%	0.3%	599	180 kg/year (0.6 kg/day)	
	closed	0.03%	0.3%	51		153 kg/year (0.51 kg/day)
Injection moulding	closed	0.03%	0.3%	51		153 kg/year (0.51 kg/day)
Plastisol spread-coating[a]	open	0.15%	1.5%	74.4	112 kg/year (0.37 kg/day)	

a) Release from other plastisol processes such as dip coating and slush moulding is expected to be similar. Release from processes such as car underbody coating and sealing (if medium-chain chlorinated paraffins are used), and rotational moulding are thought to be negligible.
b) In the PEC calculations it will be assumed that 50% of the air emissions eventually reach waste water at the site.
c) Taken to represent a small site using closed processing where fume reduction equipment may not always be used.
d) Estimated based on 45% wt. Cl products. The equivalent estimates for 52% wt. Cl products are given in Appendix G.

3.1.1.2.2 Releases from use as a plasticiser/flame retardant in other plastics and rubber

Chlorinated paraffins are used as additives in plastics other than PVC, mainly as flame retardant additives. Although they will also have some plasticising properties in these materials, plasticisers are not generally used in plastics other than flexible PVC. According to UCD (1998) over 98% of plasticiser use is in flexible PVC, thus the use of chlorinated paraffins in plastics other than PVC can be considered to be primarily as a flame retardant additive. However, the types of chlorinated paraffins used in these applications are the solid products (e.g. $>C_{20}$) with around 70% wt. Cl chlorine contents and so are not subject to this risk assessment (Euro Chlor, 1999). The use of medium-chain chlorinated paraffins as a plasticiser (in PVC) is considered in detail in Section 3.1.1.2.1.

Medium-chain chlorinated paraffins are used as a flame retardant softener (or process oil) in rubber and are added at a maximum content of around 15% by weight of the final rubber. It is also possible that small amounts of medium-chain chlorinated paraffins may be used for similar functions in other polymeric materials.

The amount of medium-chain chlorinated paraffin used for this purpose in the EU was 2,146 t/year in 1997. The individual amounts used in the various plastic types and rubber are not known, although the main use in this area is in rubber (Euro Chlor, 1999). However, since the processes involved for both rubber and plastic are generally similar (in that a compounding step involving mixing of the plasticiser with the polymer, followed by a shaping/curing operation involving heat are used), a generic approach to this area can be undertaken.

For rubber, a typical loading of up to 15% by weight of the chlorinated paraffin in the rubber is used. This is similar to the levels of medium-chain chlorinated paraffins used in PVC (see Section 3.1.1.2.1) and it will be assumed that this would also apply to any use of medium-chain chlorinated paraffins in other plastics. Thus, the amount of rubber and plastic (other than PVC) containing the medium-chain chlorinated paraffin produced in the EU would be around 14,307 t/year.

Default release estimation

Appendix 1 of the Technical Guidance Document gives default release estimates for substances used in the polymers industry. The release factors for flame retardants (Use Category 22) during the polymer processing step for thermoplastics are 0.001 (0.1%) to air (boiling point <300°C/unknown; vapour pressure <1 Pa) and 0.0005 (0.05%) to waste water (Table A.3.11 of Appendix I of the TGD). For thermosetting resins the release factor to air is zero and the release factor to waste water is 0.0005 (0.05%). The default release factors assuming that the main function is as a plasticiser are similar to those reported for plasticiser use in PVC in Section 3.1.1.2.1.

Assuming around 2,146 t/year of medium-chain chlorinated paraffins are used as a flame retardant in rubber and plastics in the EU at 15% by weight, then the amount of elastomer/polymer containing them produced in the EU is 14,307 t/year. According to the Technical Guidance Document, 10% of this i.e. 1,431 t/year would be produced in a region. Using Table B3.9 of Appendix 1 of the Technical Guidance Document, the amount of polymer/elastomer containing medium-chain chlorinated paraffins produced on a site would be 15% of this i.e. 215 t/year over 86 days. The amount of medium-chain chlorinated paraffin used to produce the polymer/elastomer on a site would be 32.3 t/year.

Based on the above figures, the following default release estimates can be calculated:

Local release:	16.2 kg/year or 0.19 kg/day to waste water
	32.3 kg/year or 0.38 kg/day to air
Regional release:	107 kg/year to waste water
	215 kg/year to air
Total EU release:	1,073 kg/year to waste water
	2,146 kg/year to air

Industry-specific release estimation

The Use Category Document on plastics additives (UCD, 1998) details possible releases to the environment from the use of flame retardants in plastics. These will be used here to determine the possible releases for use of medium-chain chlorinated paraffins in plastics. Although the processing (curing/vulcanisation) of natural and synthetic rubber takes place at lower temperatures (e.g. 125-150°C) than for many polymers, the same sorts of processes as for plastics (e.g. injection moulding, extrusion calendering etc.) can be used (Bouton, 1992; Kirk-Othmer, 1997). Therefore, as the compounding and subsequent processing of plastics and rubber are essentially similar, and use similar equipment a similar (but possibly smaller) releases would be expected from the use of medium-chain chlorinated paraffins in rubber.

In Section 2.2.2, it was reported that chlorinated paraffins could be used as a flame retardant in polystyrene. This will be used here as an example for estimating the releases to the environment from plastics other than PVC in general. The releases from use in PVC are given in Section 3.1.1.2.1. Although the calculations are carried out for polystyrene, the release estimates detailed in the UCD (1998) depend more on the processes used than the type of plastic being processed and so the figures obtained are likely to be reasonably representative of the polymers industry as a whole. As mentioned above, the processes used in manufacture of rubber are essentially similar to those used in plastic manufacture, except that they may be carried out at lower temperatures (and hence may lead to lower emissions). As many of the releases during plastic processing are to the atmosphere, these can also be considered to be a worst case estimate for the releases from rubber processing.

According to UCD (1998) nearly all plastics containing flame retardants are processed using closed systems (these are defined as methods in which the materials are converted in almost completely enclosed environments and include injection and compression moulding and extrusion). A reasonable estimate for the amount of polystyrene processed at a large site would be 623 t/year for a site using closed systems. This size of site would use around 93 t/year of medium-chain chlorinated paraffin if all the plastic contained it at 15% by weight.

Raw materials handling (formulation – step 1)

Medium-chain chlorinated paraffins are liquids of low vapour pressure. Losses to the atmosphere are likely to be negligible when the substance is handled at ambient temperature. The liquid plasticisers are usually transported and handled in bulk, using enclosed storage systems and so minimal loss by spillage can occur. The worst case release figure for loss through spillage is estimated at 0.01% (UCD, 1998).

Using this figure, the release to the environment from a polymer processing site can be estimated at 9.3 kg/year (0.031 kg/day) to waste water.

The total usage of medium-chain chlorinated paraffins in the EU in this application is 2,146 t. Thus, the EU-wide release from raw materials handling can be estimated at 215 kg/year. According to the Technical Guidance Document, the regional release will be 10% of this figure, around 21.5 kg/year.

As these release figures refer to spillage, the releases can be assumed to enter into waste water as a worst case approach.

Compounding (formulation – step 2)

Compounding of plastics is usually by a dry process, where the base polymer and additives are mixed together. The mixing process generates heat or is heated externally and so there is a possibility for volatilisation from the process. The main source of loss from the process is dust generated when adding solid components. Since medium-chain chlorinated paraffins are liquids, no dust will be generated from them and so the only source of loss is volatilisation to the atmosphere. This is estimated at 0.002% for organic flame retardants (UCD, 1998). This figure is based on the assumption that the medium-chain chlorinated paraffins used as plasticiser/flame retardants in plastic and rubber are of similar volatility to the least volatile phthalate plasticisers used in PVC (e.g. of similar volatility to DIDP (vapour pressure ~$3.3 \cdot 10^{-6}$ Pa at 20°C)). However, the medium-chain chlorinated paraffins used in rubber/other plastic all have chlorine contents >50% wt. Cl. In Section 3.1.1.2.1, it was seen that these plasticisers are of similar or slightly lower volatility than DEHP, and so it seems reasonable to base the release figure for the medium-chain chlorinated paraffin on those for DEHP rather than the less volatile DIDP. This assumption is reasonable since medium-chain chlorinated paraffins with chlorine contents >50% wt. Cl have estimated vapour pressures of the order of <$4 \cdot 10^{-5}$ Pa at 25°C (see Appendix B), which is similar to that of DEHP (vapour pressure ~$3.4 \cdot 10^{-5}$ Pa at 20°C). The figure for loss to air of DEHP during compounding is 0.01% (UCD, 1998) and this figure will be applied here for loss of medium-chain chlorinated paraffins.

The estimated release of medium-chain chlorinated paraffins from a polymer compounding site is 9.3 kg/year (0.031 kg/day), initially to air.

The total usage of medium-chain chlorinated paraffins in the EU in this application is 2,146 t. Thus the EU-wide release from polymer/elastomer compounding can be estimated at 215 kg/year. According to the Technical Guidance Document, the regional release will be 10% of this figure, around 21.5 kg/year.

These releases are thought to occur initially to air. Similar to the case discussed above for PVC, the possibility exists that as the gases cool; the medium-chain paraffin could condense out and eventually enter into waste water during cleaning etc. To take this into account in the PEC calculations, it will again be assumed that 50% of the releases initially to air will enter into waste water and 50% will remain in the air.

Conversion (processing)

The losses to the atmosphere during polymer processing in closed processes are estimated at 0.01% for an additive of similar volatility to DEHP (UCD, 1998). However, for sites producing <750 t/year of plastic, it is recommended that the release factor is increased by a factor of 10 to allow for the fact that air emission control equipment may not be present. Thus a worst case release figure of 0.1% to air will be assumed during polymer conversion.

The estimated release of medium-chain chlorinated paraffins to air from conversion at a polymer processing site is thus 93 kg/year (0.31 kg/day) to air.

The total usage of medium-chain chlorinated paraffins in the EU in this application is 2,146 t. Thus the EU-wide release from polymer/elastomer conversion (processing) can be estimated at 2,146 kg/year. According to the Technical Guidance Document, the regional release will be 10% of this figure, around 215 kg/year.

Again, it will be assumed that these air emissions will distribute 50:50 between air and water at the site as the gases cool.

Other information

Another estimate for the release to the environment from use of chlorinated paraffins in rubber has been reported (Government of Canada, 1993). This gave a Swedish estimate for the total release from the process as <0.001% of that used. No indication as to whether this was a release to waste water or to air was given.

No information is available as to the amount of medium-chain chlorinated paraffin used in rubber alone in the EU. Using the default estimate for the amount of medium-chain chlorinated paraffin used on a site of 32.3 t/year (see above) over 86 days, then the amount of medium-chain chlorinated paraffin released to the environment from such a site can be estimated at <0.323 kg/year (or <0.004 kg/day). This figure is around a factor of 10 lower than the values estimated above, based on the worst case releases from plastics processing. This may indicate that, due to the generally lower processing temperatures involved, the losses of the flame retardant from manufacture of rubber are lower than those associated with the manufacture of plastic.

3.1.1.2.3   Releases from use as a plasticiser/flame retardant in sealants/adhesives

Around 3,541 t of medium-chain chlorinated paraffins were thought to be used in the production of paints and sealants/adhesives in the EU in 1997 (see Section 2.2). No information on the amounts used in sealants/adhesives alone is available. However, Euro Chlor (1999) indicate that around 2/3 of the total are used in sealants/adhesives, and so as a worst case it will be assumed that 2,360 t of medium-chain chlorinated paraffins are used in sealants/adhesives alone.

The main function of the medium-chain chlorinated paraffin is as a plasticiser and/or flame retardant additive. It is thought that the medium-chain chlorinated paraffins used have a chlorine content of around 55-60% by weight and are used at a typical concentration of 10-14%, with a maximum of around 20% by weight of the sealant/adhesive. This means that the amount of sealant/adhesive containing medium-chain chlorinated paraffin can be estimated as around 11,800-23,600 t/year.

Default release estimation

No default release figures are given in the Technical Guidance document for this use.

Industry-specific information

Sealants are produced by mixing the required additives with a viscous liquid polymer. Both low and high shear mixers may be used, depending on the surface area of the filler used in the formulation (Palmer and Klosowski, 1997). As most sealants are moisture sensitive (particularly

the one-part sealants), no water use is likely in the process and so releases to waste water are likely to be very low.

Information has been received from several sealant manufacturers in the United Kingdom. Of the 22 companies contacted, responses were received from 10. Not all companies reported using medium-chain chlorinated paraffins but where they were used, a consistent picture of the industry was obtained. Only minor amounts of medium-chain chlorinated paraffins appear to be used in adhesives.

Medium-chain chlorinated paraffins are used in both 1-part and 2-part sealants, and similar methods are used to produce both types.

Typically, sealants are made in a batch process of around 1,000 kg at a time. The process is simple mixing, sometimes under gentle heat (e.g. up to around 40°C) and is usually carried out under vacuum to avoid moisture entering the process. A typical medium-chain chlorinated paraffin content of the sealant would be 5-20% by weight and typically 1-2 t of a sealant containing the chlorinated paraffin may be manufactured at a site per week. The amount of medium-chain chlorinated paraffins used on a site is typically of the order of 10-30 t/year.

Once formulated, the sealant is pumped directly from the mixing vessel to fill cartridges (e.g. for 1-part sealants) or tins (e.g. 2-part sealants).

Losses to waste water during the manufacture of sealants are reported to be low or zero as water is not used in the process (most sealants are moisture sensitive). Scrap material and machine cleaning can account for up to 5% solid waste. Cleaning between batches is minimised by the use of dedicated equipment or by starting with light coloured product and progressing through to darker coloured products. Generally, solid material is removed from the equipment by hand. Solvent cleaning of the equipment can also occur. These solvents are collected and disposed of at the end of their useful life by registered waste contractors. Due to its physico-chemical properties, the chlorinated paraffin is likely to be associated with the solid waste phases during the cleaning of equipment and so releases to waste water from the process are likely to be very low (the releases to water due to leaching from the sealant are considered in Section 3.1.2.1.4).

Some sealants (e.g. 1-part) are supplied in the form of cartridges typically containing around 500 g of sealant. In use, around 2-3 cm^3 of sealant are estimated to remain in the nozzle and tube when the cartridge has been emptied. This will quickly skin over and be protected inside the packaging. The final destination of these discarded cartridges will be as waste to landfill.

Other sealants (e.g. 2-part) are supplied in tins. Immediately before use, a curing agent is added to the tin and mixed with the sealant. The sealant is then filled into a cartridge on-site prior to application. Again, any unused material will quickly cure and set hard and will be disposed of in an appropriate manner. For industrial applications in the United Kingdom, the waste sealants are treated as special waste rather than general building waste.

3.1.1.2.4   Release from use as a plasticiser in paints and varnishes

The amount of medium-chain chlorinated paraffins used in paints is unknown. A combined figure of 3,541 t/year has been reported for the amounts used in the EU in paints and sealants/adhesives in 1997, and Euro Chlor (1999) indicate that 1/3 of this total is used in paints, although other industry sources (BCF, 1999) have indicated that the actual amount may be lower than this. As a worst case approach it will be assumed that 1,180 t/year is used in paints.

The function of the chlorinated paraffin in paint is to act mainly as a plasticiser. The chlorinated paraffin content of paint is usually between 5-25% by weight, with most in the region 5-15% by weight. The most common paint types in which medium-chain chlorinated paraffins may be used are chlorinated rubber-based and vinyl copolymer-based paints.

Assuming a 5-25% chlorinated paraffin content, the amount of paint produced in the EU containing medium-chain chlorinated paraffins can be estimated at around 4,720-23,600 t/year.

Default release estimation

Appendix 1 of the Technical Guidance Document gives default emission factors for both the formulation and use of paints.

Formulation

The default emission factors for formulation of paints are given in Table A2.1 of Appendix I of the TGD and are 0.001 (0.1%) to air (vapour pressure <10 Pa; use of dedicated equipment) and 0.003 (0.3%) to waste water.

The amount of paint formulated in a region is estimated to be between 472 and 2,360 t/year (contains 118 t of medium-chain chlorinated paraffins at between 5 and 25% by weight of paint). From Table B2.3 of Appendix I of the TGD, the amount of paint formulated on one site can be estimated as 2,360 t/year over 300 days (5% chlorinated paraffin content) or 472 t/year over 300 days (25% chlorinated paraffin content). Thus the amount of medium-chain chlorinated paraffin formulated at a site is 118 t/year over 300 days.

Based on the above information, the default release estimates for medium-chain chlorinated paraffins from formulation of paints are shown below:

Local release:	354 kg/year or 1.2 kg/day to waste water
	118 kg/year or 0.39 kg/day to air
Regional release:	354 kg/year to waste water
	118 kg/year to air
Total EU release:	3,540 kg/year to waste water
	1,180 kg/year to air

Processing (application of paints)

The default emission factors from industrial use of paints containing medium-chain chlorinated paraffins are given in Table A3.15. The emission factors are 0 to air (Use Category 47; vapour pressure <10 Pa) and 0.001 (0.1%) to waste water (solvent based paint; Use Category 47; water solubility <10 mg/l). The amount of paint used on an industrial site can be estimated from Table B3.13 of Appendix I of the TGD. Based on a regional paint use of 472-2,360 t/year, the amount used per site is 354 t/year (5% chlorinated paraffin) or 70.8 t/year (25% chlorinated paraffin) over 300 days. The amount of medium-chain chlorinated paraffin contained within this paint is 17.7 t.

Based on the above information, the default release estimates for medium-chain chlorinated paraffins from industrial paints are:

Local release:	17.7 kg/year or 0.059 kg/day to waste water
Regional release:	118 kg/year to waste water

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Total EU release: 1,180 kg/year to waste water

Default emission factors for private (domestic) use of construction and maintenance paints are given in Table A4.5 of the Technical Guidance Document. Here the emission factor for air is 0 (Use Category 47, vapour pressure <10 Pa) and the emission factor for release to waste water is 0.001 (0.1%) (Use Category 47; water solubility <10 mg/l; solvent based paint). The domestic usage of this type of paint is unknown but likely to be very limited (Table B4.5 of Appendix I of the TGD indicates that the fraction used in domestic applications is of the order of 0.00002-0.0004 (0.002-0.04%) of the total used). This gives the amount of paint for domestic use in a region as 0.009 t/year (25% chlorinated paraffin) or 0.9 t/year (5% chlorinated paraffin content). According to the TGD, the fraction of this paint used in the local scenario is 0.002 (i.e. 0.2%) and so the amount of paint used in the local scenario can be estimated as 1.8 kg/year (5% chlorinated paraffin) or 0.018 kg/year (25% chlorinated paraffin), over 300 days (Table B4.5 of Appendix I of the TGD). The amount of medium-chain chlorinated paraffin used within this paint is 0.005 or 0.09 kg/year. Thus, using the emission factor to water of 0.1%, the worst case estimate for release of medium-chain chlorinated paraffins to waste water from use of paints is $5 \cdot 10^{-6}$ kg/year or $9 \cdot 10^{-5}$ kg/year.

Industry-specific information

Formulation

Information on the releases to the environment from formulation and use of paints has been obtained from industry.

Medium-chain chlorinated paraffins are used only in solvent-based paints, mainly for industrial applications. Releases to the environment from formulation and use are likely to be minimal (Government of Canada, 1993; BCF, 1999). This is because the chlorinated paraffin is likely to be associated with the solid phase (e.g. dried paint) of any waste generated and so is very unlikely to enter into the aqueous effluent streams. This is also indicated to be the case in the Emission Scenario Document for Paints, lacquers and varnishes industry in Chapter 7 of the Technical Guidance Document.

Information on possible releases during formulation of paints has been obtained for the United Kingdom (BCF, 1999). This indicates that releases to the atmosphere and waste water are expected to be very low during paint formulation. The amount of (solid) waste generated during the manufacturing process was estimated as 0-2% of the total use, with the waste going mainly to landfill, with a smaller amount being incinerated.

BCF (1999) indicated that paints and coatings containing medium-chain chlorinated paraffins typically make up only a small fraction (typically <1-2%, maximum 5%) of the total amount of paint formulated on a site. The information obtained also indicated that the amount of chlorinated paraffin used at a site was very small (a total of 34 t/year of chlorinated paraffins was reported to be used over 12 sites (average usage/site = 2.8 t/site); with an estimated 30 sites in total in the United Kingdom manufacturing paints containing chlorinated paraffins). This figure is much less than the default calculations given above would indicate is used on a site.

Euro Chlor (1999) also indicated that the number of sites manufacturing paints containing medium-chain chlorinated paraffins was of the order of 10-50 in a country/region, leading to a lower consumption of medium-chain chlorinated paraffins at a worst case site than would be indicated by the default calculations above.

Based on this information, a worst case estimate for the amount of medium-chain chlorinated paraffins used on a formulation site will be taken to be around 15 t/year (~5 times the average usage/site determined by BCF (1999)). The total amount of medium-chain chlorinated paraffins used in paint in the EU is estimated at 1,180 t/year, with 10% of this (i.e. 118 t/year) being used in a region. Using the default emission factors given above (the default emission factors for formulation of paints are given in Table A2.1 of Appendix I of the TGD and are 0.001 (0.1%) to air (vapour pressure <10 Pa; use of dedicated equipment) and 0.003 (0.3%) to waste water), the following local, regional and total EU releases can be estimated from a site formulating paint containing medium-chain chlorinated paraffins:

Local release:	45 kg/year or 0.15 kg/day to waste water
	15 kg/year or 0.05 kg/day to air
Regional release:	354 kg/year to waste water
	118 kg/year to air
Total EU release:	3,540 kg/year to waste water
	1,180 kg/year to air

These values will be used later in the PEC calculations.

Processing (application of paints)

During application of the paint, losses of medium-chain chlorinated paraffins to air should be minimal due to the low vapour pressure of the substance. Losses to water are also expected to be low (due to the low water solubility of the substance) from industrial application of paints. This is also indicated in the Emission Scenario Document for paints and the default calculations given above.

In the absence of information on the releases to the environment from the use of paints containing medium-chain chlorinated paraffins, the default release estimates calculated earlier will be used in the PEC determinations.

The release from subsequent leaching from paint is considered later in Section 3.1.1.2.9.

3.1.1.2.5   Release from use as an extreme pressure additive in metal cutting/working fluids

Formulation of metal cutting/working fluids

From **Table 2.1**, around 5,950 t of medium-chain chlorinated paraffins were used in the EU to make metal cutting/working fluids in 1997. Assuming that the formulated cutting fluid contains around 5-10% chlorinated paraffin, then the total amount of cutting fluid formulated in the EU is 59,500-119,000 t/year.

Medium-chain chlorinated paraffins are used in both oil-based and water-based (emulsion) metal cutting/working fluids. In most oil-based cutting fluids, the chlorinated paraffin content is around 5-10% (typically 5%), but can be up to 70% in some heavy drawing applications. In water-based metal cutting/working fluids, the chlorinated paraffin may be present typically at around 5% in the formulation. In use, this formulation is diluted (emulsified) in water to give the final metal cutting/working fluid. The typical dilution is around 1:20 with water. Thus if the chlorinated paraffin is present at 5% in the formulation, the concentration in the fluid in use is around 0.25%.

Default release information

Default release estimates for the formulation of metal cutting/working fluids can be obtained from Table A2.2 of Appendix I of the TGD [Industry Category 8 (metal extraction, refining and processing industry); Use Category 35 (lubricants and additives); vapour pressure <1 Pa]. The default release factor to air is 0.00005 ($5 \cdot 10^{-3}$%) and the default release factor to waste water is 0.002 (0.2%). Assuming the total amount of metal cutting/working fluid formulated in the EU is 119,000 t/year (containing 5% medium-chain chlorinated paraffin) then the amount formulated in a region can be estimated at 10% of this value i.e. 11,900 t/year of fluid. The amount of cutting/working fluid formulated at a site can then be estimated from Table B2.3 of Appendix I of the TGD as 8,330 t of metal cutting/working fluid (containing 417 t of medium-chain chlorinated paraffins) over 300 days. Thus from the default release figures given in the TGD, the following estimates for medium-chain chlorinated paraffins can be obtained:

Local release:	834 kg/year or 2.8 kg/day to waste water
	20.9 kg/year or 0.07 kg/day to air
Regional release:	1,190 kg/year to waste water
	29.8 kg/year to air
Total EU release:	11,900 kg/year to waste water
	298 kg/year to air

Industry-specific release information

Information on the releases to the environment from this application is given in UCD (1997), supplemented by information provided by Euro Chlor (1998). This information will form the basis of the release estimation for this use, and will be used to derive the PECs for the various environmental compartments.

Formulation or blending of metal cutting/working fluids is normally carried out in a batch process. Firstly, the base oils to be used are metered into the mixing vessel and the oils are blended together. This is usually carried out at ambient temperature, but higher temperatures of up to 60°C can be used. Then the additives are added to the base oil either by meter from a bulk storage tank or directly (either in neat form or diluted in base oil). Many additives are difficult to handle due to their high viscosity. Such additives may be pre-heated prior to blending. The blending vessels are normally mixed using paddle mixers or jet mixers, but other methods such as air sparging, pulse-air mixing, high shear mixing and passing the fluid through a convoluted chamber to induce turbulence are sometimes used (UCD, 1997).

It has been estimated that the highest likely loss of lubricant from a formulation site would be typically in the region of 1%, with a maximum of 2% (UCD, 1997). Of this, the greatest amount would be controlled losses, for instance off-specification material that could not be re-used. This would be collected and sent for disposal. Another possible source of loss would be residues in drums sent for recycling. Losses to the atmosphere may occur from pre-heating and blending but are thought to be very low, typically 16 kg of lubricant/year for an average size blending plant (this figure refers to the release of all lubricants, not just metal cutting/working fluids containing medium-chain chlorinated paraffins). As the medium-chain chlorinated paraffin has a lower vapour pressure than the base oils used in the lubricants, the atmospheric release of the chlorinated paraffin will be much lower than this figure, and can be considered to be of negligible importance in terms of environmental exposure. Typical losses of the lubricant to waste water are thought to be around 0.25%. The maximum concentration of oil in the effluent from a well controlled plant, after treatment in an oil/water separator system would be around

5 mg/l. This figure is derived from information in the discharge consents for oil for blending sites in the United Kingdom (UCD, 1997). Similar discharge consents apply in other EU countries (Euro Chlor, 1998). The oil in the effluent is likely to also contain the chlorinated paraffin.

In the United Kingdom there are thought to be 6 large lubricant blending plants for all types of lubricants (UCD, 1997). Assuming that each plant produces cutting fluids containing medium-chain chlorinated paraffins (there is evidence to suggest that most formulators do or have used chlorinated paraffins (RPA, 1996)), the quantity of medium-chain chlorinated paraffin used at any one site can be estimated as a sixth of that estimated to be used in a country/region. Since 5,950 t/year of medium-chain chlorinated paraffins are assumed to be used in this application in the EU, then the regional use can be estimated as 595 t/year. Thus the amount of medium-chain chlorinated paraffins used at a large blending plant can be estimated at around 100 t/year. Release is likely to occur over 300 days. From the release figure given above of 0.25% to waste water, the following release estimates can be obtained:

Local release:	250 kg/year or 0.83 kg/day to waste water
Regional release:	1,488 kg/year to waste water
Total EU release:	14,875 kg/year to waste water

The amounts released to waste water are estimated to be before any on-site treatment. Well controlled plants typically have oil capture and recovery systems prior to discharge to the drainage system and thereby to the sewage treatment plant. As mentioned above, such equipment is designed to lower the concentration of dissolved oil to 5 mg/l or less. However, these lower emissions associated with well controlled plants may not be applicable to all, particularly smaller blenders (which make up around 20% of the market in the UK; Euro Chlor, 1998) and so the figures estimated above based on a 0.25% release to waste water also need to be taken into account in the assessment as a worst case approach.

Use in metal cutting/working fluids

Default release information

Appendix I of the TGD gives release factors to waste water for metal cutting/working fluid additives of 0.185 (18.5%) from oil-based fluids and 0.316 (31.6%) from water-based (emulsifiable) fluids (Table A3.7; Industry Category 8; Use Category 35). The emissions to air are estimated at 0.0002 (0.02%) from both types of fluid.

If it is assumed that the medium-chain chlorinated paraffin use is split 50:50 between the two types of fluid (industry-specific information below indicates that the split may actually be around 67:33 oil-based: water based), then 2,975 t/year of the chlorinated paraffins can be estimated to be used in each type in the EU. Similarly, the regional usage of medium-chain chlorinated paraffin in each type of metal cutting/working fluid can be estimated as 298 t/year. Thus, for oil-based fluids, the regional usage of the fluid can be estimated at 5.950 t/year (containing 5% medium-chain chlorinated paraffins). From Table B3.5 of Appendix I of the TGD the amount of fluid used on one site can be estimated as 4,463 t/year of cutting fluid (for steelworks) or 1,785 t/year (for other applications), both over 300 days. These amounts of metal cutting/working fluids would contain 223 and 89 t/year of the chlorinated paraffins for the two applications respectively.

Similarly, for the water-based (emulsion) metal cutting/working fluids, the regional usage of the fluid can be estimated at approximately 119,000 t/year of emulsion (containing 0.25%

chlorinated paraffin). From Table B3.5 of Appendix I of the TGD the amount of fluid used on one site can be estimated as 71,400 t/year (for steelworks) or 23,800 t/year (for other applications), both over 300 days. These amounts of metal cutting/working fluids would contain 179 t and 59.6 t/year of the chlorinated paraffin for the two applications respectively.

Based on these default release estimates, the following releases of medium-chain chlorinated paraffins can be calculated:

Oil-based fluids

Local release (steelworks):	41.3 t/year or 138 kg/day to waste water
	44.6 kg/year or 0.15 kg/day to air
Local release (other sites):	16.5 t/year or 54.9 kg/day to waste water
	17.8 kg/year or 0.06 kg/day to air
Regional release:	55.1 t/year to waste water
	59.6 kg/year to air
Total EU release:	550 t/year to waste water
	595 t/year to air

Water-based (emulsion) fluids

Local release (steelworks):	56.6 t/year or 189 kg/day to waste water
	35.8 kg/year or 0.12 kg/day to air
Local release (other sites):	18.8 t/year or 62.7 kg/day to waste water
	11.9 kg/year or 0.040 kg/day to air
Regional release:	94.2 t/year to waste water
	59.6 kg/year to air
Total EU release:	940 t/year to waste water
	595 t/year to air

Industry-specific release information

The major uses of medium-chain chlorinated paraffins are as additives in oil-based metal cutting/working fluids (neat oils). However, they may also be used in water-based emulsions and so both types need to be considered.

Oil-based fluids (Neat oils)

Information on the use of and release from metal working fluids in the United Kingdom has been obtained (UCD, 1997). Losses of fluid, and hence any additive contained within it, are dependent on the type of equipment available for separating the fluid from the swarf. In the United Kingdom it is thought that around 40% of the metal working activity is carried out in large machine shops with sophisticated swarf treatment, 30% in medium sized machine shops with basic swarf treatment and the remaining 30% in small machine shops with no swarf treatment. Little information is available on the size distributions in other EU countries, although the distribution in Spain is thought to be similar to that in the United Kingdom, and in Italy the proportion of large machine shops is slightly higher (60% in large machine shops, 30% in medium machine shops and 10% in small machine shops) (RPA, 1996). The estimated annual losses of cutting fluid, based on the replacement rates in the United Kingdom, are thought to be

near to 50% for a large machine shop, 75% for a medium sized machine shop and 100% from a small machine shop. Not all of this loss, however, is released to the environment. A breakdown of the total losses for a large and small machine shop using oil-based cutting fluids is shown below:

	Large facility with swarf reprocessing	Small facility - no swarf reprocessing
Misting/evaporation	2%/year to air	2%/year to air
Overalls	1%/year to water	2%/year to water
Leaks	1%/year to water*	3%/year to water*
Dragout/workpiece	1%/year to water	1%/year to water
	2%/year to chemical waste	2%/year to chemical waste
Internal reprocessing	1%/year to water*	not applicable
External reprocessing	10%/year reused/discarded as waste oil	not applicable
Dragout-swarf	30%/year (of which 90% burnt, 10% landfill)	90%/year (of which 90% burnt, 10% landfill)
Total losses	48%/year	100%/year

*   The losses may be further minimised by collecting the cutting fluid for re-use.

The major losses of oil-based metal cutting/working fluids are associated with the swarf. It is thought that the vast majority (90%) of swarf produced (and the adhering cutting fluid) is melted for re-use. Thus the cutting fluid and any additive will be destroyed in this process. In some situations, the swarf may undergo solvent cleaning prior to melting, and so some medium-chain chlorinated paraffin could end up in waste solvent in such sites. The remaining 10% of swarf is thought to be disposed of to landfill.

As can be seen from the above figures, the losses to waste water from a large and small machine shop can be estimated at 4% and 6% respectively. However, some other losses have the potential for entering waste water. For instance, misting/evaporation losses are initially to air. However, these have the potential to settle within the facility and reach waste water as a result of cleaning equipment etc. The losses due to external reprocessing of spent cutting fluid are due to line flushing etc. In a well controlled facility, this will be collected and re-used or discarded as waste oil. However, in a less well controlled facility, there remains the possibility that this could be discharged to waste water.

Another source of loss is dragout of the cutting fluid on the workpiece. This is generally removed by either alkaline washing or solvent washing and it is thought that in both cases the remaining cutting fluid is distributed between emissions to water and chemical waste. In a worst case it could be assumed that all this dragout loss occurs to waste water.

From the above discussion, it can be seen that a worst case loss from a metal working facility could be in the region of 18%. Since these worst case loss figures are more likely to apply to a small facility than a large facility, where suitable reprocessing is usually carried out, an assessment will be made of both a large facility (release to waste water 4%) and a small facility (release to waste water 18%). The situation at a medium sized facility is likely to be between these two extremes.

It is thought that a typical large-scale metal cutting/working plant in the United Kingdom would contain around 50,000 litres of cutting oil. This size will be used as the basis for the local

emission scenario for a large site. Assuming that the medium-chain chlorinated paraffin makes up around 5% of the cutting fluid, then 50,000 litres of cutting fluid would contain around 2,500 kg of medium-chain chlorinated paraffin. The possible emissions of medium-chain paraffin to waste water can be estimated at 100 kg/year, using the 4% release figure. These emissions are equivalent to 0.33 kg/day, assuming use on 300 days/year.

Information reported in RPA (1996) indicates that a small company may use <20% of the metal cutting/working fluid at a large company. Therefore, an assessment will also be carried out for a small metal cutting/working plant containing 10,000 litres of cutting fluid. Assuming a medium-chain chlorinated paraffin content of 5%, then 10,000 litres of cutting fluid would contain around 500 kg of medium-chain chlorinated paraffin. The possible emissions of medium-chain chlorinated paraffin to waste water from such a plant can be estimated at 90 kg/year, using the 18% release figure. These emissions are equivalent to 0.3 kg/day over 300 days.

The local release estimates for use of oil-based cutting fluids are summarised below:

Local release: large site = 0.33 kg/day to waste water over 300 days
small site = 0.3 kg/day to waste water over 300 days

Emulsifiable cutting fluids

Similar to the situation with the neat oil cutting fluids, the losses of emulsifiable cutting fluids to the environment depend on the type of equipment available for separating the fluid from the swarf. However, there are some differences between the two types of fluids that have to be taken into account. Firstly, losses by evaporation and by mist generation with emulsifiable fluids are higher than those associated with neat oils. However, since the emulsifiable cutting fluid is mainly water, which is more volatile than the additives present, the vapours and mists generated tend to have higher water contents than the bulk material. Thus the losses of additives may not be in proportion to the total losses of fluid. Also, the adhesion of emulsifiable cutting fluids to the swarf is less than that with neat cutting fluids (due to lower viscosity). However, recovery of emulsifiable cutting fluids from swarf is not generally practised (UCD, 1997).

A breakdown of the potential losses to the environment of emulsifiable metal working/cutting fluids is shown below (UCD, 1997).

Misting/evaporation	5% to air
Overalls	2% to water
Leaks	3% to waste oil/water
Dragout/workpiece	1% to water
	2% to chemical waste
Dragout-swarf	87% (of which 90% burnt, 10% landfill)
Total losses	100%

In use, it is important to maintain the correct oil/water ratio and an average replenishment rate of around 10% per week can be considered typical to compensate for loss of fluid by dragout and evaporative losses etc. Since there is preferential evaporative loss of water, the replenishment package used is often a diluted version of the original fluid, typically containing around 50% of the normal working concentration of the oil component. In addition, emulsifiable cutting fluids are subject to (bacterial) degradation during use and the whole system has to be replenished at a much higher frequency than with neat oils, typically at intervals of between 1 and 6 months. A

typical worst case volume of cutting fluid present in the holding tanks at a site using emulsifiable cutting fluids is around 10,000 litres of fluid (UCD, 1997).

The emulsifiable metal cutting/working fluids are made by adding the oil component (containing the chlorinated paraffin at typically 5% of the oil) to water at a dilution of around 1:20 oil: water. Thus, 10,000 litres of the emulsified fluid will contain 500 litres of oil and approximately 25 kg of medium-chain chlorinated paraffin. These concentrations will be approximately maintained in the cutting fluid by weekly additions of half-strength emulsion (to take into account the preferential evaporation of the water phase), at a rate of around 10% of the total cutting fluid volume present (i.e. 1,000 litres/week). The losses to water are likely to have a similar composition to the cutting fluid as used. From the loss figures reported above, the losses to water are estimated to be around 6% (due to overalls, leaks and dragout from the workpiece). Thus the weekly loss of cutting fluid to waste water during use can be estimated as 60 litres/week. This volume of cutting fluid would contain around 0.15 kg/week or 0.025 kg/day assuming 6 working days/week (300 days/year) of medium-chain chlorinated paraffin (UCD, 1997).

In addition to the weekly loss of fluid during use, the whole system (10,000 litres of fluid containing 25 kg of medium-chain chlorinated paraffin) will be replaced every 1-6 months (UCD, 1997). Before disposal, water-based (emulsion) cutting fluids can be treated by separating the oil and water phases before disposal by methods such as ultrafiltration. The oil phase can be collected for disposal (e.g. incineration) and the water phase then discharged to waste water. Given the physical properties of medium-chain chlorinated paraffins, it is likely that most of the chlorinated paraffin will be associated with the oil phase and so will not be released to the environment. However, it is thought that around 50% of waste emulsion is discharged to the sewage treatment plant without any pre-treatment. Thus as a worst case, as well as the 0.025 kg/day release of the medium-chain chlorinated paraffin from losses in use discussed above, an intermittent (2-6 times/year) discharge to waste water of 25 kg medium-chain chlorinated paraffin/event during final disposal of the cutting fluid needs to be considered.

Information is also available on the likely residual oil content of the water phase after treatment by ultrafiltration prior to disposal to waste. The typical residual oil content of such water is around <10-40 mg/l (BUA, 1992). If it is assumed that the chlorinated paraffin composition of this residual oil is the same as the content in the oil used to produce the cutting fluid (i.e. 5% of the oil), then the chlorinated paraffin content of the waste water can be estimated as 0.5-2 mg/l.

The local release estimates for use of emulsifiable cutting fluids are summarised below:

Local release: use of cutting fluid = 0.025 kg/day to waste water over 300 days

disposal of cutting fluid = 25 kg/day to waste water on 2-6 days/year

Total EU and regional release estimate

Since the loss and disposal patterns of oil-based and emulsion cutting fluids are different this needs to be taken into account in the estimation of the regional and continental release of medium-chain chlorinated paraffins from use of metal cutting/working fluids.

The amount of medium-chain chlorinated paraffins currently used in metal cutting/working fluids is currently 5,953 t/year. The split between use in oil-based and emulsion fluids is not known. The UCD (1997) indicates that the amount of base oil used to produce oil-based and emulsion fluids in the United Kingdom is in the ratio 15,750:7,700 t/year. Since the medium-chain chlorinated paraffin is present at a similar concentration in both the oil-based and emulsifiable cutting fluids (before dilution to the working strength), the same ratio could be used

to determine the relative amounts of chlorinated paraffin used in each type. Thus, it will be assumed that of the 5,953 t/year of medium-chain chlorinated paraffins used, approximately 3,969 t/year can be expected to be used in oil-based fluids and 1,984 t/year can be expected to be used in emulsion based fluids.

The total worst case EU release from emulsion-based fluids can be estimated assuming that 50% of the fluid is eventually released to waste water without any pre-treatment (UCD, 1997). Thus the total EU release of medium-chain chlorinated paraffins from emulsion-based fluids is estimated at 992 t/year. The regional release will be 10% of this figure, 99.2 t/year.

For the oil-based fluids, the release to the environment depends on the size of the facility. As discussed above, around 60% of oil-based fluids can be assumed to be used in large (and medium) facilities with swarf reprocessing, and the realistic worst case release to waste water from such facilities is estimated at 4%. This gives as a total release of medium-chain chlorinated paraffins from large sites using oil-based fluids of $3,969 \cdot 0.6 \cdot 0.04 = 95.3$ t/year. For the remaining 40% of oil, this will be assumed to be used in small and medium facilities, where little or no swarf reprocessing is carried out. For both these facilities, a worst case release figure of 18% to waste water will be assumed. This gives a total release of medium-chain chlorinated paraffins from small and medium sized facilities using oil-based fluids of $3,969 \cdot 0.4 \cdot 0.18 = 285.7$ t/year. Thus the overall EU release of medium-chain chlorinated paraffins to waste water from use in oil-based cutting fluids is 381 t/year. The regional release will be 10% of this figure, 38.1 t/year.

Appendix E considers the possible effects on the releases to the environment of medium-chain chlorinated paraffins resulting from the proposed risk reduction measures on short-chain chlorinated paraffins in this application.

Further information relevant to the emissions of medium-chain chlorinated paraffins from metal working fluids in the United Kingdom has recently become available (MCCP User Forum, 2003). This indicated that the practices used by the industry today do not result in discharge of aqueous effluents from metal working fluid use. Waste mineral oils are considered to be special waste and may only be disposed of via approved, regulated waste disposal routes. Oil recovery is a major route for disposal of spent metal working fluids in the United Kingdom. Waste emulsions are not allowed to be discharged to sewer or surface water without suitable treatment. The same source also estimated that less than 5 t/year of medium chain chlorinated paraffins in the United Kingdom (and less than 20 t/year in the EU) are disposed of inappropriately (e.g. released to drain without treatment). In relation to 'drag-out' losses, the report indicates that most of the swarf produced in the United Kingdom is now recycled and the adherent metal working fluids destroyed and that the release of medium-chain chlorinated paraffins from swarf is minimised by the appropriate handling of the contaminated swarf as required by existing regulations. Residual metal working fluid left on the work following processing will often be removed in a cleaning process. The resultant waste from this cleaning process is disposed of in the United Kingdom through clearly defined waste disposal routes.

Based on this information, the above release estimates may overestimate the current situation, at least in some countries, but the information available does not allow a more realistic estimate to currently be made.

3.1.1.2.6   Release from use in leather fat liquors

Around 1,048 t of medium-chain chlorinated paraffins were used in the EU in the formulation of leather fat liquors in 1997. The chlorinated paraffin content of the formulation is around 10%;

therefore the amount of leather fat liquor containing medium-chain chlorinated paraffins produced in the EU is 10,480 t/year. Around 50% of this is exported from the EU.

<u>Default release estimation</u>

Appendix I of the TGD provides default release estimates for the formulation and processing (use) of substances used in the leather processing industry (Industry Category 7).

Formulation

For the formulation stage, Table A2.1 of Appendix I of the TGD is appropriate. The default emission factors for this process are 0.001 (0.1%) to air (vapour pressure <10 Pa; produced in dedicated equipment) and 0.003 (0.3%) to waste water. The amount of leather fat liquor formulated on one site can be estimated from Table B2.3 of Appendix I of the TGD. Assuming an EU production of 10,480 t of leather fat liquors, the amount used in a region would be 1,048 t of fat liquor. All of this 1,048 t of fat liquor is estimated to be used on one site over 300 days. This amount of fat liquor contains 105 t of medium-chain chlorinated paraffins. The following figures can therefore be estimated for release of medium-chain chlorinated paraffins from the formulation step:

Local release:	315 kg/year or 1.1 kg/day to waste water
	105 kg/year or 0.35 kg/day to air
Regional release:	315 kg/year to waste water
	105 kg/year to air
Total EU release:	3,144 kg/year to waste water
	1,048 kg/year to air

Processing (use of leather fat liquors)

Around 5,240 t of leather fat liquors are assumed to be used in the EU each year. The amount used in a region is therefore 524 t of fat liquor. According to Table B3.4 of Appendix I of the TGD the amount used at a site is 262 t/year of leather fat liquor (containing 26.2 t/year of medium-chain chlorinated paraffins), over 105 days.

Table A3.6 of Appendix I of the TGD gives default emission factors for the use of substances during the processing step. For medium-chain chlorinated paraffins the emission factors are 0.001 (0.1%) to air (solubility <100 mg/l; vapour pressure <100 Pa) and 0.05 (5%) to waste water (Main Category 2 (inclusion into matrix; solubility <100 mg/l)).

The following figures can therefore be estimated for release of medium-chain chlorinated paraffins from the leather fat liquoring step:

Local release:	1,310 kg/year or 12.5 kg/day to waste water
	26.2 kg/year or 0.25 kg/day to air
Regional release:	2,620 kg/year to waste water
	52.6 kg/year to air
Total EU release:	26,200 kg/year to waste water
	526 kg/year to air

Industry-specific release estimation

Formulation of fat liquors

Information on the formulation of leather fat liquors has been provided by a major formulator (Euro Chlor, 1998). This site complies with a discharge consent of <0.5 ppm of adsorbable organic halogen (AOX) (chlorinated paraffins are the only source of halogen in this discharge). Industry indicated that a similar situation with regards to discharge is likely to exist for all European formulators (Euro Chlor, 1998). In France, the discharge limit is 1 ppm for total AOX, but other halogen sources other than medium-chain chlorinated paraffins may contribute to this limit.

A small amount of medium-chain chlorinated paraffins is sold directly to tanneries that then make their own fat liquors. The emissions from this processes are likely to be small compared to the emissions associated with the fat liquoring process itself (default release factor for formulation is 0.3% compared with the estimated 2% release factor for fat liquoring) and so will not be considered further here.

Processing (fat liquoring)

An emission scenario document is available for the leather industry (Chapter 7 of the Technical Guidance Document). This recommends a value of 15 t/day as a reasonable worst case for the mass of leather processed at a site, based on production data for Germany. Figures for typical water use are also available. These depend on whether the site carries out all stages of leather production (from processing of raw skins to production of the final leather), where a water consumption of 35 l/kg raw hide is typical, or is specialised in the refining of 'wet blue' (leather produced after the tanning step), where a water consumption of 18 l/kg leather is typical. Processing of 1 t of raw hides produces a maximum of 250 kg of 'wet blue'. Since the fat liquoring step follows the tanning stage, both types of site have the potential to use fat liquors containing medium-chain chlorinated paraffins.

Information on the amount of fat liquor used in treating leather has been provided (Euro Chlor, 1998). The typical application rate is around 70-120 g of fat liquor/kg of leather treated. Since the fat liquor typically contains around 10% by weight of the medium-chain chlorinated paraffin, the amount of the chlorinated paraffin used in this process is around 7-12 g/kg leather treated. The amount of chlorinated paraffin present in the treatment solution at the end of the process is thought to be around 2% of that used (Euro Chlor, 1998). This will be discharged to waste water.

Using this information, the following release estimates can be made, using the methods outlined in Chapter 7 of the Technical Guidance document.

Complete processing:

> Mass of raw leather processed/day = 15 t
> Mass of 'wet blue' leather produced = 3.75 t/day
> Mass of MCCPs used = 12 kg/t 'wet blue' = 45 kg/day
> Percentage released to waste water = 2%
> Mass of MCCPs released to waste water = 0.9 kg/day

Processing of 'wet blue':

> Mass of 'wet blue' processed/day = 15 t
> Mass of MCCPs used = 12 kg/t 'wet blue' = 180 kg/day
> Percentage released to waste water = 2%
> Mass of MCCPs released to waste water = 3.6 kg/day

As the overall release figure for medium-chain chlorinated paraffins from the process is around 2%, then the total release to waste water in the EU is 10.48 t/year. The estimated regional release will be 10% of this figure, 1.05 t/year.

Appendix E considers the possible effects on the releases to the environment of medium-chain chlorinated paraffins resulting from the proposed risk reduction measures on short-chain chlorinated paraffins in this application.

3.1.1.2.7   Release from production of carbonless copy paper

Around 741 t/year of medium-chain chlorinated paraffins were used in the EU to manufacture carbonless copy paper in 1997 (see Section 2.2). The medium-chain chlorinated paraffin content of the paper is around 3-4% by weight. This would give a total for the amount of paper containing medium-chain chlorinated paraffins of 18,525-24,700 t/year (Euro Chlor, 1999). This is consistent with the information given in Section 2.2.5, where it was estimated that at most, 5% of the carbonless copy paper used in the EU (i.e. 33,000 t of paper out of the total usage of 660,000 t) could contain medium-chain chlorinated paraffins.

Default release estimation

Appendix 1 of the Technical Guidance Document gives default emission factors from printing, and production of pulp, paper and board. Neither of these scenarios is appropriate to the use of medium-chain chlorinated paraffins in the manufacture of carbonless copy paper.

Industry-specific release estimation

Chapter 7 of the Technical Guidance Document contains an emission scenario document for the paper industry. In this document it is stated that the environmental impact of the application stage of coatings and the production of carbonless copy paper is considered low in comparison with the impact of release during paper recycling. The releases from recycling of carbonless copy paper containing medium-chain chlorinated paraffins are considered in Section 3.1.1.2.8.

Euro Chlor (1999) indicated that there are no available estimates or industry-specific information regarding the release to the environment from production of carbonless copy paper. Based on knowledge of the industry, it was thought that there is only a small potential for release to the environment during the coating stage of paper production. The production of the microcapsules (containing the medium-chain chlorinated paraffins) is carried out in essentially closed systems. The microcapsules are coated onto the paper as an aqueous suspension and it is possible that some of this suspension may be discharged to water after appropriate treatment, but it is not possible to estimate the quantity involved.

3.1.1.2.8   Release from recycling of carbonless copy paper

Default release estimation

Appendix I of the TGD gives default release factors for recycling (recovery) of paper (Table A5.2). The release factors are 0 to air and are around 0.1-0.2 (10-20%) to water for toners and colourants. No release factors are given for carbonless copy papers.

Around 741 t of medium-chain chlorinated paraffins were used in carbonless copy paper in the EU in 1997. The total release in the EU from recycling of carbonless copy paper can be estimated at around 74.1-148 t/year, based on the release factors given above for toners and colourants. The estimated regional release would be 10% of these figures, 7.4-14.8 t/year.

Industry-specific release estimation

The emission scenario document for the pulp, paper and board industry (Chapter 7 of the Technical Guidance Document) does contain some information on the possible releases to the environment from the recycling of carbonless copy paper. It is reported that the recycling of carbonless copy paper is perceived to cause problems for mills using waste paper because the constituents of the coatings used can prove to be difficult to remove from the paper in the de-inking process.

For carbonless copy paper it is reported that most of the colour former is hydrolysed during alkaline pulping and is released into the water. Since medium-chain chlorinated paraffins are used as carrier solvent for these colour formers, it could be assumed that all the medium-chain chlorinated paraffin will also enter into the water phase. The emission scenario document also states that at least primary sedimentation is carried out at all paper mills and that this process will remove up to 90% of poorly water soluble substances and that sludges produced in the clarification/sedimentation process are dewatered and disposed of to landfill. Thus the overall release of medium-chain chlorinated paraffins to waste water from the process could be around 10% of that used.

The emission scenario document suggests that as a worst case approach, a recycling rate of 50% of the paper should be used, and the paper containing a given substance is recycled at 10 sites (i.e. a maximum of 5% of the substance at a site). Thus the amount of medium-chain chlorinated paraffin in carbonless copy paper at a paper mill using recycled paper could be 37.05 t/year. The number of days of recycling is given as 250 days.

From the above discussion, the following emissions of medium-chain chlorinated paraffins to the environment from recycling of carbonless copy paper can be estimated:

Local release:	3,705 kg/year or 14.8 kg/day to waste water
Regional release:	3,705 kg/year to waste water
Total EU release:	37,050 kg/year to waste water
	333.5 t/year to landfill on sludges

These figures assume that 50% of the carbonless copy paper is recycled. This may overestimate the recycling rate as much of the paper is used in commercial documents that will be retained and filed, or sent for destruction (e.g. incineration in waste). However, figures on the actual recycling rate are unavailable.

Other information is available on the recycling of paper in the EU that may be useful to estimate the amount of paper containing medium-chain chlorinated paraffins that might be recycled on a

site. Within the EU, it is estimated that 30 million t of recycled fibres are used for paper making each year (IPPC, 2000), and that recycled fibres account for 45% of the total paper production in the EU. In addition it is reported that there are 1,064 paper mills in the EU, although not all of these will use recycled fibre. Assuming a 50% recycling rate for carbonless copy paper, then the amount of carbonless copy paper recycled each year (i.e. 330,000 t/year) is 1.1% of the total recycled paper.

A large paper production site in the EU may produce >250,000 t/year of paper (IPPC, 2000). If it is assumed that 1.1% of this is carbonless copy paper, the amount of carbonless copy paper recycled at a site of this size is 2,750 t/year. This calculation effectively averages out the carbonless copy paper amongst all the paper recycled. It is possible that some sites take a higher proportion of carbonless copy paper and so as a worst case it could be assumed that five times this amount of the paper recycled at the site is carbonless copy paper, i.e. 13,750 t/year. In terms of the total EU consumption of carbonless copy paper, this figure is 4.17% of that recycled (330,000 t/year) or 2.08% of the total carbonless copy paper (660,000 t/year). Since the amount of medium-chain chlorinated paraffins used in carbonless copy paper is 741 t/year, the amount of medium-chain chlorinated paraffins recycled at the site is 15.4 t/year. With a release rate to waste water of 10%, the local emission in this case would be:

Local release: 1,541 kg/year or 6.17 kg/day (assuming 250 days recycling)

This gives a broadly similar estimate to that above and will be used in the local PEC calculation.

3.1.1.2.9   Release from use in plastics/other polymers over their service life

Although medium-chain chlorinated paraffins are of low vapour pressure at ambient temperatures, the vapour pressure is not so low as to preclude the possibility of volatilisation from plastics and other polymers during their service life. This is particularly true of the medium-chain chlorinated paraffins with lower chlorine contents (see Appendix B for estimates of how vapour pressure varies with chlorine content).

Volatilisation

The loss to air of a C_{14-17}, 52% wt. Cl paraffin from PVC has been determined by Campbell and McConnell (1980). In the experiment, a plasticised PVC sheet (area 1.05 m^2) containing 8% by weight of the chlorinated paraffin was placed in a box (volume 0.125 m^3) and air (total volume 12.75 m^3) was passed through the system over 21 days. The air was scrubbed using a suitable solvent and around 1 mg of chlorinated paraffin was found to be removed (volatilised) in the air from the system. Based on the amount volatilised, the effective vapour pressure of the chlorinated paraffin was estimated to be $3 \cdot 10^{-9}$ mmHg ($4 \cdot 10^{-7}$ Pa). An emission rate for the chlorinated paraffin of around $5 \cdot 10^{-4}$ μg/s/m^2 can be estimated from this data, which is similar to the emission rates estimated for DEHP ($1.8-3.0 \cdot 10^{-4}$ μg/s/m^2) from PVC (see below). This emission factor for medium-chain chlorinated paraffins is considered further in Appendix F

The Use Category Document on plastics additives (UCD, 1998) summarises the work that has been carried out on plasticiser leaching and volatilisation from PVC products.

For volatilisation from PVC the following equation was derived for thin film applications:

rate of volatilisation (% per year) $= 1.1 \cdot 10^6 \cdot$ vapour pressure (mmHg).

In Section 1.2.8, it was shown that the vapour pressure of the components of medium chain chlorinated paraffins depends markedly on the carbon chain length and degree of chlorination. For example, the vapour pressure of a ~51-53% wt. Cl medium-chain, chlorinated paraffin was estimated to vary between $5.5 \cdot 10^{-5}$ Pa for the C_{15} component to around $1 \cdot 10^{-6}$ Pa for the C_{17} component. The vapour pressure for a 52% wt. Cl medium-chain chlorinated paraffin has been measured as $2.0 \cdot 10^{-6}$ mmHg ($2.7 \cdot 10^{-4}$ Pa) at 20°C, but this probably reflects the vapour pressure of the most volatile components rather than being representative of the whole commercial product and so would overestimate the total loss of medium-chain chlorinated paraffins from thin films. Since the majority of medium-chain length chlorinated paraffins are represented by products having between 45% wt. Cl and 52% wt. Cl, a reasonable worst case value for a representative vapour pressure can be taken as around $5 \cdot 10^{-5}$ Pa = $3.75 \cdot 10^{-7}$ mmHg (based on the estimates reported in Appendix B). Based on this vapour pressure, the rate of volatilisation estimated using the equation above is 0.4% per year. This applies to losses from thin film applications.

For general articles an emission factor of 0.05% of the annual consumption of plasticiser is recommended (UCD, 1998). This figure is appropriate for a plasticiser such as DEHP, and is based on the estimated amount volatilised (approximately 140 t/year) from the major applications, related to the annual consumption of the substance. Thus although the amount of the substance present in articles will be higher than the annual consumption (the lifetime of many PVC products is >1 year), this is accounted for in the way the emission factor has been estimated. The figure of 140 t/year for the amount of DEHP volatilised was estimated from the results of theoretical and semi-experimental studies on the volatilisation rate from PVC, along with the estimated surface area of PVC articles/products present in the EU, taking into account the lifetime of the product. The studies gave a volatilisation rate in the range $1.8 \cdot 10^{-4}$-$3.0 \cdot 10^{-4}$ µg/s/m^2, with an average value of $2.3 \cdot 10^{-4}$ µg/s/m^2 for DEHP (Cadogan et al., 1994). A similar volatilisation rate was derived earlier in this Section for a medium-chain chlorinated paraffin, indicating that the general emission factor of 0.05% of the annual consumption may also be applicable for some medium-chain chlorinated paraffins.

For most applications medium-chain chlorinated paraffins with chlorine contents of around 45% and 52% wt. Cl are used. These are usually of slightly higher volatility (for the 45% wt. Cl) or of a similar volatility (for the 52% wt. Cl) as DEHP (see Section 3.1.1.2.1 and Appendix B) and so the release factor could be increased by a factor of 2-3 to take this into account. In addition, the medium-chain chlorinated paraffins used as plasticiser/flame retardant additives in polymers other than PVC generally have higher chlorine contents (e.g. >50% wt. Cl). These substances are of similar volatility or slightly lower volatility than DEHP and so the release factor could be decreased by a similar factor. Overall, the release factor estimated for DEHP of 0.05% over the lifetime could be considered representative for the whole range of medium-chain chlorinated paraffins, taking into account some products are more and some products are less volatile than this.

Information provided by industry indicates that a polyurethane coating is typically applied to cushioned PVC flooring produced by spread coating to improve the wear properties and staining resistance (Personal Communication, 2000). It is estimated that around 50-60% of the cushion vinyl flooring may have such coatings. These coatings may reduce the potential for volatilisation loss from the flooring. This is considered further in Appendix F.

Other products, such as paints, sealants, etc., can also be expected to lose medium-chain chlorinated paraffin by volatilisation. A similar rate of volatilisation to that in PVC will be assumed. The estimated loss rate of 0.4% per year from thin films may be appropriate for paints (although as paints form a surface skin of low permeability, this should reduce the emissions

compared to those from a thin film of plastic), but will overestimate the releases from sealants (loss rate of 0.05% over the lifetime would appear more appropriate here). The release figure of 0.4% per year for thin films should be applied to the total amount of medium-chain chlorinated paraffin present in painted articles in the EU, rather than the yearly consumption figure in this area. In **Table 3.3** the releases from paints using this figure have been estimated based on a seven year lifetime for painted surfaces. It is likely that the actual releases from painted surfaces will be lower than this figure due to formation of a surface skin of low permeability.

Table 3.3 summarises that possible volatilisation losses from articles containing medium-chain chlorinated paraffins.

An alternative approach to estimating the volatilisation losses of medium-chain chlorinated paraffins from PVC and other polymer use, based on the measured emission rate of $5 \cdot 10^{-4}$ µg/s/m^2 is considered in Appendix F. This gives a release to air of around 38-61 t/year over the products lifetime (and a further 2.86 t/year from waste disposal), which is in good agreement with the figures derived in **Table 3.3**. The approach taken in Appendix F requires a large number of assumptions and so there is considerable uncertainty in the figures derived. Therefore the figures from **Table 3.3** will be used in the environmental modelling to estimate the regional concentrations.

Table 3.3   Estimated volatilisation losses of medium-chain chlorinated paraffins from polymeric materials

Use	Amount used in EU	Release factor to air	Release to air
PVC	51,827 t/year	0.05% over lifetime[a]	25.9 t/year
Paints, adhesives and sealants	1,180 t/year – paints	0.4%/year over a 7 year lifetime[b]	33.0 t/year
	2,360 - sealants	0.05% over lifetime[a]	1.18 t/year
Rubber/polymers	2,146 t/year	0.05% over lifetime[a]	1.07 t/year
Total EU			61.15 t/year
Regional total			6.12 t/year

a)   Emission factor applies to yearly consumption figure.
b)   Emission factor applies to total amount of medium-chain chlorinated paraffins present in painted articles (= amount used/year · lifetime of painted surface).

Volatilisation could also occur from other products containing medium-chain chlorinated paraffins, such as leather articles. However, there is insufficient information available about the emission rates from these types of products to make a reasonable attempt to estimate the overall releases.

Leaching

Information has been reported on the leaching of plasticiser from PVC flooring during washing (UCD, 1998). Again, this information has generally been generated for a phthalate plasticiser such as DEHP. Since leaching losses are likely to depend to some extent of the water solubility, the difference in solubility between DEHP (45-340 µg/l (Brooke et al., 1991); recommended value from Draft DEHP ESR Assessment 3 µg/l) and medium-chain chlorinated paraffins (5-27 µg/l) needs to be considered. Thus the potential for leaching of medium-chain chlorinated paraffins is similar to that determined for DEHP. Information provided by industry indicates that a polyurethane coating is typically applied to around 50-60% of cushioned PVC flooring. These coatings may reduce the potential for leaching loss from washing of the flooring.

The worst case losses to water were estimated at 0.05% for washing of interior products and 0.7% for exterior products such as roofing (UCD, 1998). The factor of 0.05% for washing interior products applies to the annual consumption of plasticiser rather than the total amount present in articles (this is accounted for in the way the emission factor was derived).

The factor of 0.7% for outdoor use was determined for loss of total phthalate plasticiser from roofing material over 4 years. Thus the average loss rate/year in the study is 0.15%/year. This factor should be applied to the actual amount of medium-chain chlorinated paraffin present in products, taking into account the products lifetime. It should also be noted that the derived emission factor will also include contributions from loss of particulates, degradation etc. from the material due to weathering or erosion and so is likely to overestimate the actual leaching loss of the medium-chain chlorinated paraffin.

Since a major use of medium-chain chlorinated paraffins is in flooring the 0.05% release factor is appropriate. As indicated above, some cushioned PVC products may have coatings that reduce the potential for leaching loss from the product, but the extent of this reduction is unknown and so adds further uncertainty to the estimates presented, and is considered further in Appendix F. For paints and, to a lesser extent, sealants, the external release factor may be more appropriate, as they are sometimes used in applications where significant exposure to water may occur (e.g. marine paints, masonry paints). For the other polymer applications, e.g. as a flame retardant in rubber and polymers other than PVC, the potential for exposure to water appears to be limited. The worst case release to the environment from leaching of medium-chain chlorinated paraffins from paints/sealants and PVC is shown in **Table 3.4**.

Table 3.4   Estimated leaching losses of medium-chain chlorinated paraffins from polymeric materials

Use	Amount used in EU	Release factor to water	Release to water
PVC	51,827 t/year	0.05% over lifetime[a]	25.9 t/year
Paints, adhesives and sealants	1,180 t/year – paints	0.15%/year over 5-7 year lifetime	8.9-12.4 t/year
	2,361 t/year – sealants	0.15%/year over 10-30 year lifetime	35.4-106 t/year
Total EU			70.2-147.9 t/year
Regional total			7.0-14.79 t/year

a) Emission factor applies to yearly consumption figure.
b) Emission factor applies to total amount of medium-chain chlorinated paraffins present in article
   (= amount used/year · lifetime of article).

An alternative approach to estimating the leaching losses from PVC and other polymer use is considered in Appendix F. This gives a release to water of around 73-93 t/year (plus a loss of around 30-37 t/year to soil, and 2 t/year to waste water from leaching from landfills), which is in reasonable agreement with the figures derived in **Table 3.3**. The approach taken in Appendix F requires a large number of assumptions and so there is a large degree of uncertainty in the figures derived. Therefore the figures from **Table 3.3** will be used in the environmental modelling to estimate the regional concentrations. The figures estimated for the leaching loss are likely to overestimate the actual loss as not all the PVC, paint or sealant containing medium-chain chlorinated paraffin will come into contact with water. There are also uncertainties in determining representative lifetimes of products such as sealants, which have a large bearing on the resulting release estimate. In addition, some of the emission factors used also include losses of particulates etc. due to weathering effects and erosion, as well as leaching loss. The environmental behaviour of medium-chain chlorinated paraffins in these particulates is unknown (see also Section 3.1.1.2.10).

3.1.1.2.10 Waste in the environment and ultimate disposal

'Waste remaining in the environment'

As well as volatilisation and leaching losses of medium-chain chlorinated paraffins from products/articles, medium-chain chlorinated paraffins may also enter into the environment as a result of 'waste' from the products themselves during their useful lifetime and disposal. Such waste could include erosion/particulate losses of polymeric products, paints and sealants as a result of exposure to wind and rain or may occur as a result of their mode of use (e.g. wear on conveyor belts, flooring etc.). Similarly, when products/articles are dismantled or disposed of at the end of their useful life there is again a potential for this type of particulate release. In either case the end result is that polymeric particles containing medium-chain chlorinated paraffins could enter into the environment.

No agreed method is currently included in the Technical Guidance Document for addressing these potential sources of release. These emissions were considered in the draft risk assessments of several 'phthalate' plasticisers. Appendix F uses a similar approach as taken in the draft risk assessment of DEHP to derive the overall release figures for medium-chain chlorinated paraffins as particulates:

> Release to air = 1.1-1.3 t/year
> Release to surface water = 275-324 t/year
> Release to waste water = 100-166 t/year
> Release to urban/industrial soil = 826-973 t/year

As these releases of medium-chain chlorinated paraffin are essentially bound within a polymer matrix, the actual bioavailability and environmental behaviour of the medium-chain chlorinated paraffin is unknown. There are no agreed methods available in the current Technical Guidance for dealing with these types of releases in the risk assessment.

Ultimate disposal

Since medium-chain chlorinated paraffins are not generally reacted or changed during their lifecycle, ultimately all the chlorinated paraffin used in products will be disposed of at the end of the products' useful life. Disposal by landfill or incineration is likely to be the ultimate destination of much of the chlorinated paraffin. For some applications, e.g. metal working fluids, some of the chlorinated paraffin could be destroyed in processes such as recycling of metal swarf. For other processes e.g. recycling of carbonless copy paper, the majority of the medium-chain chlorinated paraffin present is likely to end up in the sludge produced in the process, which will again most likely be disposed of by incineration or landfill.

As a first approximation, it can be assumed that the annual consumption of medium-chain chlorinated paraffin is used to replace the articles disposed of each year, and so the amount of medium-chain chlorinated paraffins disposed of to landfill and incineration each year is of the order of 60,000 t. The vast majority of this amount is likely to be present in PVC articles, as this is the major use of medium-chain chlorinated paraffins.

Of the possible disposal methods, incineration is likely to completely destroy the medium-chain chlorinated paraffin. In landfills, chlorinated paraffins may be expected to be relatively stable for a number of years and so could be subject to leaching or volatilisation from the landfill. It is currently not possible to quantify these releases. However, medium-chain chlorinated paraffins are expected to adsorb strongly onto soil and so leaching and volatilisation from landfill would

not be expected to be significant processes for medium-chain chlorinated paraffins compared with other sources of release (see Sections 3.1.1.6 and 3.1.1.7 and Appendix F).

3.1.1.3   Summary of release estimates

The releases of medium-chain chlorinated paraffins to the environment from their production and use are summarised in **Table 3.5**. In most cases the releases are based on information specific to the industry, supplemented with default release estimates from the Technical Guidance Document where appropriate.

The effects of the proposed risk reduction measures on short-chain chlorinated paraffins on the possible consumption, and hence release, of medium-chain chlorinated paraffins are considered in Appendix E.

In addition to these releases, there is also the possibility of medium-chain chlorinated paraffins being released to the environment as a result of weathering/erosion of particulate materials. These potential releases are estimated in Appendix F and summarised in Section 3.1.1.2.10. There is currently no agreed methodology available within the Technical Guidance Document to quantify or deal with these potential sources in the risk assessment as the actual bioavailability and environmental behaviour of the medium-chain chlorinated paraffin within the particles is unknown. As a result, any environmental modelling of these releases is highly uncertain. For this reason, the regional PEC calculations have been carried out both with and without these releases and the possible effect of including these releases on the PECs is discussed in the following Sections where appropriate.

As mentioned in Section 1.2.3, C_{17}, and to a much lesser extent, C_{16} chlorinated paraffins are present as impurities in some types of long-chain chlorinated paraffins based on a C_{18-20} carbon chain length. These substances are used in PVC applications, paints and leather fat liquors.

Table 3.5 Summary of environmental release estimates for medium-chain chlorinated paraffins

Use	Comment	Estimated local release	Estimated regional release (kg/year)	Estimated continental release[d] (kg/year)
Production (4 sites)	Site A	0.22 kg/day to waste water over 300 days	65 kg/year to waste water	37 kg/year to surface water
	Site B	0.06 kg/day to surface water over 300 days		
	Site C	0.06 kg/day to surface water over 300 days		
	Site D	$1 \cdot 10^{-5}$ kg/day to surface water over 300 days		
Use in PVC[e] – plastisol coating[h]	Compounding site (formulation)	0.025[a] kg/day to waste water over 300 days	869 kg/year to waste water and 351 kg/year to air from compounding 10,215 kg/year to waste water and 10,215 kg/year to air from conversion[f]	7,817 kg/year to waste water and 3,155 kg/year to air from compounding 91,935 kg/year to waste water and 91,935 kg/year to air from conversion[f]
	Conversion site (processing)	0.185[a] kg/day to waste water; 0.185[a] kg/day to air, over 300 days		
	Combined compounding and conversion site	0.21[a] kg/day to waste water; 0.185[a] kg/day to air, over 300 days		
Use in PVC[e] – extrusion/other	Compounding site (formulation)	0.092[a], 0.50[b] and 0.0425[c] kg/day to waste water; 0.055[a], 0.3[b] and 0.0255[c] kg/day to air, over 300 days		
	Conversion site (processing)	0.28[a], 0.3[b] and 0.255[c] kg/day to waste water; 0.28[a], 0.3[b] and 0.255[c] kg/day to air, over 300 days		
	Combined compounding and conversion site	0.372[a], 0.80[b] and 0.298[c] kg/day to waste water; 0.335[a], 0.6[b] and 0.281[c] kg/day to air, over 300 days		
Use in rubber/plastics[e]	Compounding site (formulation)	0.0465 kg/day to waste water; 0.0155 kg/day to air, over 300 days	32.25 kg/year to waste water and 10.75 kg/year to air from compounding 107.5 kg/year to waste water and 107.5 kg/year to air from conversion[f]	290.3 kg/year to waste water and 96.75 kg/year to air from compounding 966 kg/year to waste water and 966 kg/year to air from conversion[f]
	Conversion site (processing)	0.155 kg/day to waste water; 0.155 kg/day to air, over 300 days		
	Combined compounding and conversion site	0.202 kg/day to waste water; 0.171 kg/day to air, over 300 days		
Sealants/ adhesives	Formulation/use	negligible	negligible	negligible

Table 3.5 continued overleaf

Table 3.5 continued Summary of environmental release estimates for medium-chain chlorinated paraffins

Use	Comment	Estimated local release	Estimated regional release (kg/year)	Estimated continental release[d] (kg/year)
Paints and varnishes	Formulation	0.15 kg/day to waste water; 0.05 kg/day to air, over 300 days	{354 kg/year to waste water 118 kg/year to air}	{3,186 kg/year to waste water and 1,062 kg/year to air}
	Industrial application of paints (Processing)	{0.059 kg/day to waste water, over 300 days}	{118 kg/year to waste water}	{1,062 kg/year to waste water}
	Application by general public (private use)	$3 \cdot 10^{-7}$ kg/day to waste water, over 365 days		
Metal cutting/working fluids	Formulation	0.83 kg/day to waste water, over 300 days	1,488 kg/year to waste water	13,875 kg/year to waste water
	Use in oil based fluids (processing)	0.33 kg/day to waste water (large site); 0.3 kg/day to waste water (small site), over 300 days	38,100 kg/year to waste water	342,900 kg/year to waste water
	Use in emulsifiable fluids (processing)	0.025 kg/day to waste water, over 300 days plus an intermittent discharge of 25 kg/event to waste water	99,200 kg/year to waste water	892,800 kg/year to waste water
Leather fat liquors	Formulation	{1.1 kg/day to waste water; 0.35 kg/day to air, over 300 days}[i]	{315 kg/year to waste water and 105 kg/year to air}	{2,829 kg/year to waste water and 943 kg/year to air}
	Use – complete processing of raw hides	0.9 kg/day to waste water	1,050 kg/year to waste water	9,430 kg/year to waste water
	Use – processing of 'wet blue'	3.6 kg/day		
Carbonless copy paper	Recycling	6.17 kg/day to waste water	3,705 kg/year to waste water	33,345 kg/year to waste water
Polymers (PVC, other plastics, paints, sealants etc.)	Service life	not applicable	14,790 kg/year to waste water and 6,120 kg/year to air	133,110 kg/year to waste water and 55,035 kg/year to air

Table 3.5 continued overleaf

Table 3.5 continued Summary of environmental release estimates for medium-chain chlorinated paraffins

Use	Comment	Estimated local release	Estimated regional release (kg/year)	Estimated continental release[d] (kg/year)
'Waste remaining in the environment'	Service life and disposal	not applicable	111-113 kg/year to air 10,000-16,600 to waste water (split 7,000-11,620 kg/year to WWTP and 3,000-4,980 to surface water)[g] 27,500-32,400 kg/year direct to surface water 82,600-97,300 kg/year to urban/industrial soil	990-1,170 kg/year to air 90,000-149,400 to waste water (split 63,000-104,580 to WWTP and 27,000-44,820 to surface water)[g] 247,500-291,600 kg/year direct to surface water 743,400-875,700 kg/year to urban/industrial soil
Total (not including 'waste remaining in the environment')			17,027 kg/year to air 170,408 kg/year to water (split 119,286 kg/year to WWTP and 51,122 kg/year to surface water)[g]	153,193 kg/year to air 1,533,582 kg/year to water (split 1,073,482 kg/year to WWTP and 460,101 kg/year to surface water)[g]
Total (including 'waste remaining in the environment)			17,138-17,140 kg/year to air 207,908-219,408 kg/year to water (split 126,286-130,906 kg/year to WWTP and 81,622-88,502 kg/year to surface water) 82,600-97,300 kg/year to urban/industrial soil.	154,183-154,363 kg/year to air 1,871,082-1,974,582 kg/year to water (split 1,136,482-1,178,062 kg/year to WWTP and 734,601 -796,521 to surface water) 743,400-875,700 to urban/industrial soil

a) Open systems (as defined in UCD, 199
b) Partially open systems (as defined in UCD, 1998).
c) Closed systems (as defined in UCD, 1998).
d) Continental release = total EU release-regional release.
e) Releases estimated from UCD, 1998 assuming that 50% of the initial release to air will condense and eventually reach waste water.
f) Regional and continental releases from conversion assume no air emission control is applied. The estimated emissions would be 10 times lower if his was taken into account, but the actual overall proportion of the industry with such controls is unknown.
g) Releases to waste water assume a 70% connection rate to WWTP.
h) Releases from car underbody coating and sealing, and rotational moulding are thought to be negligible during the processing step.
i) Industry-specific release information is also available and has been used to estimate the PEC_{local} in preference to these default values.
{ } Denotes estimates are based on the Technical Guidance default values only.

A draft risk assessment of these products has recently been carried out (Environment Agency, 2001), using the TGD methodology. This estimated the total regional emissions of C_{16-17} chlorinated paraffins from production and use of these long-chain chlorinated paraffins as 1,160-1,616 kg/year to air, 226-254 kg/year to waste water treatment plants, 214-378 kg/year direct to surface water and 351-808 kg/year to industrial/urban soil. The corresponding continental emissions were 10,439-14,542 kg/year to air, 2,033-2,288 kg/year to waste water treatment plants, 1,922-3,398 kg/year direct to surface water and 3,160-7,275 kg/year to industrial/urban soil. These emission estimates include contributions from the emissions over the lifetime of products and also 'waste remaining in the environment'.

Based on these estimates, the C_{16-17} impurities present on long-chain chlorinated paraffins would only contribute around 0.5% to the total estimated environmental release of C_{14-17} chlorinated paraffins. As the regional concentrations used in the risk characterisation (see Section 3.3) are based on actual monitoring data, these will already include the contributions from the C_{16-17} impurities present in long-chain chlorinated paraffins and so it is not necessary to consider these releases further here.

3.1.1.4 Degradation

3.1.1.4.1 Abiotic degradation

Second order rate constants (k_{OH}) for reaction with atmospheric hydroxyl radicals of $8.0\text{-}14.4 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} have been calculated for medium-chain chlorinated paraffins with chlorine contents between 40% wt. Cl and 56% wt. Cl using the method of Atkinson (Hoechst AG, 1988 and 1991). Similar values for the hydroxyl radical rate constant can be estimated from structure using the Syracuse AOP estimation programme.

Assuming an atmospheric concentration of hydroxyl radicals of $5 \cdot 10^5$ molecules cm^{-3} allows atmospheric half-lives of 1-2 days to be estimated.

For the EUSES modelling used in this risk assessment, a value for k_{OH} of $8 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} was used. This corresponds to an atmospheric half-life of 2 days.

Howard et al. (1975) reported that medium-chain chlorinated paraffins with chlorine contents of 45% wt. Cl and 52% wt. Cl were not decomposed when exposed to high energy light (13% of energy in the 220-280 nm range) in petroleum ether. They concluded that direct photolysis of medium-chain chlorinated paraffins is unlikely to be a significant degradation pathway in the environment.

In aqueous systems, medium-chain chlorinated paraffins are not expected to degrade significantly by abiotic processes such as hydrolysis.

3.1.1.4.2 Biodegradation

Hoechst AG (1976 and 1977) reported 5-day biochemical oxygen demand (BOD_5) values for various medium-chain chlorinated paraffins. Few details of how the tests were carried out are given. The results are reported in **Table 3.6** and show little or no biodegradation when compared with the measured chemical oxygen demand (COD) values.

Table 3.6   BOD5 and COD values for various medium-chain chlorinated paraffins (Hoechst AG, 1976 and 1977)

Chemical	COD (mg O2/g)	BOD5 (mg O2/g)	Percentage biodegradation
C14-17, 41% Cl*	1,140	<10	<0.8%
C14-17, 41% Cl	590	<10	<1.6%
C14-17, 49% Cl	1,380	20	1.4%

*   Preparation containing chlorinated paraffin and polyethylene glycol.

Madeley and Birtley (1980) determined the biodegradability of several commercial medium-chain chlorinated paraffins using extended BOD tests. The substances were tested as emulsions at concentrations of 2, 10 and 20 mg/l. Both acclimated and unacclimated microorganisms were used in the tests. Acclimated microorganisms were cultured from soil collected close to a chlorinated paraffin production plant and these were acclimated to chlorinated paraffins by incubation for 8 weeks with a basal medium containing 20-50 mg/l of each chlorinated paraffin being tested. Non-acclimated microorganisms were obtained from the effluent of a laboratory-scale activated sludge unit treating domestic sewage. The results of the tests are shown in **Table 3.7**. From these results, the potential for degradation of the chlorinated paraffin appears to increase with decreasing chlorination.

Table 3.7   BOD values for medium-chain chlorinated paraffins (Madeley and Birtley, 1980)

Substance	Microorganism source	BOD (g O2/g substance)					Biodegradation[a] at day 25
		day 5	day 10	day 15	day 20	day 25	
C14-17, 40% Cl	non-acclimated	0.02	0.32	0.41	0.37	0.29	15%
	acclimated	0.10	0.30	0.49	0.54	0.42	22%
C14-17, 45% Cl	non-acclimated		0.05	0.14	0.19	0.18	10%
	acclimated		0.20	0.37	0.49	0.57	32%
C14-17, 52% Cl	non-acclimated		0.02	0.06	0.04	0.07	5%
	acclimated	0.02	0.03	0.07	0.09	0.10	7%
C14-17, 58% Cl	non-acclimated	no significant oxygen uptake					0%
	acclimated	no significant oxygen uptake					0%

a)   The approximate percentage biodegradation has been estimated from the BOD/ThOD ratio. The ThOD (theoretical oxygen demand) has been estimated (ThOD (g O2/g substance) = 16[2×c+0.5×(h-cl)]/mw; where c=number of carbon atoms, h=number of hydrogen atoms, cl=number of chlorine atoms and MW = molecular weight) for an example formula for each commercial substance as follows: 40% Cl - $C_{15}H_{28}Cl_4$ - ThOD=1.92 g O2/g substance; 45% Cl - $C_{16}H_{29}Cl_5$ - ThOD=1.77 g O2/g substance; 52% Cl - $C_{17}H_{29}Cl_7$ - ThOD=1.50 g O2/g substance; 58% Cl - $C_{15}H_{24}Cl_8$ - ThOD=1.25 g O2/g substance. Slightly different degradation percentages would be obtained if other example formulae were used.

The removal of medium-chain chlorinated paraffins has been studied using non-adapted activated sludge. Few experimental details of the test conditions used are reported. However, removal was determined by chemical oxygen demand determination, presumably of effluent or water in the system. The substances tested were Chlorparaffin 40 fl nv (C_{14-17}, 41% wt. Cl), and Hordalub 70 VT (C_{14-17}, 41% wt. Cl + polyethylene glycol). In both cases, removal was reported to be >90% over 5 and 10 days, but it was also indicated that the majority of the removal was by adsorption onto the sludge rather than biodegradation (Hoechst AG, 1976 and 1977).

The degradation of medium-chain chlorinated paraffins has been studied by Omori et al. (1987) using a variety of bacterial cultures. The medium-chain chlorinated paraffins studied had average chemical formulae of $C_{14.5}H_{26.6}Cl_{4.4}$ (43% wt. Cl) and $C_{15.4}H_{25.4}Cl_{5.6}$ (50% wt. Cl) and

degradation was studied by monitoring the release of chloride ion. Firstly, degradation of the 50% wt. Cl chlorinated paraffin was studied using resting cell cultures of *Pseudomonas aeroginosa*, *Achromobacter delmarvae*, *A. cycloclastes*, *Micrococcus* sp. and *Corynebacterium hydrocarboclastus* grown on glycerol. These bacteria had previously been shown to degrade 1-chlorohexadecane as well as some other mono- and dichlorinated alkanes. Little or no degradation (chloride release) was observed when the medium-chain chlorinated paraffin was incubated with the bacteria for 24 hours at $30^{\circ}C$.

For the cometabolic degradation studies, bacterial strains (designated HK-3, HK-6, HK-8 and HK-10) were isolated from soil using an enrichment culture containing n-hexadecane as the sole carbon source. The cometabolic biodegradation experiments were carried out using the single bacterial strains (HK-3, HK-6 or HK-8) incubated at $30^{\circ}C$ for 48 hours in mineral medium containing 0.05% (i.e. 500 mg/l) n-hexadecane and 0.1% (i.e. 1,000 mg/l) of the 50% wt. Cl product. In addition, biodegradation of both the 43.5% wt. Cl and 50% wt. Cl products (concentration equivalent to 180 mg Cl/l) was studied under similar conditions (36 hour incubations) utilizing a mixed bacterial inoculum (containing all 4 strains) previously exposed to 5,000 mg/l of n-hexadecane. In the experiments using the pure bacterial strains, both HK-3 and HK-8 showed appreciable degradation of the 50% wt. Cl medium-chain chlorinated paraffin, releasing 53 and 38 mg/l of chloride into the mineral medium (as the starting concentration of the chlorinated paraffin was around 1,000 mg/l, these figures indicate that around 8-11% of the chlorine present was released). The third strain tested, HK-6, showed less degradation (10 mg/l (2%) chloride released). It was noted that the pH fell as the dechlorination proceeded and this increase in acidity may have caused bacterial growth and hence degradation to reduce during the experiment. In the experiments using all four strains of bacteria, both medium-chain chlorinated paraffins tested showed significant degradation, with 77 mg/l and 85 mg/l of chloride being released from the 50% wt. Cl and 43.5% wt. Cl chlorinated paraffins respectively. In this case the starting chlorinated paraffin concentration was 180 mg Cl/l, and so around 43-47% of the chlorine present was released during the degradation. In further experiments using activated sludge from a municipal waste water treatment plant that had been acclimatized to n-hexadecane for 60 days, only a small amount of dechlorination (2% of the chlorine present was released) of the 50% wt. Cl medium-chain chlorinated paraffin was seen over 48 hours at $30^{\circ}C$ (Omori et al., 1987). The authors concluded that the degradation seen was consistent with that previously observed for other chlorinated alkanes in that a variety of enzymes are required to degrade chlorinated paraffins and that the most likely mode of degradation involves firstly dechlorination of the terminal methyl groups, with subsequent oxidation to form chlorinated fatty acids, which are then broken down to 2- or 3- chlorinated fatty acids via β-oxidation.

Fisk et al. (1998b) estimated half-lives for biodegradation of 12 days for ^{14}C-labelled $C_{16}H_{31}Cl_3$ and 58 days for $C_{16}H_{21}Cl_{13}$ in an aerobic sediment system containing oligochaetes (*Lumbriculus variegatus*). The extent of degradation was determined at day 0 and day 14 of the experiments based on the difference between toluene-extractable ^{14}C measurements (taken to represent unchanged chlorinated paraffin) and total ^{14}C measurements (taken to represent degraded chlorinated paraffin). However, the results of this test should be treated with caution as the identity of the ^{14}C present in the samples was not determined, and it was only assumed that the non-extractable ^{14}C represented metabolites.

3.1.1.4.3   Summary of degradation

No standard ready or inherent biodegradation tests results are available for medium-chain chlorinated paraffins. From the available information, medium-chain chlorinated paraffins can be

considered to be not biodegradable in such test systems and so a biodegradation rate constant of 0 day^{-1} will be used in the risk assessment. Adsorption onto sludge is likely to be the major removal mechanism for medium-chain chlorinated paraffins during waste water treatment processes. Similar results on biodegradation were obtained for short-chain (C$_{10-13}$) chlorinated paraffins. For the short-chain chlorinated paraffin, an equilibrium removal percentage of 93% by adsorption onto the sludge was determined in a Coupled Units test (see the short-chain chlorinated paraffins assessment for further details). Since the medium-chain chlorinated paraffins have similar, but slightly higher log Kow values (and hence Koc values) to the C$_{10-13}$ chlorinated paraffins, then a similar degree of removal by adsorption onto the sludge as found for the short-chain chlorinated paraffins would also be expected for the medium-chain chlorinated paraffins during waste water treatment. Therefore a removal rate of 93% by adsorption onto sewage sludge during waste water treatment will be used in this assessment. This value agrees well with the value of 91% removal by adsorption obtained in the SIMPLETREAT model.

There is evidence that some microorganisms may be capable of degrading medium-chain chlorinated paraffins in the environment in acclimated or cometabolic systems. The potential for biodegradation appears to increase with decreasing chlorine content. However, it is not possible from the available data to derive rate constants for biodegradation in soil, surface water and sediment systems. As a worst case approach, no biodegradation will be assumed in these media in the PEC calculations. The effect of varying the biodegradation rate on the risk characterisation is analysed in Appendix H.

Hydrolysis is not expected to be a significant degradation process for medium-chain chlorinated paraffins in the environment. An atmospheric half-life of 1-2 days is estimated for medium-chain chlorinated paraffins for reaction with hydroxyl radicals. A value for the rate constant for the reaction (k$_{OH}$) of $8 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} will be used for the environmental modelling in the risk assessment.

3.1.1.5   Uptake and accumulation

3.1.1.5.1   Bioconcentration from water

<u>Fish</u>

The accumulation of a C$_{14-17}$, 52% wt. Cl paraffin in rainbow trout (*Oncorhynchus mykiss*) has been studied over 60 days in a GLP study (Madeley et al., 1983b). The substance tested was a commercial product mixed with a n-pentadecane-8-^{14}C that had been chlorinated to a similar degree. Two concentrations were tested; 1.05 mg/l and 4.5 mg/l, both based on mean measured concentrations over the 60 day period. Acetone (500 ppm v/v - this concentration was required to maintain the test substance in suspension) was used as cosolvent and a flow-through system was used for the test. Concentrations of chlorinated paraffin were measured by both parent compound analysis and by radioactivity measurements and similar concentrations in the fish were obtained by both methods. The bioconcentration factors obtained were 32-45 l/kg on a wet weight basis at the 1.05 mg/l exposure concentration and 42-67 l/kg on a wet weight basis at the 4.5 mg/l exposure concentration. The concentrations of chlorinated paraffin used in these tests were above the water solubility of the substance in pure water. A high concentration of acetone was used in order to prepare stable test solutions, and the actual water solubility of the substance in the test system is not known. It is possible that not all the chlorinated paraffin present was in true

solution during the test and so the measured BCF values may represent the lower limit of the true BCF.

The results of a preliminary study using a $C_{14\text{-}17}$, 45% wt. Cl paraffin with rainbow trout (*Oncorhynchus mykiss*) have been reported (Madeley and Pearson, 1980). The chlorinated paraffin was introduced into the test medium as an acetone solution (the actual concentration of acetone present in the test solution was not given). In the study, the fish were exposed to nominal concentrations of either 0.1 mg/l or 1 mg/l of the medium-chain chlorinated paraffin for 28 days using flow-through conditions. The mean measured concentrations of the chlorinated paraffin in the test solutions were reported to be 0.01 mg/l and 0.18 mg/l for the two exposures, however, there was a long delay before the samples could be analysed and bacterial growth was present in the media. This casts some doubt over the validity of these measurements. The concentrations found in the fish after 28 days were 6.0 mg/kg wet weight for fish exposed to the lower concentration, and 50 mg/kg wet weight for fish exposed to the higher concentration. Thus BCFs of 50-60 l/kg were obtained based on the nominal exposure concentrations and 280-600 l/kg when based on the measured water concentrations. It is possible that not all the chlorinated paraffin present was in true solution during the test and there is some uncertainty over the measured levels in water and so the values reported may represent the lower limit of the true BCF.

Fisk et al. (1999) studied the uptake of a ^{14}C-labelled medium-chain chlorinated paraffin by eggs and larvae of Japanese medaka (*Oryzias latipes*) as part of a 20-day embryo-larval toxicity study. The substance tested had an average formula of $C_{14}H_{23.3}Cl_{6.7}$, 55% wt. Cl. The measured exposure concentrations used were 1.4, 12, 120, 420 and 1,600 µg/l. The resulting concentrations in the larvae at approximately 3-days post hatch were 0.24, 8.2, 45, 84, and 51 mg/kg, respectively, leading to BCF values of approximately 32-680 l/kg (the BCF generally decreasing with increasing concentration). Similar results were found for the eggs. Further details of this study are given in Section 3.2.1.1. The exposure period in this experiment is relatively short and no indication is available as to whether equilibrium was reached. The BCF values measured probably represent the lower limit of the true value for fish in this system.

Bengtsson et al. (1979) studied the uptake of a medium-chain chlorinated paraffin by Bleak (*Alburnus alburnus*). The chlorinated paraffin tested was a $C_{14\text{-}17}$, 50% wt. Cl substance. The tests were performed at 10°C using a semi-static procedure in which the test solutions containing 125 µg/l of the test substance were renewed every two to three days over the 14 day exposure period. A seven day depuration period followed the 14 day exposure period. The water used in the experiment was Baltic Sea water with a salinity of 7%, and acetone was present in all aquaria, including controls, at a concentration of 0.1 ml/l. The fish used in the experiment had an average weight of 4.5 g and were not fed during the exposure period. Six groups of 15 fish were used for both the exposure and control solutions. No mortalities or effects on behaviour were seen in fish exposed to the medium-chain chlorinated paraffin during the test. Uptake of the chlorinated paraffin occurred during the exposure period, with whole body levels of the medium-chain chlorinated paraffin of around 5 mg/kg fresh body weight (read from graph) being determined at 14 days. From this value a BCF of around 40 l/kg can be estimated. Little reduction in the body concentration appeared to occur during the 7 day depuration period. The analytical method used (neutron activation analysis) is not specific for the chlorinated paraffin and so may also include any chlorinated metabolites present in the fish, which may result in an overestimate of the actual chlorinated paraffin concentration in the fish if substantial metabolism was occurring. Again, in this experiment the concentration tested was slightly above the water solubility of the substance in pure water, leading to the possibility that not all the test substance

was present in true solution in the experiment. Also, the exposure period in the study is relatively short and so it is not certain that equilibrium would have been reached.

As a result of the inadequacies of the above tests, the Chlorinated Paraffins Sector Group of Euro Chlor voluntarily agreed to perform a new fish BCF test for use in this risk assessment. The study was carried out using rainbow trout (*Oncorhynchus mykiss*) and the method used was based on the OECD 305 test guideline, using a flow-through system (Thompson et al., 2000). The test substance was a chlorinated n-pentadecane-8-^{14}C (chlorine content was 51% by weight) mixed with a non-radio-labelled C_{14-17}, 51% wt. Cl chlorinated paraffin. The mixture tested contained 49% of the ^{14}C-labelled component and 51% of the non-labelled component. The test vessels used in the experiment were glass tanks with a working volume of 87 litres. One test vessel was used for each treatment group (two concentrations were tested; 1 µg/l and 5 µg/l), control and solvent control group. A continuous flow-rate of dilution water of 500 ml/min was used throughout the test.

Stock solutions of the test substance were prepared in acetone and were continually dosed, by syringe pumps, into glass chambers where they were mixed (with stirring) with the in-flowing dilution water prior to delivery to the test vessel. The same flow rate of the test substance stock solution (0.00139 ml/min or 2.0 ml/day) was used for both the 1 µg/l and 5 µg/l test concentrations. The final acetone concentration in the test solutions was 0.0028 ml/l, and this concentration was also used in the solvent control. The vessels were equilibrated to the test solutions for 6 days before the fish were added to the vessels. The concentrations present in the test vessels were measured on day -5, -4, -2 and -1 of this equilibration period (2 samples from each exposure concentration were taken on each sampling day). For the 1 µg/l concentration, the measured values were 0.86 and 1.1 µg/l, 1.0 and 1.3 µg/l, 1.3 and 1.5 µg/l, and 1.1 and 1.1 µg/l on the four sampling days respectively, and the values for the 5 µg/l concentration were 3.3 and 3.7 µg/l, 4.8 and 4.8 µg/l, 4.3 and 6.0 µg/l, and 4.8 and 5.9 µg/l respectively. These results indicated that the diluter system used was functioning correctly prior to the start of the test.

At the start of the exposure phase groups of 85 rainbow trout were added to each vessel and the exposure phase was continued for 35 days. After the exposure phase, the fish were transferred to a set of identical vessels, but which received dilution water only, for a further 42 days in order to study the depuration of the substance. The fish were analysed for the presence of the test substance using a radiochemical method (the method used would include any parent compound and any radiolabelled metabolites present). This was carried out on days 3, 7, 14, 21, 28 and 35 of the exposure phase and days 3, 7, 14, 21, 28, 35, and 42 of the depuration phase of the experiment. In addition, water samples were also analysed (again by a radiochemical method) for the presence of the test substance. These analyses were carried out on 4 days prior to the start of the fish exposure (to ensure that the test substance delivery system was functioning correctly), and then on days 0, 1, 3 and at least once per week thereafter during the exposure part of the study. The mean measured water concentrations in the test vessels during the exposure phase were 0.93 µg/l (93% of nominal 1 µg/l) and 4.9 µg/l (98% of 5 µg/l nominal), and the mean measured exposure concentrations were used in the BCF calculations. The measured water concentrations were generally ≥87% of the nominal value on all sampling dates except for on day 28 of the experiment, where the levels fell to around 46% of nominal in the low exposure group and 23% of nominal in the high exposure group. The measured levels had increased on day 29, but were still less than expected. By day 30 the measured levels recovered to be again ≥87% of the nominal values. There was no obvious reason why the levels declined on day 28, as all equipment appeared to be functioning normally.

During the test the fish were fed with a commercial fish food at a rate of 2% of their body weight/day. The dissolved oxygen concentration was in the range 7.8 to 10.2 mg/l throughout the

test and the temperature was maintained at 14.7-15.3°C. The water hardness was 43-50 mg/l as $CaCO_3$ and the pH was 6.96-7.87. One fish mortality occurred in the higher treatment group on day 3 of the study (indicating that the mortality criterion for a valid test had been met).

The analysis of the fish concentrations carried out during the experiment indicated that a steady state was being reached at both exposure concentrations (the increase in concentration between day 14 and day 21 was <6%). This was also indicated by the day 28 fish analyses, but these may have been influenced by the apparent fall in water concentration at this time. However, the day 35 data indicated that the concentrations may still have been increasing, and it was less certain that the steady state had been reached. The measured fish concentrations and the resulting BCF values are shown in **Table 3.8**. The concentrations are also shown graphically in Figure 3.1.

Table 3.8   Bioconcentration of a medium-chain chlorinated paraffin in rainbow trout (Thompson et al., 2000)

Mean measured exposure concentration (mg/l)	Exposure period (days)	Mean measured tissue concentration during uptake phase (mg/kg fresh weight)	BCF (l/kg)[c]
0.00093±0.00025	3	0.36±0.04	387
	7	0.43±0.02	462
	14	0.54±0.02	581
	21	0.57±0.06	613
	28	0.55±0.20	591
	35	0.80±0.08	860
0.0049±0.0017	3	0.71±0.34	145
	7	0.52±0.07	106
	14	0.97±0.10	198
	21	1.0±0.17[a]	204
	28	1.1±0.17	224
	35	1.3±0.19[b]	265

a) The results for the analysis of 1 out of the 4 fish sampled was considered to be an outlier (exceeding the mean concentration of the remaining fish by a factor >3) and so was not used in calculation of the mean. The mean if this value is included is 2.96±3.89, which is equivalent to a BCF of 604 l/kg.

b) The results for the analysis of 2 out of the 8 fish sampled were considered to be outliers (exceeding the mean concentration of the remaining fish by a factor >3) and so were not used in calculation of the mean. The mean if these values are included is 2.86±3.42, which is equivalent to a BCF of 583 l/kg.

c) The standard deviations of the individual BCF values were not given.

Figure 3.1   Accumlation in rainbow trout

Note: Error bars represent the mean value +/- the standard deviation.
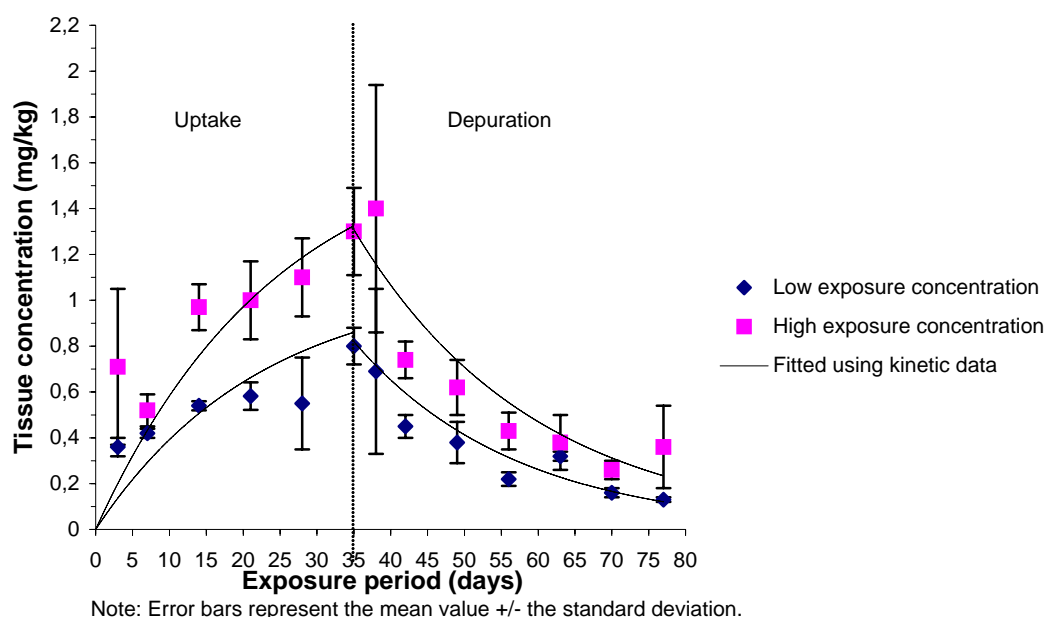
As the data indicated that steady state may not have been reached during the 35 day exposure period, the BCF was also determined by the kinetic method given in the OECD 305 test guideline. The uptake rate constant was determined to be 48.7 day^{-1} for the lower exposure concentration and 14.2 day^{-1} for higher exposure concentration. The depuration rate constant was determined to be 0.0448 day^{-1} and 0.0407 day^{-1} for the two exposure groups respectively. The fitted kinetic data are shown in Figure 3.1. Thus the kinetic BCF can be determined as 1,087 for the lower exposure group and 349 for the higher exposure group. The kinetic data also allowed estimates for the depuration half-life of 15-17 days and the time to 95% of steady state of 67-74 days to be made. The estimate for the time to 95% of steady state indicates that the exposure period employed in this study may not have been long enough for steady state to have been reached and so the kinetic BCF data are considered more reliable. It should be noted that the analytical method used does not distinguish between the radio-labelled parent compound and any radio-labelled metabolites formed (including radio-labelled carbon that is incorporated into fish tissues) and so the BCF determined may overestimate the actual accumulation potential of the substance.

Darnerud et al. (1983) studied the disposition of a radiolabelled medium-chain chlorinated paraffin (n-hexadecane-1-^{14}C, 34% wt. Cl) in carp (*Cyprinus carpio*) and bleak (*Alburnus alburnus*). Two series of experiments were carried out with carp. In the first experiment, 3 carp were injected with the medium-chain chlorinated paraffin (as a fat emulsion) in the dorsal aorta and were then transferred to tubes filled with water. The $^{14}CO_2$ excreted by the fish was then collected over a 96 hour period. In the second experiment with carp, fish were again injected with the medium-chain chlorinated paraffin and then placed in tanks with a continuous flow of water. Fish were subjected to whole-body autoradiography after 1, 5 and 13 days. In the experiments with bleak, 10 fish were exposed to a medium-chain chlorinated paraffin concentration of 125 µg/l in the water (salinity 7%) for 14 days. After this time the fish were placed in clean water for 35 days. At various times during the experiment, fish were removed from the tanks for whole-body autoradiography.

In the carp experiments, the cumulative excretion of $^{14}CO_2$ was found to be 6.4% of the injected dose over 96 hours. Whole-body autoradiography indicated that high levels of radioactivity were found in bile and intestinal contents at all post-injection times. The highest concentrations of radioactivity were found in kidney, liver, nasal mucosa and fat 1 day after injection. After 5 days, the radioactivity at these sites was still elevated, but in addition, marked uptake of radioactivity had occurred in the gills, testis and brain. At 13 days after injection, the concentrations of radioactivity in tissues had generally reduced, although elevated levels were still present in liver. In the experiments with bleak, marked uptake of radioactivity was seen in the gills, nasal cavity, skin, liver and fat, with radioactivity also present in brain, bile and intestinal contents, after 1 day exposure. After 14 days exposure the amount of radioactivity in liver and gills had increased considerably, and radioactivity was also present in brain, nasal cavity, skin and eye (particularly the outer layer of the lens). The distribution pattern of radioactivity between the various organs was found to be similar in fish placed in clean water, but by day 35 of depuration the amount of radioactivity present had decreased markedly. The presence of ^{14}C in bile and intestine of all fish indicated that bile was a significant excretion route in fish (Darnerud et al., 1983).

Invertebrates

Madeley and Thompson (1983) determined bioconcentration factors in mussels (*Mytilus edulis*) at the end of a 60 day toxicity study with a medium-chain chlorinated paraffin (GLP study). The substance used in the test was a commercial C_{14-17}, 52% wt. Cl product that was mixed with a small amount of radiolabelled chlorinated paraffin (n-pentadecane-8-^{14}C, 51% wt. Cl). The test substance was dissolved in acetone before dilution with sea water (salinity 34.0-35.5‰, pH 8.1-8.3, dissolved oxygen 6.15-8.0 mg/l, and temperature 15°C). The test used a flow-through system in order to maintain the concentration in the exposure vessels but, as the study was actually designed to determine the toxicity to mussels, relatively high nominal concentrations of 0.56 and 5.6 mg/l of the test substance were used (these are greater than the reported water solubility of 0.005-0.027 mg/l). The acetone concentration in the exposure vessels was 500 ppm (v/v) (0.5 ml/l) and a solvent control containing acetone at this concentration was run. The mean measured concentrations were 0.22 and 3.8 mg/l in the two exposure groups based on radiochemical analysis. The higher concentration tested was reported to be cloudy in appearance, indicating that undissolved test substance may have been present. The organisms were fed with algae (*Platymonas suecica*) at a rate of $1.0-1.1 \cdot 10^9$ cells/day. The algae were continuously dosed to the in-flowing dilution water. No mortality occurred in the test, but a reduction in filter feeding activity was seen at the higher test concentration. The bioconcentration factors (BCF (mg/kg wet mussel)/(mg/l test solution)) were found to depend on the exposure concentration, with higher BCFs being determined at the lower exposure concentration. This is probably the result of incomplete dissolution of the test substance at the higher concentration, and to a lesser extent at the lower concentration. The BCFs were determined as 2,182 l/kg (based on parent compound analysis) or 2,856 l/kg (based on ^{14}C-measurements) in the organisms exposed to 0.22 mg/l, and 339 l/kg (parent compound analysis) or 429 l/kg (^{14}C measurements) in the organisms exposed to 3.8 mg/l. The similarity between the values obtained by the two analytical methods indicates that the majority of the ^{14}C present in the organism must have been as parent compound rather than metabolites.

Field data

Muir et al. (2002) determined the levels of medium-chain chlorinated paraffins in surface water and various parts of the food chain in Lake Ontario and northern Lake Michigan. The samples were collected during June and August 2001. The samples collected included water, zooplankton

(4 samples collected above the thermocline), Mysis (4 samples collected as for zooplankton), Diporeia (1-2 samples; benthic invertebrate; collected from Lake Ontario only), forage fish (12 samples including smelt (*Osmerus mordax*, omnivore), slimy sculpin (*Cottus cognatus,* benthivore) and alewife (*Alosa pseudoharengus*, planktivore)), and lake trout (*Salvelinus namaycush*, 6 samples per lake).

The samples were analysed for the presence of C_{14}-, C_{15}-, C_{16}- and C_{17}-chain length chlorinated paraffins. The mean total levels of C_{14-17} chlorinated paraffins found in the various samples from Lake Ontario were 109 µg/kg wet weight (2,198 µg/kg lipid) in two samples of smelt, 108 µg/kg wet weight (~2,218 µg/kg lipid) in two samples of slimy sculpin, 35 µg/kg wet weight (1,285 µg/kg lipid) in two samples of alewife, 15 µg/kg wet weight (112 µg/kg lipid) in six samples of lake trout and 12 µg/kg wet weight (426 µg/kg lipid) in one sample of Dipoereia. Based on these data, Muir et al. (2002) estimated biomagnification factors (BMFs) for various parts of the food chain. The results of this analysis are summarised in **Table 3.9.**

Table 3.9   Estimated biomagnification factors for medium-chain chlorinated paraffins in the Lake Ontario food web (Muir et al., 2002)

Food chain	Estimated biomagnification factor (BMF) on a lipid basis[a]				
	C_{14}-chlorinated paraffin	C_{15}-chlorinated paraffin	C_{16}-chlorinated paraffin	C_{17}-chlorinated paraffin	Total C_{14-17} chlorinated paraffin
Lake trout - alewife	0.27	0.04	0.01	0	0.09
Lake trout - smelt	0.16	0.02	0.01	0	0.05
Lake trout - slimy sculpin	0.10	0.03	0.01	0	0.05
Slimy sculpin - Diporeia	2.7	9.6	14.5	11.5	5.2

a)   The BMF were determined from the concentration in predator (µg/kg lipid)/concentration in prey (µg/kg lipd)).

The estimated BMFs for lake trout are <1 for all of the food sources considered. However, the BMF is 2.7-14.5 for the slimy sculpin when Diporeia is considered as the food source. When considering these data it should be born in mind that the sample size was very small and so it is difficult to draw any definite conclusions. It should also be noted that the apparent BMF >1 for the slimy sculpin – Diporeia food chain could, in part, result from differences in the bioconcentration factors between the two species. For example the concentration of chlorinated paraffin in slimy sculpin is a result of bioconcentration in water and uptake from food (assumed to be Diporeia). Similarly the concentration in Diporeia is dependent on the uptake from water/sediment and the uptake from food. Therefore, as the concentration in each organism results from a contribution from exposure via water (bioconcentration) and via food (biomagnification), differences in concentrations in this food chain could result from differences in bioconcentration between the two species rather than biomagnification through the food chain.

When considering the actual levels in the fish, it can be seen that the levels present in slimy sculpin and smelt were very similar (indicating that the apparent BMF>1 for the slimy sculpin-Diporeia food chain results from the relatively lower levels present in Diporeia rather than high levels present in slimy sculpin), with the levels in alewife being slightly lower and the levels in trout being lower still. The authors concluded that the low biomagnification seen through these food chains is probably due to biotransformation by vertebrates as well as to low bioavailability (i.e. strong adsorption onto sediments).

It should also be noted that the estimated BMFs given in **Table 3.9** assume that there is only one food source for each predator. For example, the BMF for the slimy sculpin-Diporeia food chain essentially assumes that Diporeia are the sole food for slimy sculpin. This is unlikely to be the case in reality. For example, Brandt (2004) showed that the contribution of Diporeia to the slimy sculpin's diet varied geographically and seasonally (approximate range 25-97%) and that for Lake Michigan there had been a decline in the Diporeia populations in recent years that contributed to this variability. Other invertebrates (for example *Mysis relicta*) were shown to replace Diporeia in the diet (*Mysis* samples appear to have been collected in the Muir et al. (2002) study but no results were given).

Based on the data reported in Muir et al. (2002), bioaccumulation factors for medium-chain chlorinated paraffins have been estimated in an unpublished draft report by Environment Canada (2003). Medium-chain chlorinated paraffins could not be detected in water samples from the area and so the detection limit (0.02 ng/l) was used in the calculation. The corresponding whole body bioaccumulation factors were determined to be around $7.8 \cdot 10^5$ l/kg for lake trout, $5.5 \cdot 10^6$ l/kg for smelt, $5.4 \cdot 10^6$ l/kg for slimy sculpin and $1.7 \cdot 10^6$ l/kg for alewife. The same factors expressed on a lipid weight basis are $5.6 \cdot 10^6$ l/kg for lake trout, $1.1 \cdot 10^8$ l/kg for smelt, $1.1 \cdot 10^8$ l/kg for slimy sculpin and $6.4 \cdot 10^7$ l/kg for alewife.

As the factors reported by Environment Canada (2003) are based on field measurements they represent a combination of bioconcentration through water and uptake from food and so it could be questioned whether the concentration measured in fish should be compared directly with the concentration in water alone. It should also be noted that the values appear to be based on very few data points (single values in some cases) and it is not clear if the water samples were taken at the same time and location as the fish samples. Therefore there may be considerable uncertainty over the actual concentrations these fish were exposed to over extended time periods (i.e. the concentration in water may vary both spatially and temporally). Thus, although these data confirm that significant uptake of medium-chain chlorinated paraffins occurs in fish in the environment, there is some uncertainty over the actual bioaccumulation factors obtained.

Consideration of available data

The most reliable fish BCF value comes from the recent Thompson et al. (2000) study with rainbow trout using low concentrations of medium-chain chlorinated paraffin. Here, the kinetically determined BCFs were in the range 349-1,087 l/kg but the analytical method used did not distinguish between parent compound and metabolites and so these represent the realistic upper limit for the true BCF of the substance.

In the majority of the other bioconcentration experiments, the concentrations of medium-chain chlorinated paraffin tested were above the solubility in pure water. Acetone was used as co-solvent in the experiments, but it is likely that not all the chlorinated paraffin present in the test systems was in true solution. If this was the case then the BCF values obtained may underestimate the true BCF value. This was seen in the experiments with mussels, where the BCF was found to increase with decreasing test concentration, and so the BCF at the lower test concentration (BCF 2,182-2,856 l/kg) is considered to be more reliable. For the 60-day experiments with fish, no such concentration dependence was seen, and similar values of 32-67 l/kg were determined in all tests (using two different fish species and a test concentration range of 36). However, it is still possible that these values may underestimate the true value. One possible approach to this problem would be to assume that the organisms were only exposed to the substance at its solubility, even though the nominal concentrations were much higher. Using the solubility of 27 µg/l, for the three fish exposure concentrations of 125 µg/l, 1.05 mg/l and

4.5 mg/l (Bengtsson et al. (1979) and Madeley et al. (1983b) studies) the BCF values would be 185 l/kg, 1,244-1,750 l/kg and 7,000-11,200 l/kg respectively. It should be noted that if exposure were limited to the solubility in each case then the levels in fish might be expected to be similar for each exposure, and the BCF based on nominal concentrations should decrease with increasing exposure concentration - neither of these were seen. A possible explanation of this would be if the 'undissolved' fraction was contributing to the total level in fish (e.g. if it was absorbed onto external surfaces) or if the substance did not have long enough to equilibrate and the lower test concentrations had a dissolved fraction below the water solubility. From the available bioconcentration data it is not possible to determine which, if any, of these effects are occurring.

Other experiments with fish or fish larvae (e.g. Fisk et al. (1999) and Madeley and Pearson (1980) studies) gave BCF values around 600 l/kg for medium-chain chlorinated paraffins when tested at concentrations around the water solubility, but again there are some uncertainties around the results from these studies.

According to the Technical Guidance Document, the bioconcentration factor (BCF) for fish can be estimated from the following equations:

$$\log BCF = 0.85 \log Kow - 0.70 \qquad \text{for } \log Kow < 6$$
$$\text{or} \quad \log BCF = -0.20 \cdot (\log Kow)^2 + 2.74 \cdot \log Kow - 4.72 \qquad \text{for } \log Kow > 6$$

Since for medium-chain chlorinated paraffins the log Kow is generally >6 then the second of these two equations is more applicable. Using a log Kow value of 7 as being representative of medium-chain chlorinated paraffins, a BCF value of 45,710 l/kg can be estimated.

An alternative predictive method is available in the SRC BCFWIN program. Using the formula $C_{15}H_{26}Cl_6$ as an example, and using the log Kow value of 7, gives a predicted BCF of 1,549 l/kg. This program makes a correction for large numbers of CH_2 groups in a molecule, which reduces the predicted BCF.

From the available data, a fish BCF of 1,087 l/kg is the most reliable for use in the risk assessment. This was obtained by a kinetic method from an experiment using low concentrations of medium-chain chlorinated paraffins. This value is supported by other experimental studies (e.g. Fisk et al. (1999) and Madeley and Pearson (1980)) and is also in line with the prediction obtained from the SRC BCFWIN program.

There are some limited data available for bioconcentration in mussels. In this study, BCFs of 339-2,865 l/kg were determined. However, the concentrations tested (0.22 mg/l and 3.8 mg/l) were again well above the reported water solubility of the substance, and indeed there was visual evidence of undissolved test substance in the test solution of the highest concentration. Since mussels are filter feeders, there is the possibility that some of the uptake found could have been as a result of ingestion of particles/droplets of undissolved test substance. Also in this study, the alga used as a food source appeared to have been constantly dosed in the inflow dilution water, which also contained the test substance. Thus there is the possibility that adsorption of the substance onto the alga prior to ingestion could have occurred and provided a further route of uptake. Therefore the results of the mussel bioconcentration study, although they clearly show that uptake of medium-chain chlorinated paraffins can occur, are difficult to interpret. This is compounded by the fact that there are no standard test methods (e.g. OECD guidelines) for carrying out reliable mussel BCF studies, and there are currently no agreed methods within the Technical Guidance Document for dealing with this sort of data. Therefore, these data are not considered further in this risk assessment.

3.1.1.5.2   Accumulation from sediment and soil

<u>Worms</u>

An experiment to investigate the uptake of medium-chain chlorinated paraffins by oligochaetes (*Lumbriculus variegatus*) from sediment has been carried out (Fisk et al., 1998b). The chlorinated paraffins used were synthesised by chlorination of ^{14}C-hexadecane (labelled in the 1-position for the 35% wt. Cl product, and uniformly labelled for the 69% wt. Cl product), and had the following average formulas: $C_{16}H_{30.7}Cl_{3.3}$ 35% wt. Cl and $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl. The sediment used had the following composition: 76% sand, 21% silt and 3% clay; organic carbon content 1.3-1.5% of dry weight. For each exposure concentration, 36 jars were filled with spiked sediment to provide a 100:1 organic carbon:oligochaete lipid ratio (15 animals per jar) and the jars were placed in flow-through aquaria maintained at 11.6°C. The uptake period of the experiment was for 14 days (this was extended to 21 days in some cases), followed by a 42 day depuration period, where the animals were placed in clean sediment. Analysis of the concentrations present in sediment, interstitial water and the oligochaetes was by ^{14}C measurements using a variety of extraction methods. Biota-sediment bioaccumulation factors were determined both from the rates of uptake and depuration, and also the equilibrium concentrations found in the organisms and sediment (equilibrium was reached within 14-21 days). For the determination of the bioaccumulation factors, concentrations in the organisms were normalised to the lipid content and the sediment concentrations were normalised to the organic carbon content (also corrected for loss of ^{14}C (possibly by biodegradation or metabolism)) as determined by the difference between toluene-extractable and total ^{14}C measurements. The results of the analysis are shown in **Table 3.10**.

Table 3.10 Uptake and accumulation of ^{14}C-labelled chlorinated paraffin by *Lumbriculus variegatus*

Substance	Sediment conc. at 14 days (dry wt)	Sediment organic carbon content[b]	Pore water conc.	Lipid conc.[c]	Uptake rate constant (g/g/d)	Depuration rate constant (d^{-1})	Depuration half-life	Kinetic BAF[d]	'Steady state' BAF[d]
$C_{16}H_{30.7}Cl_{3.3}$	47.1 µg/kg	1.4%	-	2.5%	$9.3 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	33 days	4.4	0.7
	135 µg/kg	1.3%	0.1 µg/l	2.3%	$7.6 \cdot 10^{-2}$	_[a]	_[a]	_[a]	
$C_{16}H_{20.6}Cl_{13.4}$	263 µg/kg	1.5%	0.1 µg/l	2.0%	$1.3 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$	30 days	0.6	0.2

a)   The depuration data for this treatment did not show a significant linear relationship with time.
b)   On a dry sediment weight basis.
c)   Mean lipid concentration of exposed organisms.
d)   BAF is the bioaccumulation factor – defined as [concentration in organisms (µg/kg lipid (wet wt.))]/[concentration in sediment (µg/kg organic carbon (dry wt.))]. Kinetic BAF based on rate of uptake and rate of depuration. 'Steady state' BAF based on concentration measurements in organism and sediment at equilibrium (14 days).

The interpretation of these results is complicated by the fact that the measurements are based on ^{14}C-determinations and there was evidence that biotransformation was occurring in both the sediments and oligochaetes. Therefore, the results could indicate uptake, accumulation and elimination of metabolites rather than the parent compound. This may particularly be the case with the measured depuration rates and half-life, and so the kinetic BAF probably represents the upper limit of the true bioaccumulation factor of the chlorinated paraffin. However, from the results available it can be seen that the potential for uptake by organisms from sediment is reduced as the chlorine content is increased. For the determination of concentrations in the worms, the organisms were not cleansed of gut contents prior to analysis. As the sediment

concentrations were higher than the tissue levels, this may have lead to a significant overestimation of the actual concentration in the organism and hence the actual uptake of the substances

Thompson et al. (2001b) determined the uptake of a n-pentadecane-8-^{14}C, 51% wt. Cl substance by earthworms (*Eisenia fetida*) from soil as part of an earthworm toxicity study. The substance had a radiochemical purity of >96.6% and was mixed with a commercial C_{14-17}, 52% wt. Cl substance to give nominal test concentrations of 100, 1,000 and 10,000 mg/kg dry weight in the test soil. The soil used was an artificial soil consisting of 10% sphagnum moss peat, 70% quartz sand, 20% kaolinite clay and 0.25% calcium carbonate. The soil had an organic carbon content of 4.7%, a pH of 6.66-7.09 and was maintained at moisture content of 26% (a soil wet weight:dry weight ratio of 1.35) throughout the test. At the start of the test, 4 replicates of 10 adult worms each were exposed to the test substance in 500 g of soil. After 28 days, the remaining adult worms were removed and any cocoons present were allowed to hatch over the following 28 days. The concentration of the chlorinated paraffin present in the soil phase (on days 0, 28 and 56), the adult worms (on day 28) and the hatched juvenile worms (on day 56) was determined by a radiochemical method. The results are shown in **Table 3.11**.

Table 3.11 Uptake of n-pentadecane-8-^{14}C, 51% wt. Cl by earthworms

Exposure concentrations			Measured concentrations in earthworms		BCF$_{earthworm}$[a]	
Nominal	Mean measured over day 0-28	Mean measured over day 28-56	Adults at day 28	Juveniles at day 56	Adults	Juveniles
100 mg/kg dry wt.)	70 mg/kg wet wt. (79 mg/kg dry wt.)	61 mg/kg wet wt. (69 mg/kg dry wt.)	169 mg/kg wet wt.	140 mg/kg wet wt.	2.4	2.3
1,000 mg/kg dry wt.	800 mg/kg wet wt. (900 mg/kg dry wt.)	748 mg/kg wet wt. (845 mg/kg dry wt.)	802 mg/kg wet wt.	1,011 mg/kg wet wt.	1.0	1.4
10,000 mg/kg dry wt.	8,200 mg/kg wet wt. (9,300 mg/kg dry wt.)	8,050 mg/kg wet wt. (9,100 mg/kg dry wt.)	732 mg/kg wet wt.	[b]	0.089	[b]

a)   Earthworm BCF calculated as concentration in earthworm (mg/kg wet wt.)/concentration in soil (mg/kg wet wt.)
b)   No offspring were produced at this concentration.

As can be seen from **Table 3.11**, the BCF*earthworm* as calculated directly from the ratio of concentration in earthworm/concentration in soil decreases with increasing soil concentration. Although limited in number, the data appear to show that at high concentrations, the concentration in earthworm is not dependent on the bulk concentration of the substance present in soil. A possible explanation of this finding is that the uptake by the earthworm may be solely via the pore water, and at the high soil concentrations used in this study, the pore water becomes saturated with the test substance. For example, assuming a Koc value of 588,844 l/kg for medium-chain chlorinated paraffin (see Section 3.1.1.6) a Kp value of 27,676 l/kg can be estimated for a soil of 4.7% organic carbon content. Using this value to estimate the equilibrium concentration of the substance present in soil pore water indicates that the pore water would contain 2.9 µg/l, 32.5 µg/l or 336 µg/l of the test substance at soil concentrations of 79, 900 and 9,300 mg/kg dry weight respectively. The water solubility of medium-chain chlorinated paraffins is around 27 µg/l (see Section 1.2.9) and so clearly it is possible that at the high concentrations used in this study, the soil pore water could have become saturated with the chlorinated paraffin.

The other possible mode of uptake of the substance by earthworms from soil is direct ingestion of soil-bound substance. If direct ingestion of soil-bound substance was a major uptake route, then the concentration of substance present in the earthworm would be expected to be directly related to the soil concentration. The available information appears to indicate that this route of uptake is negligible compared with uptake via pore water.

Although the data from this study are limited in number, they do appear to indicate that the major route of uptake of the substance from soil by earthworms is via the soil pore water. Since the soil used in this study had a higher organic carbon content than the default value of 2% suggested in the TGD, and organic carbon content has a bearing on the resulting pore water concentrations in soil, it is important to take account of this fact when considering the data from the Thompson et al. (2001b) study. For example, the highest $BCF_{earthworm}$ obtained from the study was from the 79 mg/kg dry wt. treatment. As shown above, the estimated equilibrium pore water concentration present in the soil would be 2.9 µg/l. However, for a soil with a lower organic carbon content (e.g. 2%) the same pore water concentration would be obtained from a soil concentration of 34.2 mg/kg dry wt., or 30.2 mg/kg wet wt. Thus the $BCF_{earthworm}$ for a soil of 2% organic carbon content would be estimated to be 5.6 on a wet weight basis. In the Technical Guidance Document, uptake by earthworm from soil is considered using the following method:

$$BCF_{earthworm} = \frac{C_{earthworm}}{C_{soil}} = K_{earthworm\text{-}porewater} \times \frac{RHO_{soil} \times 10^{-3}}{K_{soil\text{-}water}}$$

where $BCF_{earthworm}$ = bioconcentration factor for earthworms on a wet weight basis
$C_{earthworm}$ = concentration in earthworm (mg/kg wet wt.)
C_{soil} = concentration in soil (mg/kg wet wt.)
$K_{earthworm\text{-}porewater}$ = earthworm-porewater partition coefficient (l/kg wet wt.)
$K_{soil\text{-}water}$ = soil-water partition coefficient = 17,666 m^3/m^3 for medium-chain chlorinated paraffins (see Section 3.1.1.6).
RHO_{soil} = bulk density of wet soil = 1,700 kg/m^3

According to the Technical Guidance Document, the value for $K_{earthworm\text{-}porewater}$ can be estimated by the following equation for substances with a log Kow ranging from 1.0-6.5 (for substances above this range, the maximum value of log Kow of 6.5 is used):

$K_{earthworm\text{-}porewater} = 0.25 \cdot Kow \cdot 0.16$

Thus for medium-chain chlorinated paraffin (log Kow value of 7), the value of $K_{earthworm\text{-}porewater}$ predicted is 126,491 l/kg wet wt. The subsequent value for the $BCF_{earthworm}$ = 12.2 on a wet weight basis.

The bioaccumulation factors measured above of *L. variegatus* can be compared directly with the estimated $K_{earthworm\text{-}porewater}$ if they are converted to represent the concentration in wet organism/pore water concentration. In order to do this, the lipid concentration of the organism (**Table 3.10**) and the Koc value for the chlorinated paraffins tested are needed. From the data given in **Table 3.10**, Koc values of 103,846 and 175,333 l/kg can be estimated for the $C_{16}H_{30.7}Cl_{3.3}$ 35% wt. Cl and $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl compounds respectively (log Koc = 5.0 and 5.2). Thus the measured 'steady state' $K_{worm\text{-}porewater}$ for *L. variegatus* (expressed as [µg/kg wet worm]/[µg/l pore water]) = 1,817 l/kg wet wt. for the $C_{16}H_{30.7}Cl_{3.3}$ 35% wt. Cl compound and 701 l/kg wet wt. for the $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl compound (higher values

would be obtained if the kinetic measurements are used). Thus, the measured partition coefficients in this case are around a factor 100 less than the one predicted from log Kow.

Further information on the Fisk et al. (1998b) study has been provided by industry (Euro Chlor, 1999). They obtained from the authors the actual concentrations in the worms at 14 days as 52.9 µg/kg wet wt. for the $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl compound and 109.6 µg/kg wet wt. for worms exposed to the higher concentration of the $C_{16}H_{30.7}Cl_{3.3}$ compound. As the sediment pore water concentration in both these experiments was determined at around 0.1 µg/l (see **Table 3.10**), the equivalent values for $K_{worm\text{-}porewater}$ are 1,096 l/kg for the $C_{16}H_{30.7}Cl_{3.3}$ 35% wt. Cl compound and 529 l/kg for the $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl compound. These are similar to the values estimated above assuming an equilibrium partitioning, and indicate that this process may adequately account for the uptake seen from sediment. Fisk et al. (1998b) also concluded that, at least for the $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl compound, the uptake could be explained in terms of uptake from pore water and that there was little evidence for additional uptake by direct ingestion of sediment.

The substances tested in the Fisk et al. (1998b) paper represent the extremes of the typical chlorine contents of the medium-chain chlorinated paraffins in commercial production (i.e. 35% wt. Cl and 69% wt. Cl compounds were tested whereas the commercial products are typically in the range 45-52% wt. Cl. (up to 63% wt. Cl)). It is clear from the available data that uptake of medium-chain chlorinated paraffins by worms decreases with increasing chlorine content. However, there is insufficient information available to estimate if the uptake of the most common commercial medium-chain chlorinated paraffins (e.g. 45% wt. Cl. and 52% wt. Cl) is likely to be less than that determined for the $C_{16}H_{30.7}Cl_{3.3}$ 35% wt. Cl compound and so for the risk assessment of secondary poisoning, a $K_{worm\text{-}porewater}$ value of 1,817 l/kg wet wt. can be estimated from this data. The corresponding value for $BCF_{earthworm}$ would be 0.17 on a wet weight basis. From the available data, the potential for uptake by worms from soil and sediment is likely to reduce with increasing chlorine content.

Overall, the available uptake data for worms in both soil and sediment indicate that accumulation can best be explained by exposure mainly via the pore water, with only a minor contribution from sediment- or soil-bound substance. Based on the available experimental data BCF values of 5.6 using the earthworm data and 0.17 using the sediment worm (*L. variegatus*) data can be estimated (both on a wet weight basis). The earthworm value is in good agreement with the value of 12.2 on a wet weight basis estimated from log Kow using the Technical Guidance methodology. A $BCF_{earthworm}$ of 5.6 on a wet weight basis will be used in the risk assessment.

Plants

As part of a plant toxicity study, Thompson et al. (2001a) examined the concentration of medium-chain chlorinated paraffin present in above ground parts of seedlings of wheat (*Triticum aestivum*), oilseed rape (*Brassica napus*) and mung bean (*Phaseolus aureus*) after exposure for 28-days via soil. The soil used in the test had an organic carbon content of 2.3% and groups of 9 seeds were exposed to nominal medium-chain chlorinated paraffin concentrations of 50, 500 or 5,000 mg/kg dry weight. The substance tested was a commercial C_{14-17}, 52% wt. Cl substance, mixed with a radio-labelled n-pentadecane-8-^{14}C, 51% wt. Cl (radiochemical purity was >96.6%). Water was provided primarily by sub-irrigation but additional water was provided by top-down watering twice a day. The test was carried out in a glass house where the temperature ranged from 16-31.8°C. Initially, 4 replicates of 9 seeds per pot were exposed per concentration. After day 14 the emerged seedlings were randomly thinned to 5 per pot. A day 28 the plants were cropped at soil level and the concentration of medium-chain chlorinated paraffin present in the above ground shoots was determined by radiochemical analysis, and a plant BCF

(concentration in shoots (mg/kg wet wt.)/concentration in soil (mg/kg wet wt.)) was calculated for each species. Further details of the test system used can be found in Section 3.2.2.2. The results are shown in **Table 3.12**.

Similar to the case with the earthworm study discussed above, the plant BCF appears to decrease with increasing soil concentration. This is as would be expected if the uptake was via the soil pore water and this became saturated at high soil concentrations. In this case, however, because the soil used has a similar organic carbon content to the TGD default, it is not necessary to correct the results to the properties of the standard default soil. A value of 0.034 will be considered as a realistic worst case value for the BCF for uptake by plants from soil.

Table 3.12 Uptake of n-pentadecane-8-^{14}C, 51% wt. Cl from soil by plants

Plant species	Concentration in soil		Concentration in shoots (mg/kg wet weight)	Plant BCF (wet wt. basis)
	mg/kg dry wt.	mg/kg wet wt.[a]		
Wheat (*Triticum aestivum*)	50	44	1.5	0.034
	500	442	14	0.032
	5,000	4425	79	0.018
Oilseed rape (*Brassica napus*)	50	44	0.48	0.011
	500	442	2.6	0.0059
	5,000	4425	27	0.0061
Mung bean (*Phaseolus aureus*)	50	44	1.1	0.025
	500	442	6.3	0.014
	5,000	4425	30	0.0068

a)   The concentrations in the soil were determined on a dry soil weight basis. The concentration on a wet weight basis is estimated using the TGD default water content for soil.

3.1.1.5.3 Dietary accumulation

The dietary accumulation of medium-chain chlorinated paraffins has been studied in juvenile rainbow trout (*Oncorhynchus mykiss*). Trout (initial weights 2-7 g) were fed with ^{14}C-labelled chlorinated paraffins (either C_{16} 35% wt. Cl or C_{16} 69% wt. Cl) spiked into food (lipid content 14%). The experiment consisted of a 40 day exposure period followed by a 160-173 day depuration period. The daily feeding rate was 1.5% of the mean body weight and two or three exposure concentrations for each substance were used (29 and 296 µg/kg food for the 35% wt. Cl substance and 21, 198 and 2,000 µg/kg food for the 69% wt. Cl substance). At these feeding rates, neither substance was found to have any negative effect on the growth of juvenile rainbow trout. At various times during the exposure and depuration phases of the experiment fish were analysed for the presence of chlorinated paraffin by ^{14}C-measurements (parent compound analysis by HPLC was also carried out on day 40 of the uptake phase and day 20 of the depuration phase). Uptake of both chlorinated paraffins was found to occur and had not reached steady state by day 40 of the experiment (exposure to the high concentration of the 69% wt. Cl substance was continued up to day 80, where steady state still was not reached). Bioaccumulation factors of 0.9-1.07 for the 35% wt. Cl substance and 0.44-0.72 for the 69% wt. Cl substance were estimated based on the rates of uptake and depuration, expressed on a lipid weight basis (the concentrations in fish were also corrected for growth dilution). The assimilation efficiencies were 33-35% for the 35% wt. Cl substance and 9.4-30% for the 69% wt. Cl substance. The carcass was found to contain the highest amounts of the ^{14}C assimilated and the whole body half-lives were determined as 37-50 days for the 35% wt. Cl

substance and 58-77 days for the 69% wt. Cl substance. The HPLC analyses carried out indicated that substantial metabolism of the chlorinated paraffin was occurring, and so the determined bioaccumulation factors represent the total uptake of parent compound and metabolites, rather than just the parent compound (Fisk et al., 1996).

The dietary accumulation of various C_{14} chlorinated paraffins in juvenile rainbow trout (*Oncorhynchus mykiss*) has been investigated in a study by Fisk et al. (1998a). The chlorinated paraffins used in the experiment were synthesised by the gas-phase free-radical chlorination of 1,13-tetradecadiene. The main product from this reaction was 1,2,13,14-tetrachlorotetradecane ($C_{14}H_{26}Cl_4$; 42% wt. Cl), but other 1,2,13,14-substituted products were also formed including two pentachlorotetradecane isomers ($C_{14}H_{25}Cl_5$; 48% wt. Cl) and two hexachlorotetradecane isomers ($C_{14}H_{24}Cl_6$; 53% wt. Cl). In the study, the products from this reaction were combined with those from the chlorination of 1,9-decadiene before being spiked onto proprietary fish food (14% lipid content). The concentration of each isomer in the food was determined by GC analysis. The fish (initial weight 2-7 g; mean lipid content 2.7-3% from day 5 to the end of the study) were then exposed to the spiked food for 40 days, followed by 80 days depuration. At various times during the experiment, 3 fish were sampled and analysed for the presence of the chlorinated paraffin isomers (parent compound analysis). No significant effects on the health of the fish (growth rate, lipid content, liver somatic indices and mortality) were seen during the experiment, and no chlorinated paraffin was detected in the control fish (detection limit ~1 µg/kg). Uptake of the C_{14} chlorinated paraffins was seen to occur during the experiment, although steady state had not been reached during the 40 days exposure. The estimated bioaccumulation factors based on kinetic measurements and the tissue concentrations (the tissue concentrations were lipid normalised and growth corrected for the kinetic measurements) after 40 days are shown in **Table 3.13**.

Table 3.13 Dietary accumulation of C_{14} chlorinated paraffins in rainbow trout (Fisk et al., 1988a)

Substance	Concentration in food	Depuration half-life (days)	Assimilation efficiency - α	Bioaccumulation factor (BAF)		
				BAF_{calc}	BAF_{equil}	BAF_{ss}
$C_{14}H_{26}Cl_4$	92 µg/kg	39±6.4	33±2.4%	1.7	2.1	0.82
$C_{14}H_{25}Cl_5$ (a)	66 µg/kg	53±12.3	51±3.9%	3.6	3.0	1.4
$C_{14}H_{25}Cl_5$ (b)	54 µg/kg	46±9.2	46±3.5%	2.9	2.6	1.2
$C_{14}H_{24}Cl_6$ (a)	63 µg/kg	29±7.2	130±12%	5.0c	1.9	2.8
$C_{14}H_{24}Cl_6$ (b)	40 µg/kg	43±8.1	27±2.4%	1.6	2.9	0.74

(a)   and (b) denote different isomers.

c)   This value could be questioned as the assimilation efficiency used in the calculation was >100%.

BAF_{calc} is estimated from rate of uptake (α×feeding rate on lipid basis)/depuration rate. These are considered to be the most reliable values.

BAF_{equil} is estimated from rate of uptake (α×feeding rate on lipid basis)/depuration rate - assuming a value for α of 0.5.

BAF_{ss} concentration in fish at 40 days (lipid corrected, not growth corrected)/concentration in food (lipid corrected) - steady state was not reached in 40 days, so the actual steady state values will be higher than this.

The most reliable data are considered to be the BAF_{calc} values as these were based on the actual kinetic parameters measured in the study and do not depend on steady state being reached within the 40-day exposure period. The half-life for depuration was found to be around 29-53 days. The results from all the C_{10}-, C_{11}- and C_{14}-chlorinated paraffins studied suggested that chlorine position along the carbon chain may have a significant influence on the bioaccumulation of chlorinated paraffins. The C_{14} chlorinated paraffins used in this study differ from those in the commercial products in that they all contain chlorine atoms on adjacent and terminal carbon

atoms (such a substitution pattern is chemically and energetically unfavourable under the reaction conditions used to produce the commercial products). Nevertheless, the results indicate that at least some C_{14} chlorinated paraffins have the potential to accumulate through the diet (BAF>1).

The dietary accumulation of a C_{14}, 63.7% wt. chlorinated paraffin has been studied in juvenile rainbow trout (*Oncorhynchus mykiss*) (Fisk et al, 2000). The substance tested was a single carbon chain length product synthesised by the free-radical chlorination of a ^{14}C-labelled C_{14}-alkane with SO_2Cl_2. The product had an average formula of $C_{14}H_{21.3}Cl_{6.7}$, but the position of the radio-label in the carbon chain was not stated. The food used during the test was a commercial fish food (41% protein, 14% lipid and 3% fibre). The chlorinated paraffin was added to the food as a suspension in hexane followed by evaporation of the solvent. Two chlorinated paraffin concentrations were tested: 1.3 mg/kg wet wt. food and 13 mg/kg wet wt. food. During the test, groups of 36 juvenile fish in flow-through tanks (initial weight 1-5 g, final weight 23-69 g, lipid content at day 40 6.1-11.0%) were fed the contaminated food (daily feeding rate was 1.5% of mean weight of fish) over a 40-day period, followed by a 160-day depuration period using clean food. At various times during the experiment fish were sampled for ^{14}C levels in the carcass (whole fish minus liver and G. I. tract). All measured concentrations were corrected for growth dilution. At day 40 of the uptake phase and day 40 of the depuration phase the amount of non-toluene-extractable ^{14}C-label present in carcass was also determined. This measurement was assumed to reflect the extent of biotransformation of the substance in fish. No effect on body and liver growth rates or liver somatic indices were seen between exposed and control populations during the test and no mortalities were seen.

The results indicated that the chlorinated paraffin uptake had not reached steady state by day 40 of the uptake phase and so the bioaccumulation factor for uptake from food was determined kinetically. The assimilation efficiencies (based on lipid corrected concentrations in fish (the fish concentrations were also adjusted for growth dilution) and food) were determined to be 10.0% at the low dose and 11% at the high dose, and the depuration rate constant was estimated to be 0.012-0.017 d^{-1} (depuration half-life ~41-58 days). There was some evidence for biotransformation of the chlorinated paraffin by the fish. Based on the measured kinetic parameters (bioaccumulation factor = assimilation efficiency·feeding rate/depuration rate constant), the bioaccumulation factor was around 0.43 at the low exposure concentration and 0.27 at the high exposure concentration. These values are based on ^{14}C measurements and so will include a contribution from any metabolites formed. It should also be noted that the fish concentrations are based on those in the carcass and so the actual concentration in whole fish (and hence bioaccumulation factor) could be higher than indicated here if the liver and G.I. tract were included. [The Fisk et al. (2000) paper also estimates bioaccumulation factors <1 from the data outlined above assuming assimilation efficiencies of 50% and 90%. However, these are example calculations only and are not considered relevant to this assessment.]

A further study into the uptake of medium-chain chlorinated paraffins by rainbow trout from food has been carried out by Cooley et al. (2001) as part of a toxicity investigation. In the study, juvenile trout were exposed to one of two short-chain chlorinated paraffins daily via food for either 21 or 85 days. The food used in the test had a lipid content of 14%. The resulting whole fish tissue concentrations and the bioaccumulation factors that can be estimated from the data are shown in **Table 3.14**. Further experimental details of this study are report in Section 3.2.1.1. Fish from several of the high exposure concentrations fed erratically during the test which means that the actual relative exposure of these fish may be lower than indicated by the concentration in food.

Table 3.14 Uptake of medium-chain chlorinated paraffins by juvenile rainbow trout from food (Cooley et al., 2001)

Chlorinated paraffin	Exposure period (days)	Concentration in food (mg/kg)	Concentration in whole fish (mg/kg)	Estimated BAF[a]
$C_{14}H_{24.9}Cl_{5.1}$	85	0.082	0.018[b]	0.22
	21	0.78	0.11[b]	0.14
	21	2.9	0.028[b]	0.010
$^{14}C\text{-}C_{14}H_{23.3}Cl_{6.7}$	85	5.7	0.57[c]	0.10
	21	29	1.3[c]	0.045
	21	78	0.22[c]	0.003

a)   BAFs have been estimated in this report from the data (BAF = concentration in fish/concentration in food).
b)   The concentration was determined by parent compound analysis.
c)   The concentration was determined by ^{14}C analysis.
d)   These concentrations are reported elsewhere in the paper as 1.8, 2.6 and 14 µg/kg respectively.

The metabolism and distribution of a radio-labelled medium-chain chlorinated paraffin has been studied in Japanese Quail (*Coturnix coturnix japonica*). The substance tested was a C_{16} compound and had an average formula $C_{16}H_{30.7}Cl_{3.3}$ (34.5% wt. Cl) and contained a ^{14}C-label in the 1-position (specific activity was 22.7 Ci/mole). The chlorinated paraffin was dissolved in a lipid emulsion before administration by gavage. The birds used in the study had an average body weight of 164.5 g. The distribution of the radio-label was determined by whole body autoradiography 1 hour, 4 hours, 1 day, 4 days and 12 days after administration of a single dose. Initially, high uptake of radioactivity was seen in tissues with high metabolic activity and high cell turnover rate (e.g. liver, kidney, gall bladder, intestinal mucosa, spleen, bone marrow and oviduct). The radioactivity found in fat generally increased with time. By days 4 and 12 the dominant levels of radioactivity were found to be in fat, follicle yolk and the contents of the uropygial gland. The excretion of $^{14}CO_2$ from the dosed birds was studied over an eight hour period after dosing. Around 38.8% of the administered dose was found in the exhaled air as $^{14}CO_2$ and 13.5% of the administered radio-label was found in faeces and urine. The amounts of radio-label present in egg yolk, albumen and eggshells were determined 5 to 10 days after administration, with 6.6% of the administered radioactivity being present in egg yolk after 10 days, 0.8% present in albumen after 5 days and 0.6% present in eggshells after 5 days (Biessmann et al., 1982).

Darnerud and Brandt (1982) investigated the distribution and metabolism of the same radiolabelled $C_{16}H_{30.7}Cl_{3.3}$ (34.5% wt. Cl) substance in mice. The medium-chain chlorinated paraffin was dissolved in intralipid or dimethyl sulphoxide and administered to the mice either intravenously in a tail vein or perorally by gastric intubation. Autoradiography showed that the distribution of radioactivity after administration was characterised by high uptake in tissues associated with high metabolic activity, with comparatively low levels of radioactivity seen in white fat deposits. A marked uptake of radioactivity was seen within 24 hours of administration in liver, kidney, spleen, bone marrow, brown fat, intestinal mucosa, pancreas, salivary glands and harderian gland. After 12 days elevated levels of radioactivity were also seen in adrenal cortex, abdominal fat and bile, and after 30 days the level of radioactivity in brain was prominent and equalled that of the liver. No significant differences were seen in the distribution patterns in mice given the peroral dose compared with the intravenous dose, except that higher levels of radioactivity were seen in the stomach and intestinal contents of the perorally administered mice. It was found that 32.8-44.3% of the administered dose of radioactivity was excreted as $^{14}CO_2$ within 12 hours of administration. The retention of radioactivity in the adrenal cortex and brain

was thought to be as result of incorporation of radioactivity into the synthesis of endogenous substances via ^{14}C-acetyl CoA.

In another study by Biessmann et al. (1983), the distribution and metabolism of a more highly chlorinated C_{16} paraffin (average formula $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl) was studied using female quail (average weight 165 g) and mice (average weight 22 g). In this case the ^{14}C-label was uniformly distributed throughout the carbon chain. The chlorinated paraffin was dissolved in lipid emulsion administered either intravenously or per orally. In quail, uptake of radioactivity 4 hours after administration was seen in liver, intestine, gall bladder, egg yolk, kidney, ovary, blood, hypophysis and retina, but 12 days after administration significant radioactivity was seen only in the uropygial gland, white fat, liver and yolk. A similar pattern was seen in mice, with the addition that corpora lutea also showed a high uptake of radioactivity. In contrast with the 34.5% wt. Cl substance tested above, only a small amount (0.9-1.6% of the total) of the radioactivity was exhaled as $^{14}CO_2$ over the first 8 hours after dosing in both quail and mice. This could indicate that the 69% wt. Cl substance is metabolised to a lesser extent than the 34.5% wt. Cl substance, but this interpretation is complicated by the fact that the 34.5% wt. Cl substance was ^{14}C-labelled in the 1-position, whereas the 69% wt. Cl substance was uniformly labelled and so the results for the two substances are not directly comparable. Elimination of radioactivity after 96 hours was found to be mainly in faeces (43-66% of the total), with a smaller amount in urine (2.9-3.2%). A difference in excretion rate via faeces over the first 8 hours was found between the p.o. dosed and the i.v. dosed mice and quail which indicated that the substance was incompletely adsorbed by the p.o. route.

Birtley et al. (1980) studied the uptake of a medium-chain chlorinated paraffin in rats. The substance tested was a commercial C_{14-17}, 52% wt. Cl product mixed with a ^{36}Cl-labelled product (again C_{14-17}, 52% wt. Cl) synthesised by chlorination of a n-paraffin feedstock. In this study, the medium-chain chlorinated paraffin was administered in the diet (the lipid content of the diet was not given) at 0.4 mg/kg food for 10 weeks or 40 mg/kg food for 8 weeks. Equilibrium levels of radioactivity in liver and abdominal fat were found to be reached within 1 week and 7 weeks respectively. No radioactivity was found in brain or adrenal glands. The half-life for removal of radioactivity from abdominal fat was around 8 weeks, and the level of radioactivity in the liver was below the detection limit within 1 week, when the medium-chain chlorinated paraffin was removed from the diet. The equilibrium concentration of radioactivity in the abdominal fat was similar to, but never exceeded, the concentration in diet.

Poon et al. (1995) also studied the uptake of a commercial C_{14-17}, 52% wt. Cl product by rats via the diet (the lipid content of the diet was not given). In this case parent compound analysis was used to determine the concentrations of the chlorinated paraffin in fat and liver. In the study, both male and female rats were given food containing either 5, 50, 500 or 5,000 mg/kg food of the chlorinated paraffin for 13 weeks. At the end of the study, the concentrations found in body fat were again found to be similar to the concentration in the diet, reaching 4, 30-39, 417-642, and 5,430-5,581 mg/kg lipid for the four doses respectively. The concentrations found in the liver were much lower than found in the fat.

3.1.1.5.4 Summary of accumulation

The available data indicate that medium-chain chlorinated paraffins are taken up by organisms from water, sediment/soil and food.

Uptake from water

It is difficult to derive a reliable value for the fish BCF from some of the available data. A recent study designed to address many of the problems associated with the earlier studies has determined a BCF of 1,087 l/kg and this will be used in the assessment. The value was derived using radiochemical analyses and so represents the accumulation of the parent compound itself and any metabolites formed and so may overestimate the true BCF of the substance.

The available food uptake studies indicate that the 35% wt. Cl, 52% wt. Cl and 69% wt. Cl products can be taken up by organisms from food. The potential for uptake from food appears to reduce with increasing chlorine content. The majority of the studies are based on ^{14}C-measurements and indicate that substantial metabolism is 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 addition to bioconcentration, the Technical Guidance Document now provides methods to take into account biomagnification in the assessment of secondary poisoning. The Scientific Committee on Toxicity, Ecotoxicity and the Environment has also identified this as an important consideration for medium-chain chlorinated paraffins (CSTEE, 2002). The method requires a biomagnification factor (BMF) for fish, preferably expressed on a lipid-normalised basis. According to the Technical Guidance Document, an appropriate BMF for medium-chain chlorinated paraffins would be either 1 (based on the fish BCF of 1,087 l/kg) or 10 (based on a log Kow of 7) as a default value. The BMF value of 1 takes precedence since it is associated with a measured fish BCF. However, the lipid-normalised accumulation factors determined for medium-chain chlorinated paraffins with fish in laboratory feeding studies are generally in the range 0.44 to 5.0 (the high value of 5.0 can be questioned as it is based on an assimilation efficiency of >100%), with most values appearing to be around 1-3, depending on the chlorinated paraffin used and the method of calculation. This suggests that the actual BMF for medium-chain chlorinated paraffins may be higher than the recommended default value.

It should be recognised that the assessment of bioaccumulation/biomagnification according to the methods given in the Technical Guidance Document is at a relatively early stage of development. There is a general lack of experience in addressing some of the uncertainties that are associated with the methods used in fish feeding studies, and the following important points need to be considered:

- There is a fundamental difference in biomagnification/accumulation factors obtained from field studies/measurements and those obtained from laboratory feeding studies. Field-derived factors will take into account accumulation from water and by food, whereas laboratory feeding studies only consider the food route. No distinction is made in the methods given in the Technical Guidance Document between these two types of factors (this is considered further in Section 3.1.5.1).

- Many of the data are lipid-normalised. For some of these studies (e.g. those by Fisk et al. (1996), Fisk et al. (1998a) and Fisk et al. (2000)) the fish food used in the study had a lipid content of 14%, which was generally higher than that in the fish (e.g. 2.7-3.0% in the Fisk et al. (1998a) study and 6-11% in the Fisk et al. (2000) study). Thus if the accumulation factors were expressed in terms of a whole fish and whole food basis, the factors would be around 1.3-4 times lower than determined on a lipid basis and the reported accumulation factors would be below 1. However, conversely, it could be argued that in the environment the food for a predatory species would be generally of lower lipid content than found in laboratory fish food (and may be of lower lipid content than the predatory species itself). It is therefore not possible to infer from these results (or other laboratory-based results using proprietary

food of high lipid content) that the accumulation factor on a whole body and food basis would be below 1 in the environment. In terms of the Technical Guidance Document, the methods suggest that the lipid-normalised BMFs should be used.

- The uptake of a chemical from food depends on many factors including the feeding rate, the digestibility of the food, the lipid content of the food and the size of the organism (Environment Agency, 2003; Hendriks et al., 2001). The current methods proposed in the Technical Guidance Document give little or no guidance on how these factors should be considered within the risk assessment framework. Therefore the use of data from the available feeding studies in the current methods given in the Technical Guidance Document needs careful consideration.

- Several of the studies have been corrected for growth dilution. The Technical Guidance Document is unclear on whether this is an appropriate basis on which to calculate accumulation or biomagnification factors. It could be argued that such a correction, in some circumstances, may make it virtually impossible for a steady state to be reached in fish that are growing. For example, it is possible to conceive of a situation where the actual concentrations in the fish remain constant from one sampling period to the next (i.e. steady state may have been reached) but if the fish grew by 10% over the same sampling period then the growth corrected concentrations would appear to increase by 10% as a result only of the calculation method involved. Environment Agency (2003) has reanalysed the growth corrected data for medium-chain chlorinated paraffins from the Fisk et al. (1996, 1998a and 2000) studies and estimated that the non-growth-corrected fish BMFs from the studies would be around 0.081-0.23 on a lipid basis in the Fisk et al. (1996) study, 0.34-1.48 on a lipid basis in the Fisk et al., 1998a study and 0.033-0.061 on a lipid basis in the Fisk et al. (2000) study. It should be noted, however, that since the original raw concentration – time data were lacking in the papers (they generally reported only the derived kinetic parameters) the reanalysis is only approximate and may be subject to large errors

- Several of the studies investigating the kinetics of uptake have, in some cases, calculated relatively high accumulation factors when assuming assimilation efficiencies higher than those found in the experiment. These are, however, hypothetical calculations only as the actual assimilation efficiency was also determined in almost all of these studies. Thus, the kinetic data most relevant to this assessment from these studies are those based on the actual assimilation efficiencies measured.

- Many of the studies measuring the accumulation factor based on the concentration in fish at the end of the exposure period do not appear to have reached steady state. These data may therefore underestimate the actual accumulation factor. Accumulation factors determined by kinetic methods do not suffer from this problem. Despite this, there are some accumulation factors in the range 1-3 on a lipid basis based on measurements of the non-steady-state concentration in fish after 40 days' exposure.

- Many of the results have been obtained using ^{14}C-measurements and will include contributions from metabolites and so overestimate the accumulation of medium-chain chlorinated paraffins themselves. However, the data of Fisk et al. (1998a) were generated based on parent compound analysis, and accumulation factors up to 3.6 on a growth-corrected lipid basis were determined in this study.

- In feeding studies the rate of uptake of the chemical is dependent on the feeding rate. This is assumed to be a function of the amount of food added to the fish each day but in some studies (e.g. Cooley et al., 2001) it is clear that the spiked food had some effects on the actual feeding of the fish and may mean that the actual exposure in some studies could be lower (and hence accumulation factor higher) than indicated by the nominal feeding rate.

- Most of the data are available for C_{14}- chain lengths. The accumulation behaviour in fish of the longer chain lengths present in medium-chain chlorinated paraffins is less well studied but accumulation factors of up to 1.07 in fish have been measured for a C_{16}, 35% wt. Cl substance.

- 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 reported in Section 3.1.5.2 (the levels found in herring were higher than those found in seals). Similarly, recent field studies by Muir et al. (2002) showed no indications of biomagnification of medium-chain chlorinated paraffins in three lake trout– fish food chains but did appear to show BMFs >1 for medium-chain chlorinated paraffins in a fish–invertebrate food chain. Furthermore, there was some indication from the Muir et al. (2002) data that although biomagnification did not appear to be occurring, the actual bioaccumulation factor for medium-chain chlorinated paraffins 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 summary, the measurement of the accumulation/biomagnification factor is very difficult for complex substances such as medium-chain chlorinated paraffins and so there are some uncertainties associated with many of the determinations. Taking into account all of the factors described above, it is not possible to determine reliable BMF values suitable for use in the risk assessment based on current understanding of the methods used in the available studies. Indeed many of the points outlined above are not specific to medium-chain chlorinated paraffins. Rather they refer to how such data in general should be generated and treated within the current framework for secondary poisoning outlined in the Technical Guidance Document and this is an area that is probably best addressed outside of this specific assessment.

The available data for medium-chain chlorinated paraffins do show that uptake into fish from food occurs in the laboratory and, although this uptake can be significant in some cases, an accumulation factor around 1-3 would seem to be an appropriate worst case estimate.

In summary, a BCF of 1,087 l/kg and an accumulation factor from food of between 1 and 3 on a lipid basis will be used for the fish food chain risk assessment (the accumulation factor range reflects the uptake seen (for whatever reason) in some laboratory studies; the actual appropriate basis for determining such accumulation factors in laboratory studies is unclear at present).

Uptake from soil

A $BCF_{earthworm}$ of 5.6 on a wet weight basis has been derived from the available uptake data and will be used in the risk assessment of secondary poisoning for the earthworm food chain. The potential for uptake by worms from soil and sediment appears to reduce with increasing chlorine content of the medium-chain chlorinated paraffin.

Uptake from soil into above-ground parts of plants has also been observed, and a BCF of 0.034 on a wet weight basis has been determined for this process.

3.1.1.6   Adsorption

The Koc value for medium-chain chlorinated paraffins can be estimated using the QSAR equation for predominantly hydrophobic chemicals given in the Technical Guidance Document:

$$\log Koc = 0.81 \log Kow + 0.10$$

Using a log Kow value of 7.0, a Koc value of 588,844 l/kg can be estimated. This is in reasonable agreement with the Koc values determined by Fisk et al. (1998b) in sediment (Koc = 103,846 l/kg for the $C_{16}H_{30.7}Cl_{3.3}$ 35% wt. Cl and 175,333 l/kg for $C_{16}H_{20.6}Cl_{13.4}$ 69% wt. Cl), based on ^{14}C measurements. A recent definitive determination of Koc values using short-chain chlorinated paraffins has indicated that the above equation is applicable to chlorinated paraffins (Thompson et al., 1998), and so the predicted value with be used here in the assessment.

Using the 588,844 l/kg value the following partition coefficients can be estimated for soil, sediment and suspended sediment using the methods given in the Technical Guidance Document. These values will be used in the environmental modelling for medium-chain chlorinated paraffins.

Soil (2% organic carbon)	Kp_{soil} = 11,777 l/kg	$K_{soil-water}$ = 17,666 m^3/m^3
Sediment (5% organic carbon)	$Kp_{sediment}$ = 29,442 l/kg	$K_{sed-water}$ = 14,721 m^3/m^3
Suspended sediment (10% organic carbon)	Kp_{susp} = 58,884 l/kg	$K_{susp-water}$ = 14,721 m^3/m^3

For medium-chain chlorinated paraffins, a range of octanol-water partition coefficients would be expected, representing the differing hydrophobic nature of the various components of the commercial product. For the assessment, a log Kow value of 7 is taken as being representative for the group as a whole. The actual measured values vary between log Kow ~5.5 and 8.2. Thus some components of the commercial products may have values for the adsorption partition coefficients higher or lower than the values shown above, but in all cases, a high degree of adsorption onto soil, sediment and suspended sediment would be predicted. Appendix H considers the effect of varying the Koc value on the predicted environmental concentrations.

The high Koc value estimated for medium-chain chlorinated paraffins indicates that the substance is expected to be relatively immobile in soil and would not be expected to leach from soil into groundwater. Vertical movement of medium-chain chlorinated paraffins adsorbed onto soil particulates via macropores may provide a transport mechanism in soil.

3.1.1.7 Environmental distribution

The potential environmental distribution of medium-chain chlorinated paraffins has been studied using a generic level III fugacity model. The model used was a four compartment model (FUGMOD version 1, January 1992) that has been circulated for use within the OECD HPV program. The model was run using the default settings in the model and the following chemical specific input data were used:

water solubility	0.027 mg/l
vapour pressure	0.00027 Pa
log Kow	7
Degradation half-life in air	48 hours
Degradation half-life in other media	very large (e.g. $1 \cdot 10^{11}$ hours)

The model was run four times with a nominal release rate of 1000 kg/hour initially entering the air, soil or water compartments in different proportions. The results of the modelling exercise are shown in **Table 3.15**. The full model output is given in Appendix C. The same results were obtained when the distribution was calculated with the EQC model (version 1.0).

Table 3.15 Fugacity modelling for medium-chain chlorinated paraffins

Release compartment	Percentage distribution			
	Air	Water	Soil	Sediment
100% to air	0.001%	0.004%	99.6%	0.38%
100% to water	$7 \cdot 10^{-4}$%	0.44%	55.5%	44.1%
100% to soil	$1 \cdot 10^{-5}$%	0.003%	99.7%	0.34%
50% to air and 50% to water	0.001%	0.012%	98.3%	1.7%

The results of the fugacity modelling indicate that medium-chain chlorinated paraffins are likely to be associated with the soil and sediment compartments. When the substance is released to air, the model predicts that this will end up mainly in soil, probably as a result of atmospheric deposition processes. When the substance is released to water, the model predicts that a substantial amount of the substance will be associated with sediment, but some would also be expected to occur in the water phase. A substantial amount of the substance released to water is predicted to enter the soil phase, presumably as a result of volatilisation to the atmosphere and subsequent deposition. When the substance is released to soil, it is predicted to remain mainly in the soil compartment, but a small amount may also enter the sediment compartment, possibly as a result of wash-off from the soil to water.

3.1.2   Aquatic compartment (inc. sediment)

3.1.2.1   Calculation of PEC$_{local}$

Using the emission data given in **Table 3.5** for the estimated amounts released at a site for production and the various uses of medium-chain chlorinated paraffin, it is possible to estimate a PEC for surface water by assuming that the amount released/site enters into waste water and this enters into a waste water treatment plant. The Technical Guidance Document suggests that the size of the waste water treatment plant should be around 2,000 m^3/day, and the effluent from the plant will be diluted by a factor of 10 in the receiving water. It is assumed that no biodegradation occurs during waste water treatment.

Based on the physico-chemical properties of medium-chain chlorinated paraffins (vapour pressure = $2.7 \cdot 10^{-4}$ Pa; water solubility = 0.027 mg/l; Henry's law constant ~4.9 Pa m^3 mol^{-1}; octanol water partition coefficient (log value) = 7) the predicted behaviour of the substance during waste water treatment (as estimated in EUSES) is:

% to air	0.107%
% to sludge	90.8%
% degraded	0%
% to water	9.08%

However, information on the short-chain chlorinated paraffins indicates that the removal by adsorption onto sludge may be higher, around 93%, based on the results of a coupled unit test. Since medium-chain chlorinated paraffins are likely, if anything, to adsorb more strongly onto sludge, then the results obtained for the short-chain chlorinated paraffins will be used in preference to the values obtained by EUSES, i.e. for the PEC calculations in the following sections, 7% release to surface water from the waste water treatment plant will be assumed.

Where site specific information is available on the size of waste water treatment plant and subsequent dilution, these will be used in preference to the generic information. This is currently only the case for production sites. For many of the down-stream uses of medium-chain chlorinated paraffins, several sites are likely to be involved and so a generic approach to the size of waste water treatment plant and dilution in the receiving water is appropriate.

Once released to surface water, the substance will adsorb onto suspended sediment. The following equation from the Technical Guidance has been used in all calculations to take this into account:

$$Clocal_{water} = \frac{Clocal_{eff}}{(1 + Kp_{susp} \times SUSP_{water} \times 10^{-6}) \times DILUTION}$$

where
$Clocal_{water}$ = local concentration in surface water during an emission episode
$Clocal_{eff}$ = concentration in effluent from waste water treatment plant
Kp_{susp} = solids-water partition coefficient for suspended matter = 58,884 l/kg for medium-chain chlorinated paraffins
$SUSP_{water}$ = concentration of suspended matter in surface water = 15 mg/l
$DILUTION$ = dilution factor for effluent in receiving water = 10 for generic scenarios (site specific information used where appropriate).

The final $PEC_{local(water)}$ is estimated from:

$$PEC_{local(water)} = Clocal_{water} + PEC_{regional(water)}$$

where
$PEC_{regional(water)}$ = 0.389 µg/l (based on the EUSES calculation: see Section 3.1.2.2) or 0.1 µg/l (based on measured data: see Section 3.1.2.3)

Finally the PEC for sediment is estimated from:

$$PEC_{local(sed)} = \frac{K_{susp-water} \times PEC_{local(water)} \times 1000}{RHO_{susp}}$$

where
$K_{susp-water}$ = suspended matter – water partition coefficient = 14,721 m^3/m^3
RHO_{susp} = bulk density of suspended matter = 1,150 kg/m^3

3.1.2.1.1   Production sites

Site specific emission information is currently available for four of the five current production sites in the EU[9] (releases from the remaining site are likely to be similar to the other four). The estimated releases at the four sites are given in Section 3.1.1.1.2. The resulting PECs estimated from these values, using the known dilution rates at the sites, are shown in **Table 3.16**.

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[9] Entec (2004) indicates that there is now a further production site in the EU as a result of the recent enlargement of the EU. This site has not been considered further in this assessment.

Table 3.16 Summary of PECs estimated for production sites

	Site A	Site B	Site C	Site D
C$local_{water}$ (µg/l)	0.0064	0.09	0.17	6.4×10^{-6}
PEC$_{local(water)}$ (µg/l)	0.39[a] or 0.11[b]	0.48[a] or 0.19[b]	0.56[a] or 0.27[b]	0.39[a] or 0.1[b]
PEC$_{local(sediment)}$ (mg/kg wet wt.)	5.05[a] or 1.41[b]	6.14[a] or 2.44[b]	7.14[a] or 3.46[b]	4.97[a] or 1.28[b]

a)   Based on PEC$_{regional(water)}$ = 0.389 µg/l.
b)   Based on PEC$_{regional(water)}$ = 0.1 µg/l.

3.1.2.1.2   Use in PVC

In Section 3.1.1.2.1, releases of medium-chain chlorinated paraffins to water have been estimated from several stages of production of PVC. These release estimates have been used here, along with the behaviour in the generic waste water treatment plant to estimate the PEC$_{local}$ water for these stages. The calculations are summarised in **Table 3.17** and **Table 3.18**.

Table 3.17 PEC$_{local(water)}$ and PEC$_{local(sediment)}$ for use in PVC

	Use in PVC – plastisol processes		
	Compounding site (formulation)	Conversion site (processing)	Combined compounding and conversion site
Local release to waste water (g/day)	25	185	210
No of days of release/year	300	300	300
Size of WWTP (m³/day)	2,000	2,000	2,000
Influent concentration (µg/l)	12.5	92.5	105
% to water during WWTP	7	7	7
C$local_{eff}$ (µg/l)	0.88	6.48	7.35
Dilution factor	10	10	10
C$local_{water}$ (µg/l)	0.047	0.344	0.39
PEC$_{local(water)}$ (µg/l)	0.44[a] or 0.147[b]	0.73[a] or 0.44[b]	0.78[a] or 0.49[b]
PEC$_{local(sediment)}$ (mg/kg wet wt.)	5.57[a] or 1.88[b]	9.37[a] or 5.68[b]	9.96[a] or 6.27[b]

a)   Based on PEC$_{regional(water)}$ = 0.389 µg/l.
b)   Based on PEC$_{regional(water)}$ = 0.1 µg/l.
O   Open system;
PO   Partially open system;
C   Closed system (as defined in UCD, 1998).

Table 3.18 PEC$_{local(water)}$ and PEC$_{local(sediment)}$ for use in PVC

	Use in PVC – primary plasticiser								
	Compounding site (formulation)			Conversion site (processing)			Combined compounding and conversion site		
	O	PO	C	O	PO	C	O	PO	C
Local release to waste water (g/day)	92	500	42.5	280	300	255	372	800	298
No of days of release/year	300	300	300	300	300	300	300	300	300
Size of WWTP (m³/day)	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Influent concentration (µg/l)	46	250	21.25	140	150	127.5	186	400	149
% to water during WWTP	7	7	7	7	7	7	7	7	7
C$local_{eff}$ (µg/l)	3.22	17.5	1.49	9.80	10.5	8.93	13.0	28	10.4
Dilution factor	10	10	10	10	10	10	10	10	10
C$local_{water}$ (µg/l)	0.171	0.93	0.079	0.52	0.56	0.47	0.69	1.49	0.55
PEC$_{local(water)}$ (µg/l)	0.56[a] or 0.27[b]	1.32[a] or 1.03[b]	0.47[a] or 0.18[b]	0.91[a] or 0.62[b]	0.95[a] or 0.66[b]	0.86[a] or 0.57[b]	1.08[a] or 0.79[b]	1.88[a] or 1.59[b]	0.94[a] or 0.65[b]
PEC$_{local(sediment)}$ (mg/kg wet wt.)	7.16[a] or 3.46[b]	16.9[b] or 13.2[b]	5.98[a] or 2.30[b]	11.6[a] or 7.94[b]	12.1[a] or 8.45[b]	11.0[a] or 7.30[b]	13.8[a] or 10.1[b]	24.0[a] or 20.4[b]	12.0[a] or 8.32[b]

a) Based on PEC$_{regional(water)}$ = 0.389 µg/l.
b) Based on PEC$_{regional(water)}$ = 0.1 µg/l.
O   Open system;
PO Partially open system;
C   closed system (as defined in UCD, 1998).

3.1.2.1.3   Use in rubber/plastics (other than PVC)

In Section 3.1.1.2.2, releases of medium-chain chlorinated paraffins to water have been estimated from the use in rubber and plastics other than PVC. These release estimates have been used here, along with the behaviour in the generic waste water treatment plant to estimate the PEC$_{local}$ water for these uses. The calculations are summarised in **Table 3.19**. The calculations are based on the releases expected from plastic processing. The releases, and hence PECs expected from the processing of rubber would be expected to be lower than these values due to the lower processing temperatures generally used.

Table 3.19 PEC$_{local}$ for water and sediment for use in rubber and plastics

	Compounding site (formulation)	Conversion site (processing)	Combined conversion and processing site
Local release to waste water (g/day)	46.5	155	202
No of days of release/year	300	300	300
Size of WWTP (m³/day)	2,000	2,000	2,000
Influent concentration (µg/l)	23.3	77.5	101
% to water in WWTP	7	7	7
C$local_{eff}$ (µg/l)	1.63	5.43	7.07
Dilution factor	10	10	10
C$local_{water}$ (µg/l)	0.086	0.29	0.38
PEC$_{local(water)}$ (µg/l)	0.47[a] or 0.19[b]	0.68[a] or 0.39[b]	0.77[a] or 0.48[b]
PEC$_{local(sediment)}$ (mg/kg wet wt.)	6.07[a] or 2.38[b]	8.68[a] or 4.99[b]	9.83[a] or 6.14[b]

a)   Based on PEC$_{regional(water)}$ = 0.389 µg/l
b)   Based on PEC$_{regional(water)}$ = 0.1 µg/l.

3.1.2.1.4   Use in sealants/adhesives

The releases of medium-chain chlorinated paraffins to water from sites formulating or using sealants/adhesives are likely to be very low. No PEC$_{local}$ is therefore calculated for this use.

3.1.2.1.5   Use in paints and varnishes

In Section 3.1.1.2.4, releases of medium-chain chlorinated paraffins to water have been estimated from formulation and use of paints using the default release estimates from the Technical Guidance Document, along with knowledge of the likely amounts of medium-chain chlorinated paraffins formulated on a site. These default release estimates have been used here, along with the behaviour in the generic waste water treatment plant to estimate the PEC$_{local}$ water for these stages. The data available so far indicates that the releases of medium-chain chlorinated paraffins to water from the formulation and use of paints should be very low. The default calculations are summarised in **Table 3.20**.

Table 3.20 PEC$_{local}$ for water and sediment for formulation and use in paints.

	Paint formulation site (formulation)	Industrial application of paints (processing)	Application of paints by general public (private use)
Local release to waste water (kg/day)	0.15	0.059	$3 \cdot 10^{-7}$
No of days of release/year	300	300	365
Size of WWTP (m³/day)	2,000	2,000	2,000
Influent concentration (µg/l)	75	29.5	$1.5 \cdot 10^{-4}$
% to water in WWTP	7%	7	7%
C$local_{eff}$ (µg/l)	5.25	2.07	$1.05 \cdot 10^{-5}$
Dilution factor	10	10	10
C$local_{water}$ (µg/l)	0.28	0.11	$5.6 \cdot 10^{-7}$
PEC$_{local(water)}$ (µg/l)	0.67[a] or 0.38[b]	0.50[a] or 0.21[b]	0.39[a] or 0.1[b]
PEC$_{local(sediment)}$ (mg/kg wet wt.)	8.55[a] or 4.86[b]	6.37[b] or 2.69[b]	4.97[a] or 1.28[b]

a)   Based on PEC$_{regional(water)}$ = 0.389 µg/l.
b)   Based on PEC$_{regional(water)}$ = 0.1 µg/l.

3.1.2.1.6   Formulation and use in metal cutting/working fluids

In Section 3.1.1.2.5, releases of medium-chain chlorinated paraffins to water have been estimated from formulation and use in metal cutting/working fluids. These release estimates have been used here, along with the behaviour in the generic waste water treatment plant to estimate the PEC$_{local}$ water for these stages. The calculations are summarised in **Table 3.21**.

Table 3.21 PEC$_{local}$ for water and sediment for use in metal cutting/working fluids

	Formulation site (formulation)	Use in oil-based fluids (processing)		Use in emulsifiable fluids (processing)	
		Large site	Small site	Continuous use	Intermittent discharge
Local release to waste water (kg/day)	0.83	0.33	0.30	0.025	25
No of days of release/year	300	300	300	300	2-6
Size of WWTP (m³/day)	2,000	2,000	2,000	2,000	2,000
Influent concentration (µg/l)	415	165	150	12.5	12,500
% to water in WWTP	7	7	7	7	7
C$local_{eff}$ (µg/l)	29.1	11.6	10.5	0.88	875
Dilution factor	10	10	10	10	10
C$local_{water}$ (µg/l)	1.54	0.61	0.56	0.046	46.5
PEC$_{local(water)}$ (µg/l)	1.93[a] or 1.64[b]	0.998[a] or 0.71[b]	0.95[a] or 0.66[b]	0.43[a] or 0.15[b]	46.9[a] or 46.6[b]
PEC$_{local(sediment)}$ (mg/kg wet wt.)	24.7[a] or 21.0[b]	12.8[a] or 9.09[b]	12.1[a] or 8.45[b]	5.56[a] or 1.92[b]	600[a] or 597[b]

a)   Based on PEC$_{regional(water)}$ = 0.389 µg/l.
b)   Based on PEC$_{regional(water)}$ = 0.1 µg/l.

For the intermittent release scenario for metal cutting/working fluids, the Technical Guidance Document does not provide any guidance on how this should be treated. The value reported in

Table 3.21 assumes that the substance in water instantly equilibrates with the sediment. However, in reality, this is unlikely to occur as the release will be over a short period of time. An alternative approach would be to average the concentration over the year and add this to the concentration arising from the continuous use in the metal working fluids (5.56 mg/kg wet weight or 1.92 mg/kg wet weight). This would give a PEC$_{local(sediment)}$ of 15.4 mg/kg wet weight or 11.7 mg/kg wet weight, assuming that the intermittent disposal occurs 6 times/year.

In addition to the information given in **Table 3.21**, it is possible to estimate PECs from other sources. From Section 3.1.1.2.5, it was reported that at well controlled formulation sites, oil capture and recovery systems will be used prior to discharge of effluent to the sewage treatment plant. The equipment used is designed to lower the dissolved oil concentration to 5 mg/l or less. If it is assumed that the medium-chain chlorinated paraffin content of this oil is the same as in the lubricant being blended at the site (e.g. 5%), then the chlorinated paraffin content of the effluent could be 250 µg/l. A typical aqueous discharge from a formulation site could be of the order of 1×10^6 l/year (or 3,333 l/day over 300 days) (UCD, 1997). Thus if this discharge is to the 'standard' sewage treatment plant of 2,000 m^3/day, the effluent from the site will be diluted by a factor of 600 in the total influent to the plant. Thus the influent concentration in the waste water treatment plant would be 0.42 µg/l. Using the same methodology as outlined in **Table 3.21**, the $Clocal_{eff}$ = 0.029 µg/l, $Clocal_{water}$ = 0.0015 µg/l, PEC$_{local(water)}$ = 0.39 µg/l or 0.1 µg/l and PEC$_{local(sediment)}$ = 4.98 mg/kg wet wt. or 1.30 mg/kg wet wt. In this case the release from the site would make only a minor contribution to the PEC$_{local}$ for water and sediment, which are dominated by the regional concentrations.

The potential effects of the proposed risk reduction measures for short-chain chlorinated paraffins in this use on the PECs for medium-chain chlorinated paraffins are considered in Appendix E.

3.1.2.1.7   Formulation and use in leather fat liquors

In Section 3.1.1.2.6, releases of medium-chain chlorinated paraffins to water have been estimated from formulation and use of leather fat liquors containing medium-chain chlorinated paraffins. These release estimates have been used here, along with the behaviour in the generic waste water treatment plant to estimate the PEC$_{local}$ water for these stages. The calculations are summarised in **Table 3.22**.

The potential effects of the proposed risk reduction measures for short-chain chlorinated paraffins in this use on the PECs for medium-chain chlorinated paraffins are considered in Appendix E.

Table 3.22 PEC$_{local}$ for water and sediment for formulation and use of leather fat liquors

	Formulation site (formulation)		Use site (processing)	
	industry-specific information	default generic calculation	complete processing of raw hides (processing)	processing of 'wet blue' (processing)
Local release to waste water (kg/day)		1.1	0.9	3.6
No of days of release/year		300	300	300
Size of WWTP (m³/day)	2,000	2,000	2,000	2,000
Influent concentration (µg/l)	50[c]	550	450	1,800
% to water in WWTP	7	7	7	7
C$local_{eff}$ (µg/l)	3.5	38.5	31.5	126
Dilution factor	10	10	10	10
C$local_{water}$ (µg/l)	0.19	2.04	1.67	6.69
PEC$_{local(water)}$ (µg/l)	0.58[a] or 0.29[b]	2.43[a] or 2.14[b]	2.06[a] or 1.77[b]	7.08[a] or 6.79[b]
PEC$_{local(sediment)}$ (mg/kg wet wt.)	7.40[a] or 3.71[b]	31.1[a] or 27.4[b]	26.3[a] or 22.7[b]	90.6[a] or 86.9[b]

a) Based on PEC$_{regional(water)}$ = 0.389 µg/l.
b) Based on PEC$_{regional(water)}$ = 0.1 µg/l.
c) Industry-specific information indicates that the maximum concentration of medium-chain chlorinated paraffins in the waste water from a formulation site is likely to be <500 µg/l. In the absence of water flow rates from a typical site, it has been assumed that the waste water from a site is diluted by a factor of 10 in the influent to the waste water treatment plant. This value will be used in the risk assessment.

3.1.2.1.8   Recycling of carbonless copy paper

In Section 3.1.1.2.8, releases of medium-chain chlorinated paraffins to water have been estimated from the recycling of carbonless copy paper containing medium-chain chlorinated paraffins. This estimated release of medium chain chlorinated paraffins from a large site (250,000 t/year of paper) was 6.17 kg/day to waste water.

In order to calculate the PEC for recycling of carbonless copy paper, knowledge of the water use in the process is needed. The emission scenario document for the pulp, paper and board industry gives water usage figures of 5-15 m³/t paper recycled from the flotation processes, whereas washing can use between 5-100 m³/t paper. The total water usage for the production of specific types of paper are 40-75 m³/t for printing and writing paper, 57 m³/t for tissue paper and 24-35 m³/t for newsprint.

In order to estimate the worst case concentration at a recycling site it will be assumed that a water consumption rate of 35 m³/t is applicable, giving a total water usage rate of $8.75 \cdot 10^6$ m³/year for this volume of paper. According to the emission scenario document, some paper recycling plants may carry out only primary treatment before discharge of effluent to surface water via a municipal waste water treatment plant (the release estimate is based on the amount released after this primary treatment process (see Section 3.1.1.2.8)). Further, the emission scenario document also indicates that if the effluent is emitted to a waste water treatment plant off-site, the size of the treatment plant is likely to be larger than average due to the large volume of waste water generated. PECs are therefore calculated assuming that no further waste water treatment other than primary treatment occurs on-site, and that the effluent from the plant is treated at an off-site waste water treatment plant where the effluent is further diluted by a small amount (2 times), i.e. the waste water from the paper recycling site is a major contributor to the off-site waste water treatment plant, which is in line with the approach

recommended in the Technical Guidance Document. The resulting PECs are shown in **Table 3.23.**

Table 3.23 PEC$_{local}$ for water and sediment for recycling of carbonless copy paper

	Recycling of carbonless copy paper
Local release to waste water (kg/day)	6.17
No of days of release	250
Volume of waste water	8,750,000 m^3/year = 35,000 m^3/day
C$local_{eff}$ from site	0.176 mg/l
Dilution factor of site effluent in influent to waste water treatment plant	2
Influent concentration to WWTP	0.088 µg/l
% to water in WWTP	7%
C$local_{eff}$ from WWTP	6.2 µg/l
Dilution factor	10
C$local_{water}$	0.33 µg/l
PEC$_{local(water)}$	0.72 µg/l[a] or 0.43 µg/l[b]
PEC$_{local(sediment)}$	9.19 mg/kg wet wt.[a] or 5.50 mg/kg wet wt.[b]

a)   Based on PEC$_{regional(water)}$ = 0.389 µg/l.
b)   Based on PEC$_{regional(water)}$ = 0.1 µg/l.

3.1.2.2   Calculation of PEC$_{regional}$ and PEC$_{continental}$

The predicted concentrations of medium-chain chlorinated paraffins in the regional and continental scenarios have been estimated by EUSES, using the release data outlined in **Table 3.5**. As explained in Section 3.1.1.3, the calculations have been carried out both with and without the regional contribution from 'waste remaining in the environment', as the applicability of the current modelling methods to this contribution is highly uncertain. A print out of the results for the calculation (not including the 'waste remaining in the environment') is given in Appendix A.

The estimated PEC$_{regional}$ and PEC$_{continental}$ are shown in **Table 3.24**.

Table 3.24 Estimated PEC$_{regional}$ and PEC$_{continental}$ for the aquatic compartment

Compartment	PEC	Value (not including 'waste remaining in the environment')	Value (including 'waste remaining in the environment')
Surface water	PEC$_{regional(water)}$	0.389 µg/l	0.682-0.745
	PEC$_{continental(water)}$	0.053 µg/l	0.093-0.10
Sediment	PEC$_{regional(sed)}$	8.80 mg/kg wet wt	15.4-16.9
	PEC$_{continental(sed)}$	1.21 mg/kg wet wt	2.11-2.31

The potential effects of the proposed risk reduction measures for short-chain chlorinated paraffins in this use on the PECs for medium-chain chlorinated paraffins are considered in Appendix E. Appendix H considers the potential effects of the uncertainties and variability in some of the physico-chemical properties on the estimated concentrations.

3.1.2.3   Measured levels in water and sediment

The analysis of medium-chain chlorinated paraffins in environmental media is complicated by the fact that there are a large number of possible chlorinated paraffins (of different carbon chain length, degrees of chlorination and position of the chlorine atoms along the carbon chain) present in any given commercial product. Thus care has to be taken when comparing the results from one survey with those of another, since different reference compounds may have been used and hence different chemical species may have been measured. The main analytical methods used in the environmental analyses are discussed in Appendix D.

3.1.2.3.1   Levels in water

The levels of medium-chain chlorinated paraffins measured in surface water are summarised in **Tables 3.24 to 3.30**.

Recently an in-depth study of the levels of medium-chain chlorinated paraffins in industrial areas of the United Kingdom has been carried out (CEFAS, 1999). The main purpose of the study was to determine the concentrations of medium-chain (and short-chain where found) chlorinated paraffins in surface water, sediment, biota and soil associated with their industrial use. The sampling sites were chosen with regards to their proximity to known sources/users of medium-chain chlorinated paraffins. Samples were collected during early summer 1998 and were filtered (<0.45 µm) before analysis and so the reported values represent the dissolved concentration in water. It is possible that the filtering (glass microfibre pre-filter in series with a 0.45 µm PTFE filter) may have also removed some of the dissolved medium-chain chlorinated paraffin from solution (by adsorption). However, recovery experiments were carried out using pure water spiked with the medium-chain chlorinated paraffin, which were filtered in the same way as the environmental samples, and these recoveries in the range 47-83% (mean value 68±12%) for the method overall (CEFAS, 2000), indicating that the method used was acceptable. The levels found in surface water are shown in **Table 3.25**. The levels found in sediment, biota and soil are reported later in the appropriate sections of this report.

In this study, medium chain chlorinated paraffins were not detected in any of the surface water samples taken. Chlorinated paraffins were found at levels of 0.2-1.7 µg/l in some samples from a site near to engineering (metal working) activity, but these were identified as being short chain length chlorinated paraffins.

Table 3.25 Levels of medium-chain chlorinated paraffins in surface water in the United Kingdom, related to sources

Industry	Sampling site	Concentration of medium-chain chlorinated paraffin (µg/l)
Polymers/tarpaulins	1.8 km upstream from STP	<0.1
	400 m upstream from STP	<0.1
	100 m downstream from STP	<0.1
	300 m downstream from STP	<0.1
	1.8 km downstream from STP	<0.1
Synthetic rubber manufacture	1 km upstream of STP	<0.1
	STP outfall on canal	<0.1
	100 m downstream from STP on canal	<0.1

Table 3.25 continued overleaf

Table 3.25 continued Levels of medium-chain chlorinated paraffins in surface water in the United Kingdom, related to sources

Industry	Sampling site	Concentration of medium-chain chlorinated paraffin (µg/l)
	300 m downstream from STP on canal	<0.1
	300 m downstream from STP on river	<0.1
	700 m downstream from STP on river	<0.1
	1.8 km downstream	<0.1
Metal working	stream, 400 m downstream of site	<0.1
	stream, 800 m downstream of site	<0.1
	estuary, 10 sites	<0.1
Lubricant blending/ metal working	Upstream of STP	<0.1
	100m downstream of STP	<0.1
	300 m downstream of STP	<0.1
	downstream of STP	<0.1
Sealant and adhesive manufacture	Upstream of STP	<0.1
	100 m downstream of STP	<0.1
	300 m downstream of STP	<0.1
	downstream of STP	<0.1
Rubber product manufacturer	Upstream of STP	<0.1
	100 m downstream of STP	<0.1
	300 m downstream	<0.1
	Downstream of STP	<0.1
	Downstream of STP	<0.1
Manufacturer of building sealants/lubricant blending	Upstream of STP	<0.1
	100 m downstream of STP	<0.1
	300 m downstream of STP	<0.1
	Downstream of STP	<0.1
Control site - no known uses	Upstream of STP	<0.1
	100 m downstream of STP	<0.1
	300 m downstream of STP	<0.1
	1.2 km downstream of STP	<0.1
Manufacturer of chlorinated paraffins	2 km from STP discharge point	<0.1
	Lock	<0.1
	400 m from lock	<0.1
	1.8 km from lock	<0.1
	2 km from lock	<0.1
	Bank, opposite lock	<0.1
	Upstream of lock	<0.1

Table 3.25 continued overleaf

Table 3.25 continued Levels of medium-chain chlorinated paraffins in surface water in the United Kingdom, related to sources

Industry	Sampling site	Concentration of medium-chain chlorinated paraffin (μg/l)
Paint manufacturer	Upstream of discharge	<0.1
	500 m downstream of discharge	<0.1
	600 m downstream of discharge	<0.1
	800 m downstream of discharge	<0.1
	1 km downstream of discharge	<0.1
	Downstream of discharge	<0.1
Lubricant manufacturer (and other industries)	Canal, 1 km west of discharge	<0.1
	Canal, 500 m west of discharge	<0.1
	Canal, 4 km east of discharge	<0.1
	Brook, 300 m upstream of STP	<0.1
PVC cable manufacturer	Upstream of STP	<0.1
	100 m downstream of STP	<0.1
	300 m downstream of STP	<0.1
	Downstream of STP	<0.1
Metal working/leather finishing	Upstream of STP	<0.1
	100 m downstream of STP	<0.1
	300 m downstream of STP	<0.1
	Downstream of STP	<0.1
PVC production/paint manufacture	Upstream of STP	<0.1
	At STP outfall	<0.1
	100 m downstream of STP	<0.1
	800 m downstream of STP	<0.1
Leather finishing chemicals formulation site	2.3 km upstream of STP	<0.1
	100 m upstream of STP	<0.1
	600 m downstream of STP	<0.1
	1.7 km downstream of STP	<0.1
Producer of PVC compound	Upstream of STP	<0.1
	100 m downstream of STP	<0.1
	300 m downstream of STP	<0.1
Background site	3 sites	<0.1

The analysis of medium-chain chlorinated paraffins was also carried out at several locations in the United Kingdom in the summer of 1986 (ICI, 1992). The results are shown in **Table 3.26**, along with the levels of the short-chain (C_{10-13}) chlorinated paraffins. [The levels of the short-chain chlorinated paraffins are included here to enable some conclusions to be drawn about the likely concentrations of medium-chain chlorinated paraffins in the measurements of Campbell and McConnell included later in this Section (**Tables 3.28-3.30**).] As can be seen from **Table 3.26**, the medium-chain chlorinated paraffins were found in all the samples analysed

at concentrations ranging between 0.62 and 3.75 µg/l. The majority of the samples appear to have been collected in urban/industrial areas.

Levels of medium-chain chlorinated paraffins have been measured at several sites in Germany and the results are shown in **Table 3.27** (Ballschmiter, 1994; Hoechst AG, 1987). The levels measured in 1987 are similar to, but slightly higher than, those found in the United Kingdom in 1986. However the levels measured in 1994 are generally lower, indicating that reduced usage and/or improved handling of these products had occurred over that period. It should also be born in mind that different analytical methods were used for the two sets of measurements, which could also account for some of the differences seen between the 1987 and 1994 data.

Levels of total short- and medium-chain (i.e. C_{10-20}) chlorinated paraffins have been measured in marine and freshwaters remote from industry and freshwaters in industrialised areas in the United Kingdom (Campbell and McConnell, 1980). These results are shown in **Tables 3.28** to **3.30**. As these levels refer to the total chlorinated paraffin in the C_{10-20} range, it is not possible to say anything definite about the amounts of medium-chain chlorinated paraffins present. However, analysing the results reported in **Table 3.26**, it can be seen that the C_{14-17} chlorinated paraffins make up around $^2/_3$-$^3/_4$ of the combined total for short- and medium-chain chlorinated paraffins in those samples. Therefore, if the same approximate distribution applies to the data in **Tables 3.28** to **3.30**, then the likely concentrations of medium-chain chlorinated paraffins present can be inferred.

Table 3.26 Measured levels of medium-chain (and short-chain) chlorinated paraffins in surface water in the United Kingdom (ICI, 1992)

Location	Concentration (µg/l)	
	Medium-chain (C_{14-17})	Short-chain (C_{10-13})
Derwent Reservoir, UK, 1986.	1.46	
River Trent, Newark, UK, 1986.	0.86	
Trent and Mersey Canal, UK, 1986.	0.62	
River Derwent, Derby, UK, 1986.	0.64	
Walton on Trent, UK, 1986.	1.07	0.41
River Ouse, Goole, UK, 1986.	0.94	
River Don, Rotherham, UK, 1986.	1.13	0.72
River Aire/Ouse, UK, 1986.	1.13	0.12
River Ouse, York, UK, 1986.	1.36	0.46
River Cover, Wilton, UK, 1986.	0.84	0.19
River Ure, Mickley, UK, 1986.	1.46	
River Trent, Gainsborough, UK, 1986.	2.49	0.65
River Trent, Burton, UK, 1986.	2.46	1.45
River Rother, UK, 1986.	2.11	
River Trent/Humber, UK, 1986.	3.75	0.29
Hull Docks, UK, 1986.	2.69	0.71

Table 3.27 Levels of medium-chain chlorinated paraffins in surface water in Germany (Hoechst AG, 1987; Ballschmiter, 1994)

Location	Concentration (µg/l)	
	1987	1994
River Lech at Augsburg		<0.05
River Lech at Gersthofen (upstream from a chlorinated paraffin production plant)	4.5	0.094
River Lech at Langweid (downstream from a chlorinated paraffin production plant)	4.0	0.185
River Lech at Rain		0.170
River Danube at Marxheim (downstream from the mouth of the River Lech)	20	0.072
River Danube at Marxheim (upstream from the mouth of the River Lech)	4.0	≤0.055

The C_{10-20} chlorinated paraffins were detected in around half of the marine waters sampled, in the range 0.5-4 µg/l. By inference, the levels of medium-chain chlorinated paraffins are probably in the range 0.3-3 µg/l.

In fresh and other non-marine water samples from areas remote from industry, the C_{10-20} chlorinated paraffins were detected in just under half the samples in the range 0.5-1 µg/l. This corresponds to probable medium-chain chlorinated paraffin concentrations of 0.3-0.7 µg/l.

In surface waters in industrialised areas, the levels of C_{10-20} chlorinated paraffins are higher than those found in marine and remote waters, and the frequency of detection is also higher. The levels measured for the combined short- and medium-chain chlorinated paraffins are in the range 0.5-6.0 µg/l. This corresponds to probable medium-chain chlorinated paraffin concentrations in the range 0.3-4 µg/l. Although it is not clear if any of the samples were taken near to sources of discharge of chlorinated paraffins, it is thought that the Wyre estuary did receive chlorinated paraffin production plant effluent at the time of sampling.

Table 3.28 Concentration of total short- and medium-chain chlorinated paraffins (C_{10-20}) in marine waters in and around the UK (Campbell and McConnell, 1980)

Location	Concentration of C_{10-20} chlorinated paraffins (µg/l)
Irish Sea: Site a	1.0
Irish Sea: Site b	0.5
Irish Sea: Site c	0.5
Irish Sea: Site d	0.5
Irish Sea: Site e	ND
Irish Sea: Site f	ND
Barmouth Harbour	0.5
Menai Straights, Caernarvon	0.5
Tremadoc Bay, Llandanwg	ND
North Minch, Ardmair	0.5
North Minch, Port Bùn a' Ghlinne	ND

Table 3.28 continued overleaf

Table 3.28 continued   Concentration of total short- and medium-chain chlorinated paraffins (C10-20) in marine waters in and around the UK (Campbell and McConnell, 1980)

Location	Concentration of C10-20 chlorinated paraffins (g/l)
North Minch, Port of Ness	0.5
Goile Chròic, Lewis	0.5
Sound of Taransay, Harris	4.0
Sound of Arisaig	1.0
North Sea: N55o 5.7' W1o 9.3'	ND
North Sea: N57o 26.2' W1o 17.0'	ND
North Sea: N57o 56.5' W1o 22.0'	ND

ND   Not detected (detection limit = 0.5 μg/l).

Table 3.29   Concentration of combined short- and medium-chain chlorinated paraffins (C10-20) in fresh and other non-marine waters remote from industry in the United Kingdom (Campbell and McConnell, 1980)

Location	Concentration of C10-20 chlorinated paraffins (μg/l)
River Banwy, Llangadfan	0.5
River Lea, Welwyn	ND*
River Lea, Batford	ND*
River Clwyd, Ruthin	ND
Bala Lake	1.0
River Dee, Corwen	ND
River Wnion, Merioneth	0.5
Firth of Lorne, Ganevan	0.5
Loch Linnhe, Corran Narrows	ND
Firth of Clyde, Ashcraig	ND
Firth of Clyde, Girvan	0.5
An Garbh Allt	0.5
Five drinking water reservoirs, Manchester area	ND

ND   Not detected (detection limit = 0.5 μg/l).
ND*   Not detected (detection limit 1.0 μg/l).

Table 3.30   Concentration of combined short- and medium-chain chlorinated paraffins (C10-20) in waters in industrialised areas in the UK (Campbell and McConnell, 1980)

Location	Concentration of C10-20 chlorinated paraffin (μg/l)
River Aire, Leeds	2.0
River Aire, Woodlesford	2.0
River Ouse, Boothberry edge	1-2
River Trent, West Bromwich	1-2
River Trent, Walton-upon-Trent	2-3

Table 3.30 continued overleaf

Table 3.30 continued Concentration of combined short- and medium-chain chlorinated paraffins (C$_{10-20}$) in waters in industrialised areas in the UK (Campbell and McConnell, 1980)

Location	Concentration of C10-20 chlorinated paraffin (g/l)
River Trent, Swarkestone	1-2
River Trent, Newark	4.0
River Trent, Gainsborough	2.0
River Trent, confluence with Humber	6.0
Humber Estuary, Hull	1-2
Humber Estuary, Grimsby	3.0
Mersey Estuary, New Brighton	3.0
Mersey Estuary, Liverpool Pier Head	4.0
River Thames, Oxford	2.0
River Thames, Sanford	1-2
Wyre Estuary	ND-1.5
River Tees, Low Dinsdale	ND
River Tees, North Gare breakwater	0.5
River Tees, Middlesbrough	ND

ND   Not detected (detection limit = 0.5 µg/l).

Murray et al. (1987a and 1987b) reported the results of monitoring studies carried out near to a chlorinated paraffin manufacturing site in the United States. The effluent from the plant, after undergoing physical treatment, was discharged into Sugar Creek, via a surface impoundment lagoon and small ditch. The results are shown in **Table 3.31**.

Table 3.31 Measured levels of medium-chain chlorinated paraffins near a production site in the United States (Murray et al., 1987a and 1987b)

Location	Concentration
Surface lagoon near to its effluent to ditch	not detected (<0.15 µg/l) – dissolved 3.3 µg/l – particulate
Surface lagoon near to influent from plant	trace (0.15-0.5 µg/l) – dissolved 2.4 µg/l – particulate
Middle of surface lagoon	trace (0.15-0.5 µg/l) – dissolved 2.6 µg/l – particulate
Ditch, immediately above point of discharge into Sugar Creek	trace (0.15-0.5 µg/l) – dissolved 1.5 µg/l – particulate
Sugar Creek, upstream of discharge	not detected (<0.05 µg/l) – dissolved not detected (<0.05 µg/l) – particulate
Sugar Creek, just upstream of discharge	not detected (<0.05 µg/l) – dissolved trace (0.05-0.17 µg/l) – particulate
Sugar Creek, just downstream of discharge	not detected (<0.05 µg/l) – dissolved 0.16-0.20 µg/l – particulate
Sugar Creek, downstream of discharge	not detected (<0.05 µg/l) – dissolved 0.20-0.24 µg/l – particulate

Dissolved   Concentration in dissolved phase.
Particulate   Concentration in particulate phase (>0.45 µm).

As can be seen from **Table 3.31**, the highest concentrations of medium-chain chlorinated paraffins are associated with the surface impoundment lagoon. The concentrations in the river downstream from the plant are around 0.2 µg/l, with the majority of the substance associated with the particulate matter (>0.45 µm).

A similar study was also undertaken by Murray et al. (1987a and 1987b) near to a metal working facility that was thought to be using lubricating oils containing chlorinated paraffins. Due to analytical interferences, it was not possible to detect chlorinated paraffins in surface water at the site, however, a level of C_{14-17} chlorinated paraffins of 1.3 µg/l was detected in process waste streams inside the plant.

Tomy et al. (1998) report the results of Metcalfe-Smith et al. (1995), who measured levels of C_{10}-C_{17} chlorinated paraffins of 12.7 µg/l in the effluent from a chlorinated paraffin manufacturing plant in Canada. The level of C_{14-17} chlorinated paraffin reported in the receiving water (St. Lawrence River) downstream of the plant was <1 µg/l.

As reported in Section 3.1.1.5.1, the level of medium-chain chlorinated paraffins in Lake Ontario is reported to be <0.02 ng/l (Environment Canada, 2003).

Surveys of levels of chlorinated paraffins (unspecified chain length) in surface waters have been carried out at numerous sites in Japan in 1979 and 1980. Chlorinated paraffins were not detected (detection limit 10 µg/l) in any of the 51 surface water samples taken in 1979 or any of the 120 surface water samples taken in 1980 (Environment Agency Japan, 1991).

A study of the inputs of chlorinated paraffins to a sewage treatment plant in Germany has been published (Rieger and Ballschmiter, 1995). The sewage treatment plant processed 100,000 m³/day of municipal, industrial and mixed waste water. Medium-chain chlorinated paraffins were not detected (detection limit 0.1 mg/kg dry matter) in any of the sewage sludge samples taken at the plant (only short-chain chlorinated paraffins were found). Water samples taken from upstream and downstream of the plant also showed no detectable concentrations of medium-chain chlorinated paraffins (detection limit 5 µg/l).

3.1.2.3.2   Measured levels in sediment

The levels of medium-chain chlorinated paraffins in sediment are summarised in **Tables 3.32-3.36**.

Recently an in-depth study of the levels of medium-chain chlorinated paraffins in industrial areas of the United Kingdom has been carried out (CEFAS, 1999). The main purpose of the study was to determine the concentrations of medium-chain (and short-chain where found) chlorinated paraffins in surface water, sediment, biota and soil associated with their industrial use. The sampling sites were chosen with regards to their proximity to known sources/users of medium-chain chlorinated paraffins. Samples were collected during early summer 1998. The levels found in sediment are shown in **Table 3.32**. The levels found in surface water, biota and soil are reported in the appropriate sections of this report.

The levels measured in the CEFAS (1999) study are reported on a dry weight basis. In order to make these levels comparable with the PEC estimates, they need to be expressed on a wet weight basis. No details of the water contents were given in the paper and so the default water content from the Technical Guidance Document (80% by volume, 62% by weight). Thus dry weight values can be converted to approximate wet weight values by dividing by 2.6. The estimated wet weight values are shown in **Table 3.32** alongside the measured dry weight values.

Table 3.32 Levels of chlorinated paraffins in sediment in the United Kingdom, related to sources (CEFAS, 1999)

Industry	Comment	Sampling site	Measured concentration of chlorinated paraffin (mg/kg dry weight)	Estimated concentration (mg/kg wet weight)
Polymers/ tarpaulins	Identified as medium- or long-chain	1.8 km upstream from STP	<0.2	<0.08
		400 m upstream from STP	0.7	0.27
		100 m downstream from STP	0.5	0.19
		300 m downstream from STP	0.6	0.23
		1.8 km downstream from STP	0.8	0.31
Synthetic rubber manufacture	Identified as medium-chain, ~50% wt. Cl	1 km upstream of STP	<0.2	<0.08
		STP outfall on canal	0.5	0.19
		100 m downstream from STP on canal	0.3	0.12
		300 m downstream from STP on canal	2.8	1.1
		300 m downstream from STP on river	2.0	0.77
		700 m downstream from STP on river	1.3	0.5
		1.8 km downstream	2.7	1.0
Lubricant blending/ metal working	Identified as medium-chain ~50% wt. Cl. Actual levels may be higher as destructive interference was seen in the analyses.	Upstream of STP	6.0	2.3
		100m downstream of STP	3.8	1.5
		300 m downstream of STP	60.2	23.2
		downstream of STP	65.1	25.0
Rubber product manufacturer	Identified as medium-chain, ~40-50% wt. Cl	Upstream of STP	<0.2	<0.08
		100 m downstream of STP	<0.2	<0.08
		300 m downstream	43.9	16.9
		Downstream of STP	<0.2	<0.08
		Downstream of STP	16.2	6.2
Manufacturer of building sealants/ lubricant blending	No chlorinated paraffins detected	Upstream of STP	<0.2	<0.08
		100 m downstream of STP	<0.2	<0.08
		300 m downstream of STP	<0.2	<0.08
		Downstream of STP	<0.2	<0.08
Control site - no known uses.	Identified as medium chain, ~45% wt. Cl	Upstream of STP	<0.2	<0.08
		100 m downstream of STP	32.2	12.4
		300 m downstream of STP	60.4	23.2
		1.2 km downstream of STP	45.0	17.3
Manufacturer of chlorinated paraffins	Identified as a mixture of short- and medium-chain	2 km from STP discharge point	39.4	15.2
		Lock	53.3-63.0	20.5-24.2
		400 m from lock	3.8	1.5

Table 3.32 continued overleaf

Table 3.32 continued Levels of chlorinated paraffins in sediment in the United Kingdom, related to sources (CEFAS, 1999)

Industry	Comment	Sampling site	Measured concentration of chlorinated paraffin (mg/kg dry weight)	Estimated concentration (mg/kg wet weight)
Manufacturer of chlorinated paraffins	Identified as a mixture of short- and medium-chain	1.8 km from lock	2.0	0.77
		2 km from lock	1.6	0.62
		Bank, opposite lock	1.5	0.58
		Upstream of lock	6.3	2.4
Paint manufacturer	Identified as medium-chain	Upstream of discharge	<0.2	<0.08
		500 m downstream of discharge	<0.2	<0.08
		600 m downstream of discharge	0.3	0.12
		800 m downstream of discharge	6.1	2.3
		1 km downstream of discharge	6.4	2.5
		Downstream of discharge	0.4	0.15
Lubricant manufacturer (and other industries)	Identified mainly as short- chain, medium- chain also present	Canal, 1 km west of discharge	0.6	0.23
		Canal, 500 m west of discharge	n.q.	-
		Canal, 4 km east of discharge	0.5	0.19
		Brook, 300 m upstream of STP	1.6	0.62
		Brook, 100 m downstream of STP	0.5	0.19
		Brook, 300 m downstream of STP	1.0	0.38
PVC cable manufacturer	Identified as medium-chain, ~52% wt. Cl	Upstream of STP	<0.3	<0.12
		100 m downstream of STP	5.7	2.2
		300 m downstream of STP	12.8	4.9
		Downstream of STP	19.0	7.3
Metal working/ leather finishing	Mixture of short- and medium-chain, ~<60% wt. Cl. Actual levels may be higher as destructive interference was seen in the analyses.	Upstream of STP	0.8	0.31
		100 m downstream of STP	1.8	0.69
		300 m downstream of STP	1.8	0.69
		Downstream of STP	4.9	1.9
		Downstream of STP	2.5	0.96
PVC production/ paint manufacture	Identified as a mixture of short- and medium-chain	Upstream of STP	0.7	0.27
		At STP outfall	n.q.	-
		100 m downstream of STP	21.1	8.12
		800 m downstream of STP	<0.2	<0.08
		2.5 km downstream of STP	5.3	2.0
Leather finishing chemicals formulation site	Identified mainly as medium-chain	2.3 km upstream of STP	1.1	0.42
		100 m upstream of STP	13.5	5.2

Table 3.32 continued Levels of chlorinated paraffins in sediment in the United Kingdom, related to sources (CEFAS, 1999)

Industry	Comment	Sampling site	Measured concentration of chlorinated paraffin (mg/kg dry weight)	Estimated concentration (mg/kg wet weight)
Leather finishing chemicals formulation site	Identified mainly as medium-chain	600 m downstream of STP	1.1	0.42
		1.7 km downstream of STP	0.8	0.31
		2.0 km downstream of STP	1.9	0.73
		Downstream of STP	1.0	0.38
		3.0 km downstream of STP	<0.4	<0.15
Producer of PVC compound	Identified as mainly medium-chain	Upstream of STP	1.3	0.5
		100 m downstream of STP	18.0	6.9
		300 m downstream of STP	25.6	9.8
		500 m downstream of STP	58.4	22.5
Background site	No chlorinated paraffins identified	4 sites	<0.2	<0.08

n.q.   Not quantifiable.

The levels of medium-chain chlorinated paraffins have been measured in several sediments in Germany (Ballschmiter, 1994). The results are shown in **Table 3.33**. Medium-chain chlorinated paraffins were detected in a wide range of locations at concentrations up to 370 µg/kg dry weight.

The levels of medium-chain (C_{14-18}) chlorinated paraffins have been also measured near to a chlorinated paraffin production site in Germany (Hoechst AG, 1987; Ballschmiter, 1994). The results are shown in **Table 3.33**. The levels measured in the River Lech in 1987 were similar in upstream (2,200 µg/kg dry wt.) and downstream (1,700 µg/kg dry wt.) samples, and similar concentrations were also found in another sample taken from the River Danube, down stream of the confluence of the River Lech (1,800 µg/kg dry wt.). A similar trend was also seen in the measured levels found in water in the area (see Section 3.1.2.3.1). The results indicate that the production plant was only a minor contributor to the levels found. The levels present in the area were found to have reduced in the 1994 survey.

Table 3.33 Levels of medium-chain chlorinated paraffins in German sediments

Location	Concentration (µg/kg dry weight)	
	1987[a]	1994[b]
Bodensee (middle)		70 (0-5 cm depth) <10 (5-12 cm depth)
River Rhein (141 km) at Rheinfelden		60
River Rhein (152 km) at Rheinfelden, upper layer		140
River Rhein (152 km) at Rheinfelden, lower layer		85
River Rhein (853.8 km), near German-Dutch border		205
River Rhein (863.8 km), near German-Dutch border		145

Table 3.33 continued overleaf

Table 3.33 continued   Levels of medium-chain chlorinated paraffins in German sediments

Location	Concentration (µg/kg dry weight)	
	1987[a]	1994[b]
River Main (16.2 km)		260
River Main (at Griesheim)		190
River Main (55 km)		160
Outer Alster, Hamburg		370
River Elbe, Hamburg (610 km)		130
River Elbe, Hamburg (629.9 km)		230
River Lech, upstream from chlorinated paraffin production plant	2,200	<10
River Lech, downstream from chlorinated paraffin production plant	1,700	325

a)   Hoechst AG, 1987.
b)   Ballschmiter, 1994.

The levels of total chlorinated paraffin (short-, medium- and long-chain) have been determined in estuarine sediments from Western Europe. In all, samples from 22 locations were analysed and the mean total levels found in the <63 µm sediment fraction was 10.5 µg/kg dry weight in the Mersey and Seine estuaries, 5.5 µg/kg dry weight in the Schelde estuary, 4.8 µg/kg dry weight in the Liffey river estuary, 3.3 µg/kg dry weight in the Forth estuary and 1.2 µg/kg dry weight in the Humber estuary. Chlorinated paraffins were not detected (detection limit 0.5 µg/kg dry weight) at the remaining 16 sites. Long-chain length chlorinated paraffins were thought to be the predominant type of chlorinated paraffin found in the samples, with only traces of medium-chain chlorinated paraffins being seen in the samples (no indication was given in the report as to what the levels of medium-chain chlorinated paraffins were) (van Zeijl, 1997).

The levels of combined short- and medium-chain (i.e. C_{10-20}) chlorinated paraffins have been measured in several types of sediment in the United Kingdom, often from the same areas where water concentrations were also measured (Campbell and McConnell, 1980). The results of these analyses are shown in **Tables 3.34 to 3.36**. It is not clear from the paper if the levels found are expressed on a wet weight or dry weight of sediment basis.

Table 3.34   Concentration of combined short- and medium-chain chlorinated paraffins (C_{10-20}) in marine sediments around the UK (Campbell and McConnell, 1980)

Location	Concentration of C_{10-20} chlorinated paraffins (µg/kg)
Irish Sea: Site a	100
Irish Sea: Site b	ND
Irish Sea: Site c	NM
Irish Sea: Site d	100
Irish Sea: Site e	ND
Irish Sea: Site f	ND
Barmouth Harbour	500
Menai Straights, Caernarvon	ND

Table 3.34 continued overleaf

Table 3.34 continued Concentration of combined short- and medium-chain chlorinated paraffins (C10-20) in marine sediments around the UK (Campbell and McConnell, 1980)

Location	Concentration of C10-20 chlorinated paraffins (g/kg)
Tremadoc Bay, Llandanwg	ND
North Minch, Ardmair	ND
North Minch, Port Bùn á Ghlinne	ND
North Minch, Port of Ness	ND
Goile Chròic, Lewis	ND
Sound of Taransay, Harris	ND
Sound of Arisaig	ND
North Sea: N55° 5.7' W1° 9.3'	ND
North Sea: N57° 26.2' W1° 17.0'	ND
North Sea: N57° 56.5' W1° 22.0'	50

ND   Not detected (detection limit = 50 µg/kg).
NM   Not measured.

Table 3.35 Concentration of combined short- and medium-chain chlorinated paraffins (C10-20) in fresh and other non-marine sediments remote from industry in the UK (Campbell and McConnell, 1980)

Location	Concentration of C_{10-20} chlorinated paraffins (µg/kg)
River Banwy, Llangadfan	ND
River Lea, Batford	1,000
River Clwyd, Ruthin	ND
River Dee, Corwen	300
River Wnion, Merioneth	ND
Five drinking water reservoirs, Manchester area	ND*

ND   Not detected (detection limit = 50 µg/kg).
ND* Not detected (detection limit 250 µg/kg).

Table 3.36 Concentration of combined short- and medium-chain chlorinated paraffins (C10-20) in sediments in industrialised areas in the UK (Campbell and McConnell, 1980)

Location	Concentration of C_{10-20} chlorinated paraffin (µg/kg)
River Aire, Leeds	10,000
River Ouse, Goole	2,000
River Trent, West Bromwich	6,000
River Trent, Walton-upon-Trent	1,000
River Trent, Swarkestone	14,000
River Trent, Newark	8,000
River Trent, Gainsborough	3,000
Humber Estuary, Hull	2,000
Humber Estuary, Stone Creek	2,000

Table 3.36 continued overleaf

Table 3.36 continued Concentration of combined short- and medium-chain chlorinated paraffins (C10-20) in sediments in industrialised areas in the UK (Campbell and McConnell, 1980)

Location	Concentration of C10-20 chlorinated paraffin (g/kg)
Mersey Estuary, New Brighton	3,000
Mersey Estuary, Liverpool Pier Head	8,000
River Thames, Sanford	1,000
Wyre Estuary	ND-1,600
Mersey Estuary, 14 sediment samples	ND
River Tees, Low Dinsdale	300
River Tees, North Gare breakwater	50
River Tees, Middlesbrough	15,000

ND   Not detected (detection limit = 50 μg/kg).

The highest levels (up to 15 mg/kg) of combined short- and medium-chain chlorinated paraffins have been found in sediments from industrialised areas, but they have also been detected in several samples from areas remote from industry. The sediment levels from industrial areas are around 1,000 times the levels found in water in the same area. When considering the monitoring data, it should be borne in mind that the detection limit for sediment (50 μg/kg) is approximately 100 times that for water (0.5 μg/l) in these experiments.

Short- and medium-chain (C_{10-20}) chlorinated paraffins have been detected at levels between 4,000 and 10,000 μg/kg in sewage sludge from the Liverpool area, but levels were below the detection limit (50 μg/kg) in sewage sludge from the Manchester area (Campbell and McConnell, 1980).

Chlorinated paraffins (no information given as to type or chain length) were found in 24 out of 51 sediment samples from Japan in 1979 at levels of 600-10,000 μg/kg dry wt. In a similar survey for 1980, chlorinated paraffins were found in 31 out of 120 sediment samples at levels of 500-8,500 μg/kg dry wt. For both sets of analyses, the detection limit was 500 μg/kg dry wt. (Environment Agency Japan, 1991).

Murray et al. (1987a and 1987b) reported the results of monitoring studies carried out near to a chlorinated paraffin manufacturing site and an industry using metal working fluids in the United States. Medium-chain chlorinated paraffins (C_{14-17}, 50-60% wt. Cl) were detected at levels of 21,000-50,000 μg/kg dry weight in sediment from an impoundment lagoon at the production site. Much lower levels (6.8-8.2 μg/kg dry weight) were detected in stream sediments downstream from the site. Due to analytical interferences, it was not possible to detect chlorinated paraffins at the site using metal working fluids.

Tomy et al. (1998) report the results of Metcalfe-Smith et al. (1995), who found that levels of C_{14}-C_{17} chlorinated paraffins were below the detection limit (<3.5 mg/kg dry weight) in sediments from the St. Lawrence River, Canada, taken downstream from a chlorinated paraffin manufacturing plant.

Muir et al. (2002) investigated the historical profile of the levels of medium-chain chlorinated paraffins in a sediment core from Lake St. Francois in the St. Lawrence River. The study analysed six slices of the core corresponding to a time period between 1972 and 1995. The highest levels of medium-chain chlorinated paraffins (concentration was around 1.2 mg/kg dry weight) were found in the core with a median date of 1972±4 years. The concentration in other

years was around 1 mg/kg dry weight in 1976, 0.7 mg/kg dry weight in 1981, 0.75 mg/kg dry weight in 1986, 0.4 mg/kg dry weight in 1990 and 0.7 mg/kg dry weight in 1995 (all values read from a graph). The predominant medium-chain chlorinated paraffins found had chain lengths of C_{14} and C_{15}, and the chain length and chlorination pattern of medium-chain chlorinated paraffins found in surface samples was the same as found in the deeper layers indicating that little change in the chain length profile had occurred over around 25 years burial.

Chlorinated paraffin levels of 30 mg/kg in sewage sludge (containing 5% solid matter) from an industrialised area of Zürich and 5 µg/kg in sediment from Lake Zürich have been measured, based on reference to a commercial C_{14-18}, 52% wt. Cl chlorinated paraffin. Chlorinated paraffin levels of 200 µg/kg were also determined in a sample of human adipose tissue (Schmid and Müller, 1985).

Greenpeace (1995) published the results of a survey of total chlorinated paraffin levels in mud samples from Rotterdam Harbour, Hamburg Harbour and from mud flats at Kaiser Wilhelm Koog and Den Helder. The total levels measured ranged between 25 and 125 µg/kg. Medium-chain chlorinated paraffins were thought to account for 13-78% of the total chlorinated paraffins present. Using these percentages, the concentrations of medium-chain chlorinated paraffin can be estimated as 7-10 µg/kg in Rotterdam Harbour samples, 8 µg/kg in the Hamburg Harbour sample, 3 µg/kg in the sample from Den Helder and 98 µg/kg in the sample from Kaiser Wilhelm Koog. It is not clear from the paper if the levels are reported on a wet or dry weight basis.

3.1.2.3.3   Comparison of measured and predicted concentrations

Bearing in mind the possible limitations in the analytical methods used, there is reasonably good agreement between the levels of medium-chain chlorinated paraffins found in surface waters in the various surveys. It can be concluded that the levels found in the 1980's in areas close to industrial activity were of the order of 0.5-4 µg/l, with lower levels of the order of 0.1-0.5 µg/l being found in areas more remote from industry. These levels are reasonably consistent with the PECs estimated for local sources and at the region level (around 0.389 µg/l). It should be born in mind that, for many of the measurements, it is not clear if the reported levels refer to the concentration in the dissolved phase or to the total (i.e. dissolved phase + particulate phase).

More recent measurements (1994 in Germany and 1998 in the United Kingdom), indicate that the concentration of medium-chain chlorinated paraffins in the dissolved phase in surface water is much lower than found in the older surveys. Possible reasons for this include the use of better analytical methods (that are less prone to interferences from other substances) and/or a general reduction in the amounts of medium-chain chlorinated paraffins entering into the environment as a result of improved waste management practices at sites where they are produced or used.

A monitoring survey of concentrations in water and sediment associated with several industrial uses of medium-chain chlorinated paraffins has recently been completed in the United Kingdom. The results of this survey are summarised in **Tables 3.25** and **3.32**. The concentrations found in surface water were generally lower (<0.1 µg/l in the dissolved phase) than the predicted levels. This may indicate that the assumptions used in this assessment overestimate the releases to the environment (however the same assumptions were also used for the predicted sediment concentrations, where good agreement was found between calculated and measured concentrations), or may reflect the fact that the water measurements were taken on single spot samples, which would be highly dependent on the disposal activities in operation at the site at the time of sampling. Therefore, although these samples are suggestive of lower releases, they

cannot be used to overwrite the local release estimates at all sites of release in the EU. However, the measured levels in water do indicate that the regional concentration in the United Kingdom is around 0.1 µg/l as a worst case as the samples were taken from industrial areas and the regional background concentration would not be susceptible to temporal changes in site activity. Although smaller in scope, a similar 'background' level is evident from the 1994 levels measured in Germany. Information on the breakdown of use of medium-chain chlorinated paraffins by country has been provided (see Section 2) and indicates that the United Kingdom is a major (but not the highest) user of medium-chain chlorinated paraffins and so the situation found in the United Kingdom may be representative of a reasonable worst case for the $PEC_{regional}$ for surface water for Europe as a whole.

For the sediment level, reasonably good agreement is obtained between the measured concentrations and the predicted concentrations, particularly in the recent survey of the United Kingdom. The levels measured upstream from the sites of discharge were generally in the range <0.08-5.2 mg/kg wet weight (approximate mean level of 0.7 mg/kg wet wt) and could be taken to represent the 'background' level in industrialised areas. These levels can be compared with the estimated $PEC_{regional}$ of 8.80 mg/kg wet wt., and are consistent with a regional water concentration of around 0.1 µg/l (e.g. using the equations given in the Technical Guidance Document, a surface water concentration of 0.1 µg/l leads to estimated sediment concentrations of around 1.3 mg/kg wet wt. for suspended sediment and 1.1 mg/kg wet wt. for bulk sediment). For the sediment samples taken downstream from sources of release the levels were in the range 1-25 mg/kg wet wt. These values compare reasonably well with the estimated PEC_{locals} for these activities, even though the water samples taken at the site indicated that the levels in water were generally not detectable. This may reflect the fact that sediment levels are much less dependent on the releases occurring at the time of sampling than are the water samples.

In summary, the $PEC_{regional}$ for surface water could be taken as 0.1 µg/l rather than the estimated value of 0.389 µg/l. At present both values will be considered in the PEC calculations in order that the significance of the values on the overall results of the assessment can be clearly seen, but the value of 0.1 µg/l will be used in the risk characterisation. Similarly for sediment, both the estimated $PEC_{regional}$ of 8.80 mg/kg/wet wt. and measured value of around 0.7 mg/kg wet wt. will be taken into account in the calculations in the risk assessment. For the local assessment the estimated PEC_{local}s will be used, supported by the measured values where appropriate.

Some concerns have been raised about the possibility of natural organohalogens or other substances interfering with analytical measurement of environmental concentrations. These are addressed in Section 3.3.5

3.1.3   Terrestrial compartment

3.1.3.1   Predicted levels

The estimated concentrations of medium-chain chlorinated paraffins in soil are shown in **Table 3.37**. These have been estimated using the EUSES programme. The vast majority of the medium-chain chlorinated paraffin is likely to enter soil via adsorption onto and subsequent spreading of sewage sludge, but for uses where atmospheric emissions occur (e.g. PVC and plastics), then these releases can also contribute to the concentrations found in soil over time.

No degradation in soil was assumed in the model, and the local concentrations are calculated based on 10 years continual application of sewage sludge containing the chlorinated paraffin.

After this time period the fraction of the steady state concentration reached is estimated as $4.1 \cdot 10^{-3}$ (0.4%) for agricultural soil and $5.6 \cdot 10^{-3}$ (0.6%) for grassland. This indicates that over prolonged periods of exposure (either through atmospheric deposition and/or sewage sludge application) higher concentrations than predicted here could theoretically build up in the soil compartment if there is no removal mechanism for medium-chain chlorinated paraffins from soil.

For the intermittent release scenario in **Table 3.37**, the calculation of the concentration on sludge assumes that 93% the chemical released on that day is adsorbed onto the amount of sludge produced in the waste water treatment plant on that day. However, the sludge retention time of sludge in the default waste water treatment plant is 9.2 days and so the calculation has assumed that this sludge is diluted by a factor of around 9.2 prior to being spread onto the land (the instantaneous estimated concentration on sludge is 28,700 mg/kg dry weight and so a value of 3,120 mg/kg dry weight is used in the subsequent calculations).

Table 3.37 Estimated concentrations in soil

Scenario	Step	Conc. in dry sewage sludge (mg/kg)	Predicted soil concentration (mg/kg wet wt)		
			Agric. soil 30 days ave.	Agric. soil 180 days ave.	Grassland 180 days ave.
Production	Site A	0[a]	negligible[d]	negligible[d]	negligible[d]
	Site B	0[a]	negligible[d]	negligible[d]	negligible[d]
	Site C	0[a]	negligible[d]	negligible[d]	negligible[d]
	Site D	0[a]	negligible[d]	negligible[d]	negligible[d]
Use in PVC – plastisol applications	Compounding - O	28.7	1.52 (0.51)[b]	1.52 (0.51)[e]	1.27 (0.26)[e]
	Conversion – O	213	4.23 (3.21)[b]	4.23 (3.21)[e]	2.36 (1.35)[e]
	Combined compounding/ conversion – O	241	4.65 (3.64)[b]	4.65 (3.64)[e]	2.53 (1.51)[e]
Use in PVC – extrusion/other	Compounding - O	106	2.65 (1.64)[b]	2.65 (1.64)[e]	1.72 (0.71)[e]
	Compounding – PO	575	9.54 (8.53)[b]	9.54 (8.53)[e]	4.49 (3.48)[e]
	Compounding – C	48.9	1.82 (0.81)[b]	1.82 (0.81)[e]	1.39 (0.38)[e]
	Conversion – O	322	5.83 (4.82)[b]	5.83 (4.82)[e]	3.00 (1.99)[e]
	Conversion – PO	345	6.17 (5.16)[b]	6.17 (5.16)[e]	3.14 (2.13)[e]
	Conversion – C	293	5.41 (4.40)[b]	5.41 (4.40)[e]	2.83 (1.82)[e]
	Compounding/conversion – O	428	7.38 (6.37)[b]	7.38 (6.37)[e]	3.63 (2.61)[e]
	Compounding/conversion – PO	920	14.6 (13.6)[b]	14.6 (13.6)[e]	6.53 (5.51)[e]
	Compounding/conversion – C	343	6.13 (5.12)[b]	6.13 (5.12)[e]	3.12 (2.11)[e]
Use in plastics/rubber	Compounding	53.5	1.88 (0.87)[b]	1.88 (0.87)[e]	1.41 (0.40)[e]
	Conversion	178	3.72 (2.71)[b]	3.72 (2.71)[e]	2.15 (1.14)[e]
	Compounding/conversion	232	4.51 (3.5)[b]	4.51 (3.5)[e]	2.47 (1.46)[e]
Use in sealants	Formulation and use	-	negligible[d]	negligible[d]	negligible[d]
Use in paints	Formulation	172	3.63 (2.62)b	3.63 (2.62)e	2.11 (1.10)e
	Industrial application	67.8	2.09 (1.08)b	2.09 (1.08)e	1.50 (0.49)e

Table 3.37 continued overleaf

Table 3.37 continued Estimated concentrations in soil

Scenario	Step	Conc. in dry sewage sludge (mg/kg)	Predicted soil concentration (mg/kg wet wt)		
			Agric. soil 30 days ave.	Agric. soil 180 days ave.	Grassland 180 days ave.
	Domestic application	3.45×10⁻⁴	negligibled	negligibled	negligibled
Use in metal cutting/working fluids	Formulation	954	15.1 (14.1)[b]	15.1 (14.1)[e]	6.7 (5.68)[e]
	Use in oil-based fluids (large)	379	6.67 (5.66)[b]	6.67 (5.66)[e]	3.32 (2.31)[e]
	Use in oil-based fluids (small)	345	6.16 (5.15)[b]	6.16 (5.15)[e]	3.12 (2.11)[e]
	Use in emulsifiable fluids	28.7	1.52 (0.51)[b]	1.52 (0.51)[e]	1.27 (0.26)[e]
	Use in emulsifiable fluids – intermittent release	3,120	47 (46)[b]	47 (46)[e]	19.4 (18.4)[e]
Use in leather fat liquors	Formulation	115	2.80 (1.78)[b]	2.80 (1.78)[e]	1.79 (0.78)[e]
	Use – complete processing of raw hides	1,030	16.3 (15.3)[b]	16.3 (15.3)[e]	7.17 (6.16)[e]
	Use – processing of wet blue	4,140	61.8 (60.8)[b]	61.8 (60.8)[e]	25.4 (24.4)[e]
Use in carbonless copy paper	Paper recycling	203[c]	4.07[c] (3.06)[b,c]	4.07[c] (3.06)[b,c]	2.29[c] (1.28)[b,c]

a) Sewage sludge from production sites is not applied to agricultural land.
b) Values in ( ) recalculated using the measured regional natural soil concentration of 0.088 mg/kg wet wt. (see Section 3.1.3.2).
c) Primary treatment (sludge to landfill) followed by biological waste water treatment (sludge to soil).
d) The process makes no significant contribution to the levels in soil.
O Open systems;
PO Partially open systems;
C Closed systems (as defined in UCD, 1998).

For the regional sources the following concentrations in soil were calculated (see Appendix A):

agricultural soil $PEC_{regional(soil)}$ = 50.4 mg/kg wet wt.
industrial/natural soil $PEC_{regional(soil)}$ = 1.10 mg/kg wet wt.

The above regional concentrations do not include the contribution from 'waste remaining in the environment'. When this is included in the calculation the regional concentrations become:

agricultural soil $PEC_{regional(soil)}$ = 53.8-55.8 mg/kg wet wt.
industrial soil/urban $PEC_{regional(soil)}$ = 147-173 mg/kg wet wt
natural soil $PEC_{regional(soil)}$ = 1.85-2.01 mg/kg wet wt.

In the regional model, agricultural soil received input from both sewage sludge and aerial deposition, whereas the natural soil received input from aerial deposition only. Higher concentrations have been estimated in the regional model than in some of the local scenarios given in **Table 3.37**. This is because the concentrations calculated in the regional model are 'steady-state' concentrations, and reflect the possible build up in soil due to continuous application over many years (rather than 10 years as is used in the local calculations). The model does not give any indication as to the time period that may be necessary for these concentrations to be reached (for instance if 0.4% of steady-state is reached in 10 years, then the time taken to reach steady-state concentrations could be of the order of several thousands of years).

3.1.3.2 Measured levels

No measured levels of medium-chain chlorinated paraffins in soil were located in the literature. A monitoring survey of concentrations of medium-chain chlorinated paraffins (and other chlorinated paraffins) in sewage sludge, soil and earthworms associated with some uses of medium-chain chlorinated paraffins in the United Kingdom has recently been completed (CEFAS, 1999) and the results are summarised in **Table 3.38**. The samples used in the study were collected in the early summer of 1998. The levels found in digested sewage sludge prior to application onto soil were in the range 2.9-93 mg/kg dry weight and the levels found in soil where the sludge was applied were generally not detected (<0.1 mg/kg dry weight which is equivalent to <0.088 mg/kg on a wet weight basis).

Table 3.38 Levels in sewage sludge, agricultural land and earthworms from the United Kingdom (CEFAS, 1999)

Location	Comment	Sample type	Concentration[a]
South West	Sewage treatment plant associated with polymers/tarpaulin industry. Soil received repeated application of fertiliser made from sludge.	Digested sewage sludge	2.9 mg/kg dry weight
		Dried digested sewage sludge (fertiliser)	27.7 mg/kg dry weight
		Soil receiving fertiliser	<0.1 mg/kg dry weight
		Earthworms	<0.1 mg/kg fresh weight
South East	Sewage treatment plant associated with synthetic rubber and other varied industries. Digested sewage frequently applied to soil.	Digested sewage sludge	12.1 mg dry weight
		Soil receiving sewage sludge	<0.1 mg/kg dry weight
		Earthworms	0.7 mg/kg fresh weight
Wales	Sewage treatment plants associated with formulation and use of metal working fluids. Digested sewage applied to soil January 1998. Tentatively identified as short-chain[a].	Digested sewage sludge	11.8 mg/kg dry weight
		Soil receiving sewage sludge	<0.1 mg/kg dry weight
		Earthworms	<0.1 mg/kg fresh weight
West Midlands	Sewage treatment plant associated with formulation and use of metal working fluids. Digested sewage frequently applied to soil. Known to have been applied January 1998.	Digested sewage sludge	17.1 mg/kg dry weight
		Soil receiving sewage sludge	<0.1 mg/kg dry weight
		Earthworms	0.3 mg/kg fresh weight
East Midlands	Sewage treatment plant associated with rubber production. Several applications of sludge made during February 1998.	Digested sewage sludge	3.4 mg/kg dry weight
		Soil receiving sewage sludge	<0.1 mg/kg dry weight
		Earthworms	<0.1 mg/kg fresh weight
East Anglia	Industry source unknown. Digested sewage frequently applied to soil.	Digested sewage sludge	1.8 mg/kg dry weight
		Soil receiving sewage sludge	<0.1 mg/kg dry weight
		Earthworms	0.5 mg/kg fresh weight
North West	Sewage treatment plant associated with formulation and use of metal working fluids, and other industries. Digested sewage frequently applied to soil. Several applications made during 1997/1998	Digested sewage sludge	6.7 mg/kg dry weight
		Soil receiving sewage sludge	<0.1 mg/kg dry weight
		Earthworms	<0.1 mg/kg fresh weight
North East	Sewage treatment plant associated with PVC/other industries. Digested sewage frequently applied to soil.	Digested sewage sludge	93.1 mg/kg dry weight
		Soil receiving sewage sludge	<0.1 mg/kg dry weight
		Earthworms	1.7 mg/kg fresh weight

a)   The actual identity of the residues present (i.e. medium-chain or short-chain chlorinated paraffin) were difficult to assign due to the high concentration of co-extracted lipid-soluble material.

3.1.3.3   Comparison of measured and predicted concentrations

The concentrations measured in sewage sludge are in reasonable agreement with some of the predicted levels given in **Table 3.37**, but the resulting measured concentration in agricultural soil is lower than the predicted concentration. This is particularly marked for the predicted regional concentration. One reason for this is may be due to an unrealistic removal (degradation) rate for medium-chain chlorinated paraffins in the EUSES model. The calculations in the model, particularly at the regional level, are very sensitive to the degradation rate (the default degradation rate constant is $6.93 \cdot 10^{-7}$ days^{-1}, corresponding to a half-life of 2,740 years). The effect of varying the degradation rate in the regional model is shown in Appendix H. From this analysis, a biodegradation half-life of the order of 2 years results in the predicted concentrations that are consistent with the available monitoring data. Information on the actual degradation of medium-chain chlorinated paraffins in soil would be useful to indicate whether or not the substance is likely to build up in the soil as indicated by the current model.

Since the actual time from the last application of sludge to the soil and the collection of soil samples is unknown, it is not possible to estimate from the measured data the likely concentration resulting 30 days after application (as is needed for the PEC$_{local}$) for agricultural soil. Therefore the predicted PEC$_{locals}$ given in **Table 3.37** will be used at present in the risk characterisation. However, it is clear from the measured data from fields where sludge containing medium-chain chlorinated paraffins has been applied over many years that the regional 'background' concentration is <0.1 mg/kg dry weight (or <0.088 mg/kg wet weight) in agricultural soil, which is much lower than the predicted value. Similar to the case with the surface water and sediment compartments, this value will be used for the estimated PEC$_{regional}$s for agricultural and natural soil in the further calculations and in the risk characterisation.

The estimated regional concentration in industrial/urban soil is very high (147-173) when the 'waste remaining in the environment' contribution is included in the calculation, which reflects potentially high emissions from this source. However, there are some uncertainties over the actual (bio)availability of the medium-chain chlorinated paraffins released to the environment in this form, and over the applicability of the available models to predict the resulting environmental concentrations. As discussed above, the half-life for degradation/removal in soil has a large impact on the predicted concentrations for soil. If a removal half-life of 2 years is used in the calculation (as suggested by the analysis carried out in Appendix H), then these regional concentrations in industrial/urban soil would be reduced to 0.7-0.8 mg/kg wet wt. Again, there are large uncertainties inherent in this calculation.

3.1.4   Atmospheric compartment

3.1.4.1   Predicted levels

The concentrations of medium-chain chlorinated paraffins in the atmosphere have been predicted using EUSES. The local concentrations arise from direct emissions of medium-chain chlorinated paraffins from the various industrial processes involved (emissions to air from waste water treatment plants are considered to be negligible due to the physico-chemical properties of the substance). At the regional and continental level, diffuse source releases have also been considered in the model. These releases were identified in Section 3.1.1. The full output of the model is given as Appendix A. The predicted atmospheric concentrations are shown in **Table 3.39**. The regional air concentration is estimated as $3.35 \cdot 10^{-6}$ mg/m^3 or

$5.64\text{-}6.12 \cdot 10^{-6}$ mg/m^3 when the contribution from "waste remaining in the environment" is included.

Table 3.39 Estimated air concentrations of medium-chain chlorinated paraffins

Scenario	Step	Estimated Atmospheric release	Air concentrations (C$_{local}$) (mg/m^3)		PEC$_{air, ann}$ (mg/m^3)
			Emission episode	Annual average	
Production	5 Sites	0 kg/day	negligible[a]	negligible[a]	negligible[a]
Use in PVC – plastisol coating	Compounding - O	0 kg/day	negligible[a]	negligible[a]	negligible[a]
	Conversion – O	0.185 kg/day	$5.1 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$
	Compounding/conversion - O	0.185 kg/day	$5.1 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$
Use in PVC – extrusion/other	Compounding - O	0.055 kg/day	$1.5 \cdot 10^{-5}$	$1.3 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$
	Compounding - PO	0.3 kg/day	$8.3 \cdot 10^{-5}$	$6.9 \cdot 10^{-5}$	$7.2 \cdot 10^{-5}$
	Compounding – C	0.026 kg/day	$7.1 \cdot 10^{-6}$	$5.8 \cdot 10^{-6}$	$9.2 \cdot 10^{-6}$
	Conversion – O	0.28 kg/day	$7.8 \cdot 10^{-5}$	$6.4 \cdot 10^{-5}$	$6.7 \cdot 10^{-5}$
	Conversion – PO	0.3 kg/day	$8.3 \cdot 10^{-5}$	$6.9 \cdot 10^{-5}$	$7.2 \cdot 10^{-5}$
	Conversion – C	0.255 kg/day	$7.1 \cdot 10^{-5}$	$5.8 \cdot 10^{-5}$	$6.1 \cdot 10^{-5}$
	Compounding/conversion – O	0.335 kg/day	$9.3 \cdot 10^{-5}$	$7.7 \cdot 10^{-5}$	$8.0 \cdot 10^{-5}$
	Compounding/conversion - PO	0.6 kg/day	$1.7 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
	Compounding/conversion - C	0.281 kg/day	$7.8 \cdot 10^{-5}$	$6.4 \cdot 10^{-5}$	$6.7 \cdot 10^{-5}$
Use in plastics/rubber	Compounding	0.016 kg/day	$4.3 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	$6.9 \cdot 10^{-6}$
	Conversion	0.155 kg/day	$4.3 \cdot 10^{-5}$	$3.5 \cdot 10^{-5}$	$3.8 \cdot 10^{-5}$
	Compounding/conversion	0.171 kg/day	$4.8 \cdot 10^{-5}$	$3.9 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$
Use in sealants	Formulation and use	0 kg/day	negligible[a]	negligible[a]	negligible[a]
Use in paints	Formulation	0.05 kg/day	$1.4 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$
	Industrial application	0 kg/day	negligible[a]	negligible[a]	negligible[a]
	Domestic application	0 kg/day	negligible[a]	negligible[a]	negligible[a]
Use in metal cutting/working fluids	Formulation	0 kg/day	negligible[a]	negligible[a]	negligible[a]
	Use in oil-based fluids (large)	0 kg/day	negligible[a]	negligible[a]	negligible[a]
	Use in oil-based fluids (small)	0 kg/day	negligible[a]	negligible[a]	negligible[a]
	Use in emulsifiable fluids	0 kg/day	negligible[a]	negligible[a]	negligible[a]
	Use in emulsifiable fluids – intermittent release	0 kg/day	negligible[a]	negligible[a]	negligible[a]
Use in leather fat liquors	Formulation	0.35 kg/day	$9.7 \cdot 10^{-5}$	$8.0 \cdot 10^{-5}$	$8.3 \cdot 10^{-5}$
	Use – complete processing of raw hides	0 kg/day	negligible[a]	negligible[a]	negligible[a]
	Use – processing of wet blue	0	negligible[a]	negligible[a]	negligible[a]
Use in carbonless copy paper	Paper recycling	0	negligible[a]	negligible[a]	negligible[a]

a)   The process makes no significant contribution to the levels in air.
O   Open systems;
PO   Partially open systems;
C   Closed systems (as defined in UCD, 1998).

3.1.4.2   Measured levels

No measured levels for medium-chain chlorinated paraffins in air have been found in the literature.

3.1.5   Non-compartmental specific exposure relevant to the food chain

3.1.5.1   Predicted levels

The levels of medium-chain chlorinated paraffins in fish and earthworms for the secondary poisoning assessment have been calculated by EUSES using the methods given in the Technical Guidance Document. The calculations have been carried out twice: firstly using the estimated $PEC_{regional}$s of 0.389 µg/l for surface water and 50.4 mg/kg wet wt. for agricultural soil (slightly higher values would be obtained if the estimated $PEC_{regional}$s with the contribution from 'waste remaining in the environment' were used); and secondly using regional concentrations based on the measured data of 0.1 µg/l for surface water and 0.088 mg/kg wet wt. for agricultural soil. The latter values are considered to be most appropriate for consideration in the risk characterisation.

For the concentration in fish, a measured BCF of 1,087 l/kg was used in the calculations. The Technical Guidance Document indicates that as well as the bioconcentration factor, the biomagnification factor (BMF) for fish should also be considered in determination of the PEC for secondary poisoning, i.e.

$$PEC_{oral} = PEC_{water} \cdot BCF \cdot BMF.$$

According to the Technical Guidance Document, a BMF of 1 would be appropriate for medium-chain chlorinated paraffins (based on the fish BCF of 1,087 l/kg). However, the available data for accumulation of medium-chain chlorinated paraffins indicate that uptake from food does occur, and can in some cases be significant. This implies that a PEC estimated using the BCF alone (i.e. setting the BMF to 1) may underestimate the concentration in predators exposed via both food and water. Therefore, as discussed in Section 3.1.1.5, a BMF in the range 1 to 3 would be more appropriate as a worst case estimate. This range of BMF values has been used in the calculation of the PECs for fish. The predicted concentrations using this method are shown in **Table 3.40**.

It should be noted, however, that the above equation given in the Technical Guidance Document may not be appropriate when considering actual data from laboratory feeding studies. The intention in the Technical Guidance Document is to model the concentration in fish resulting from simultaneous exposure via both water and food, and this is represented by the scheme below. The term 'food accumulation factor' (FAF) is used in this scheme to distinguish it from the BMF given in the equation from the Technical Guidance Document.

Water   BCF$_{fish}$ Fish (PEC$_{oral, predator}$)   Fish-eating predator

BCF$_{aquatic\ organism}$

Aquatic organism (prey   FAF$_{fish}$
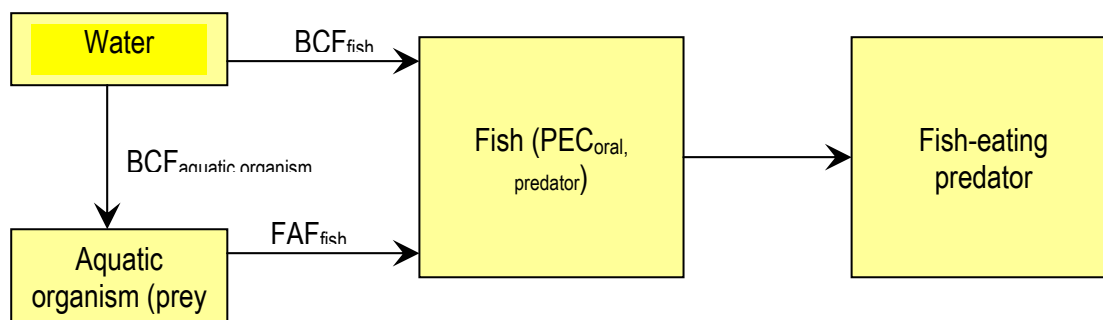
$$PEC_{oral, predator} = (PEC_{water} \times BCF_{aquatic\ orgnism} \times FAF_{fish}) + (PEC_{water} \times BCF_{fish}) \text{ -equation 1.}$$

Assuming that the 'aquatic organism' in the food chain is also a fish (as assumed in the Technical Guidance Document), then this equation simplifies to the following.

$$PEC_{oral, predator} = PEC_{water} \times BCF_{fish} \times (1 + FAF_{fish}) \text{ -equation 2.}$$

Using a FAF (BMF) of 1-3 as before, the resulting PECs in predatory fish using equation 2, and assuming that 50% of the exposure comes from local sources and 50% comes from regional sources (the Technical Guidance Default), are shown in **Table 3.40** (marked as 'alternate method'). It should be noted that there has been no formal discussion (or agreement) of this 'alternate' method at Technical Committee Meeting level and so the results from these calculations should be treated with caution. However, the calculations lead to essentially similar conclusions as obtained using the standard methodology in the Technical Guidance Document.

An interesting consequence of equation 2 is that it does not require a FAF (or BMF) to be above 1 for food uptake to be important to the overall body burden in predatory fish. For example, FAF values between 0.1 and 1 result in predicted concentrations ranging from 1.1 to 2 times those predicted from the BCF alone. This should not be confused with increasing concentrations found in sequential trophic levels (i.e. biomagnification), because the simplistic calculations used here neglect the fact that the prey fish/organism in the calculations will also have a contribution from food. More complicated food web approaches that consider several trophic levels are needed to fully assess these aspects. This aspect was commented on by the CSTEE in their review of the assessment of short-chain chlorinated paraffins (CSTEE, 2003) and is equally relevant for the assessment of medium chain chlorinated paraffins.

CSTEE (2003) carried out some preliminary modelling for short-chain chlorinated paraffins using a food chain consisting of algae and three levels of consumer. The model used was based on the system dynamic model published by Carbonell et al. (2000), and assumed a BCF for fish of 7,000 and 1,000 l/kg, a BCF for algae of 200 and 1,000 (the algal BCFs were not specific to short-chain chlorinated paraffins but were taken from work carried out with other substances (e.g. Sijm et al. (1998) and Hendriks et al. (2001)), and depuration half-lives of 10 and 20 days. The model was run several times using various combinations of the data and several results indicated that the body burdens resulting from the accumulation from food were up to one order (or in some case more) of magnitude higher than those resulting from bioconcentration alone. Therefore the CSTEE concluded that it was relevant to consider food uptake when considering the bioaccumulation potential for short-chain chlorinated paraffins. Similar conclusions would also be expected to be relevant for medium-chain chlorinated paraffins.

For the levels in earthworms, an earthworm-soil bioaccumulation factor of 5.6 kg/kg wet wt. was used, as estimated in Section 3.1.1.5. As was noted in Section 3.1.1.5, the bioaccumulation potential of medium-chain chlorinated paraffins, although still appreciable, appears to be lower than would be expected based on the high log Kow value, and also appears to reduce with increasing degree of chlorination. The predicted concentrations are shown in **Table 3.40**.

The concentrations of medium-chain chlorinated paraffins in food and other media for human consumption have been estimated using EUSES and are shown in **Table 4.2** in Section 4.

Table 3.40 Estimated concentrations in fish and earthworms for secondary poisoning

Scenario	Step	Predicted concentration in fish[f] (mg/kg wet wt)				Predicted concentration in earthworms(mg/kg wet wt)	
		Based on estimated regional water conc.[d]		Based on measured regional water conc.[e]		Based on estimated regional soil conc.[d]	Based on measured regional soil conc.[e]
		TGD method	Alternate method	TGD method	Alternate method		
Production	Site A	0.43-1.29	0.86-1.72	0.11-0.33	0.22-0.44	negligible[c]	negligible[c]
	Site B	0.46-1.38	0.92-1.84	0.15-0.45	0.30-0.60	negligible[c]	negligible[c]
	Site C	0.50-1.50	1.00-2.00	0.19-0.57	0.38-0.76	negligible[c]	negligible[c]
	Site D	0.42-1.26	0.84-1.68	0.11-0.33	0.22-0.44	negligible[c]	negligible[c]
Use in PVC – plastisol coating	Compounding - O	0.43-1.29	0.86-1.78	0.13-0.39	0.26-0.52	145	1.7
	Conversion – O	0.58-1.74	1.16-2.32	0.26-0.78	0.52-1.04	153	9.3
	Compounding/conversion – O	0.60-1.80	1.20-2.40	0.28-0.84	0.56-1.12	154	10.4
Use in PVC – extrusion/other	Compounding - O	0.50-1.50	1.00-2.00	0.19-0.57	0.38-0.76	149	4.8
	Compounding – PO	0.84-2.52	1.68-3.36	0.52-1.56	1.04-2.08	168	24.1
	Compounding – C	0.46-1.38	0.92-1.84	0.14-0.42	0.28-0.56	146	2.5
	Conversion – O	0.66-1.98	1.32-2.64	0.34-1.02	0.68-1.36	157	13.7
	Conversion – PO	0.67-2.01	1.34-2.68	0.36-1.08	0.72-1.44	158	14.7
	Conversion – C	0.63-1.89	1.26-2.52	0.32-0.96	0.64-1.28	156	12.6
	Compounding/conversion – O	0.73-2.19	1.46-2.92	0.42-1.26	0.84-1.68	162	18.1
	Compounding/conversion – PO	1.09-3.27	2.18-6.54	0.77-2.31	1.54-3.08	182	38.3
	Compounding/conversion – C	0.67-2.01	1.34-4.02	0.36-1.08	0.72-1.44	158	14.6
Use in plastics/rubber	Compounding	0.46-1.38	0.92-2.76	0.15-0.45	0.30-0.60	146	2.7
	Conversion	0.55-1.65	1.10-3.30	0.24-0.72	0.48-0.96	152	7.8
	Compounding/conversion	0.59-1.77	1.18-3.54	0.28-0.84	0.56-1.12	154	10.0

Table 3.40 continued overleaf

Table 3.40 continued Estimated concentrations in fish and earthworms for secondary poisoning

Scenario	Step	Predicted concentration in fish[f] (mg/kg wet wt)				Predicted concentration in earthworms(mg/kg wet wt)	
		Based on estimated regional water conc.[d]		Based on measured regional water conc.[e]		Based on estimated regional soil conc.[d]	Based on measured regional soil conc.[e]
		TGD method	Alternate method	TGD method	Alternate method		
Use in sealants	Formulation and use	negligible[c]	negligible[c]	negligible[c]	negligible[c]	negligible[c]	negligible[c]
Use in paints	Formulation	0.55-1.65	1.10-2.20	0.23-0.69	0.46-0.92	151	7.6
	Industrial application	0.47-1.41	0.94-1.88	0.16-0.48	0.23-0.64	147	3.3
	Domestic application	negligible[c]	negligible[c]	negligible[c]	negligible[c]	negligible[c]	negligible[c]
Use in metal cutting/working fluids	Formulation	1.11-3.33	2.22-4.44	0.80-2.40	1.60-3.20	183	39.7
	Use in oil-based fluids (large)	0.70-2.10	1.40-2.80	0.38-1.14	0.76-1.52	160	16.1
	Use in oil-based fluids (small)	0.67-2.01	1.34-2.68	0.36-1.08	0.72-1.44	158	14.7
	Use in emulsifiable fluids	0.44-1.32	0.88-1.76	0.13-0.39	0.26-0.52	145	1.7
	Use in emulsifiable fluids – intermittent release	0.84-2.52	1.68-3.36	0.52-1.56	1.04-2.08	272[a]	129[a]
Use in leather fat liquors	Formulation	0.51-1.53	1.02-2.04	0.19-0.57	0.38-0.76	149	5.2
	Use – complete processing of raw hides	1.17-3.51	2.34-4.68	0.86-2.58	1.72-3.44	187	43.0
	Use – processing of wet blue	3.41-10.2	6.82-13.64	3.10-9.30	6.20-12.4	314	171
Use in carbonless copy paper	Paper recycling	0.54[b]-1.62[b]	1.08[b]-2.16[b]	0.23[b]-0.69[b]	0.46[b]-0.92[b]	152[b]	8.8[b]

a)   Assumes dilution of sewage sludge at WWTP before application to soil (see Section 3.1.3.1).
b)   Primary treatment (sludge to landfill) followed by biological waste water treatment (sludge to soil).
c)   The process makes no significant contribution to the levels in fish/earthworms.
d)   Using the estimated PEC$_{regional}$s of 0.389 µg/l for water and 50.4 mg/kg wet wt. for soil.
e)   Using the measured regional concentrations of 0.1 µg/l for water and 0.088 mg/kg wet wt. for soil.
f)   The range of concentrations reflects the range of the BMF used (1- 3).
O   Open systems; PO = Partially open systems; C = Closed systems (as defined in UCD, 1998).

3.1.5.2 Measured levels

Recently an in-depth study of the levels of medium-chain chlorinated paraffins in industrial areas of the United Kingdom has been carried out (CEFAS, 1999). The main purpose of the study was to determine the concentrations of medium-chain (and short-chain where found) chlorinated paraffins in surface water, sediment, biota and soil associated with their industrial use. The sampling sites were chosen with regards to their proximity to known sources/users of medium-chain chlorinated paraffins. Samples were collected during early summer 1998. The levels found in biota are shown in **Table 3.41**. The levels found in surface water, sediment and soil (including earthworms) are reported in the appropriate Sections of this report.

Table 3.41 Levels of chlorinated paraffins in fish and benthos in the United Kingdom, related to sources (CEFAS, 1999)

Industry	Comment/tentative identification[a]	Sample	Concentration of chlorinated paraffin (mg/kg fresh weight)
Polymers/ tarpaulins		Fish: roach muscle	<0.2
Synthetic rubber manufacture		Fish: perch muscle	<0.2
Metal working		Fish: flounder muscle	<0.1
Lubricant blending/ metal working	Possibly medium-chain - levels could not be accurately quantified due to interferences.	Benthos: 90% Hindinae + Lymnaeidae	0.3
		Fish: roach muscle	0.6
		Fish: eel muscle	0.7
		Fish: pike liver	2.8
Sealant and adhesive manufacture	Possibly short-chain.	Benthos: 25% Spaeridae, 13% Hindinae, 9% Gammanidae, 25% Asellidae, 17% Planerbidae, 9% Valvatidae, 2% Sialidae	0.3
		Fish: roach liver	<0.1
Rubber product manufacturer	Possibly medium-chain.	Benthos: 2% Viviparidae, 16% Lymnaeidae, 5% Gammanidae, 16% Asellidae, 3% Zygoptera, 5% Corixidae, 16% Chironomidae, 8% Caddis, 3% Beetle, 16% Hindinae, 8% Hydrobiidae.	0.1
		Fish: roach muscle	<0.1
		Fish: eel liver	<0.2
Manufacturer of building sealants/ lubricant blending		Fish: roach muscle	<0.1
Control site - no known uses.	Possibly medium-chain	Benthos: 18% Chironomidae, 71% Lymnaeidae, 7% Asellidae, 4% Sphaendae	0.5
		Fish: carp muscle	0.5
Manufacturer of chlorinated paraffins	Possibly mixture of short- and medium-chain	Benthos: 90% Chironomidae, 8% Gamanidae, 2% Lymnaeidae	0.1
		Fish: eel liver	0.2

Table 3.41 continued overleaf

Table 3.41 continued Levels of chlorinated paraffins in fish and benthos in the United Kingdom, related to sources (CEFAS, 1999)

Industry	Comment/tentative identification[a]	Sample	Concentration of chlorinated paraffin (mg/kg fresh weight)
Lubricant manufacturer(and other industries)	Possibly short-chain.	Benthos: 95% Gammanidae, 5% Chironomidae	0.1
PVC cable manufacturer	Possibly medium-chain.	Benthos: 90% Spaeridae, 5% Lymnaeidae, 5% Hirudinae	0.8
Metal working/ leather finishing	Possibly mixture of short- and medium-chain.	Benthos: 50% Asellidae, 40% Chironomidae, 5% Tipulidae, 4% Hirudinae, 1% Lymnaeidae	0.5
Metal working sites	Possibly short-chain.	Benthos: 60% Oligochaetes, 20% Chironomidae, 16% Lymnaeidae, 4% Sphaeridae.	<0.05
		Fish: whole, Stone Loach	5.2
PVC production/ paint manufacture	Possibly mixture of short- and medium chain.	Benthos: 95% Asellidae, 5% Oligochaetes	0.7
Leather finishing chemicals formulation site		Benthos: 65% Sphaeridae, 265 Lymnaeidae, 3% Planorbidae, 2% Corixidae, 2% Sialidae, 2% Hinidinae, 2% Valvatidae	<0.05
		Fish: roach muscle	<0.05
		Fish: eel liver	<0.05
Background site		Fish: eel muscle	<0.05

a)   The actual identity of the residues present were difficult to assign due to the high concentration of co-extracted lipid-soluble material. Tentative identity based on the chlorinated paraffins found in sediment in the area.

Levels of combined short- and medium-chain (i.e. C_{10-20}) chlorinated paraffins have been measured in seal, marine shellfish and salt and freshwater fish from around the United Kingdom (Campbell and McConnell, 1980). The results of the analyses are shown in **Table 3.42**. The same authors also determined the levels of C_{10-20} chlorinated paraffins in several other parts of the (human) food chain. The results of these analyses are shown in **Table 3.43 to 3.46**.

Table 3.42 Concentrations of combined short- and medium-chain chlorinated paraffins (C_{10-20}) in aquatic organisms (Campbell and McConnell, 1980).

Species	No. of specimens	Concentration of C_{10-20} chlorinated paraffin	
		Mean (µg/kg)	Range (µg/kg)
Plaice (*Pleuronectes platessa*)	6	30	ND-200
Pouting (*Trisopterus luscus*)	4	100	ND-200
Mussel (*Mytilus edulis*)	9	3,250	100-12,000
Pike (*Esox lucius*)	2	25	ND-50
Grey seal (liver and blubber) (*Halichoerus grypus*)	4	75	40-100

ND Not detected (detection limit = 50 µg/kg).

Table 3.43 Concentration of combined short- and medium-chain chlorinated paraffins (C$_{10-20}$) in seabirds' eggs[a] (Campbell and McConnell, 1980)

Concentration (µg/kg)	No of eggs containing C$_{10-20}$ chlorinated paraffins
Not detected (<50 µg/kg)	7
50	3
100	3
200	5
300	1
400	2
600	1
>600 (=2,000 µg/kg)	1

Species included in study were: Cormorant (*Phalocrocorax carbo*); Gannet (*Morus bassanus*); Great skua (*Catharacta skua*); Guillemot (*Uria aalge*); Kittiwake (*Rissa tridactyla*); Puffin (*Fratecula arctica*); Manx shearwater (*Puffinus puffinus*); Razorbill (*Alca torda*) and Shag (*Phalacrocorax aristotelis*).

Table 3.44 Concentration of combined short- and medium-chain chlorinated paraffins (C$_{10-20}$) in birds (Campbell and McConnell, 1980)

Species	Organ	Concentration of C$_{10-20}$ chlorinated paraffins (µg/kg wet weight)
Heron (*Ardea cinerea*)	Liver	100-1,200
Guillemot (*Uria aalge*)	Liver	100-1,100
Herring gull (*Larus argentatus*)	Liver	200-900

Table 3.45 Concentration of combined short- and medium-chain chlorinated paraffins (C$_{10-20}$) in human foodstuffs (Campbell and McConnell, 1980)

Foodstuff class	No of samples analysed[*]	Average concentration of C$_{10-20}$ chlorinated paraffins (µg/kg)
Dairy products	13	300
Vegetable oils and derivatives	6	150
Fruit and vegetables	16	5
Beverages	6	ND

ND   Not detected (detection limit = 50 µg/kg),
*   Detected in approximately 70% of samples analysed.

Table 3.46 Concentration of combined short- and medium-chain chlorinated paraffins (C$_{10-20}$) in sheep from areas near to and remote from a chlorinated paraffin production plant (Campbell and McConnell, 1980)

Location of sheep	Organ analysed	Average concentration of C$_{10-20}$ chlorinated paraffin (µg/kg)
Remote from industry	Liver, brain, kidney, mesenteric fat	ND
Close to a chlorinated paraffin production plant	Heart	ND
	Liver	200
	Lung	ND

Table 3.46 continued overleaf

Table 3.46 continued   Concentration of combined short- and medium-chain chlorinated paraffins (C10-20) in sheep from areas near to and remote from a chlorinated paraffin production plant (Campbell and McConnell, 1980)

Location of sheep	Organ analysed	Average concentration of C10-20 chlorinated paraffin (g/kg)
	Mesenteric fat	50
	Kidney	50
	Perinephritic fat	ND

ND   Not detected (detection limit = 50 µg/kg).

Levels of total (C$_{10-24}$) chlorinated paraffins in food, fish and marine animals have been reported by Greenpeace (1995). The total levels measured (on a fat weight basis) were 271 µg/kg in mackerel, 62 µg/kg in fish oil (herring), 98 µg/kg in margarine containing fish oil, 16-114 µg/kg in common porpoise, 963 µg/kg in fin whale, 69 µg/kg in pork, 74 µg/kg in cows milk and 45 µg/kg in human breast milk. Medium-chain chlorinated paraffins were thought to make up between 6 and 29% of the total chlorinated paraffins found. The concentrations of medium-chain chlorinated paraffins present can be estimated from the data as 46 µg/kg in mackerel, 12 µg/kg in fish oil, 28 µg/kg in margarine, 3-7 µg/kg in porpoise, 144 µg/kg in fin whale, 11 µg/kg in pork fat, 16 µg/kg in cows milk and 7 µg/kg in mothers' milk. Further details of the analysis of the mothers' milk samples have recently become available (UBA, 2001). The analysis of mothers' milk was carried out on pooled samples from six fish-eaters (who ate fish a minimum of once per week) and two non-fish-eaters (who ate fish a maximum of once a month). Similar results were obtained for both groups (the total chlorinated paraffin content of the fish-eating group was 50.4 µg/kg lipid, compared to 40.5 µg/kg lipid in the non-fish-eaters; the low sample size meant that it was not possible to determine if any significant differences were apparent between the two groups). The fat content of the mother's milk was 2.8% in the fish-eaters and 4.3% in the non-fish-eaters. The average chlorine content of the chlorinated paraffins detected was reported to be around 33% (although a value of 50% appears to have been assumed in the determination of chlorinated paraffin concentrations of the samples). The occurrence of medium-chain chlorinated paraffins in mother's milk and cow's milk are considered further in the Human Health Assessment. Industry commissioned an independent critique of the analytical method used in this study. This highlighted the potential uncertainties with the method and the findings are summarised in Appendix D.

A recent study has found medium-chain chlorinated paraffins to be present in human breast milk samples from the United Kingdom (Thomas and Jones, 2002). In all, 22 breast milk samples were analysed (8 from Lancaster and 14 from London, randomly chosen from a limited number of samples collected for a different study). Medium-chain chlorinated paraffins were found in one sample from London at a concentration of 61 µg/kg lipid but were below the limit of detection in the remaining 21 samples (the limit of detection of these samples varied with sample size but ranged from 16 µg/kg to 740 µg/kg lipid; these are higher than the levels in breast milk reported in other studies).

In addition to human breast milk, Thomas and Jones (2002) also determined the levels of medium-chain chlorinated paraffins in a sample of cow's milk from Lancaster and single butter samples from various regions of Europe (Denmark, Wales, Normandy, Bavaria, Ireland, and Southern and Northern Italy). Medium-chain chlorinated paraffins were present in the cow's milk sample at a concentration of 63 µg/kg lipid and were found in the butter samples from Denmark at 11 µg/kg, Wales at 8.8 µg/kg and Ireland at 52 µg/kg lipid. The detection limit for the other butter samples ranged between 8.0 and 11 µg/kg.

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Thomas et al. (2003) carried out a follow-up study on the levels of medium-chain chlorinated paraffins in breast milk samples from the United Kingdom using a more sensitive analytical procedure. In this study relatively large samples of human milk-fat were collected from the London (twenty samples) and Lancaster (five samples) areas of the United Kingdom between late 2001 and June 2002 (it should be noted that some of the samples from London were from the same mother; five samples were provided from one mother over a three-day period, two samples were provided from another mother over a two-day period, a further two samples were provided by another mother over a five-day period, and a further two samples were provided by another mother over an unknown period). The analysis was carried out using high resolution gas chromatography (HRGC) coupled with electrochemical negative ionisation (ECNI)-high resolution mass spectrometry (HRMS) detection. The analytical standards used were a commercial short-chain and medium-chain chlorinated paraffin (C_{10-13}, 60% wt. Cl and C_{14-17}, 52% wt. Cl). In addition to total medium-chain chlorinated paraffins, twelve samples (four from Lancaster and eight from London) were also analysed in more detail to determine the various types of chlorinated paraffin (in terms of chlorine number and carbon chain length distributions) present in the samples.

Medium-chain chlorinated paraffins were found to be present in all twenty five samples analysed. The median, 95th percentile value and range of concentrations found was 21 µg/kg lipid, 127.5 µg/kg lipid and 6.2-320 µg/kg lipid respectively. The levels found in the samples from Lancaster were not thought to be significantly different from the levels found in the samples from London. The more detailed analysis of the types of chlorinated paraffins present indicated that the pattern of medium-chain chlorinated paraffins found in the milk-fat samples was heavily skewed towards the C_{14}-chain length compared to the distribution found in the medium-chain chlorinated paraffin used as the analytical standard[10].

In a survey of 108 fish samples from Japan, chlorinated paraffins (of unspecified type) were not found in any of the samples analysed (detection limit 500 µg/kg wet wt.) (Environment Agency Japan, 1991).

Murray et al. (1987a) reported the results of monitoring of chlorinated paraffin levels in mussels (*Unionidae* sp.) collected downstream of a chlorinated paraffin manufacturing site in the United States. The level of medium-chain (C_{14-17}, 50-60% Cl) chlorinated paraffin detected was 170 µg/kg compared with <7 µg/kg upstream of the discharge.

Jansson et al. (1993) reported the occurrence of chlorinated paraffins (of unspecified chain length, with 6-16 chlorine atoms/molecule) at levels of 570-1,600 µg/kg lipid in fish and 130-280 µg/kg lipid in seal from in and around Sweden. In addition they also reported levels of chlorinated paraffins of 2,900 µg/kg lipid in rabbit muscle, 4,400 µg/kg lipid in moose muscle, 140 µg/kg in reindeer suet and 530 µg/kg in osprey muscle in pooled samples from the same area. The results are shown in **Table 3.47**.

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[10] The C_{14-17}, 52% wt Cl substance used as an analytical standard was sourced from the United States. Thomas et al. (2003) indicated that discussions between European and US producers of medium-chain chlorinated paraffins had identified a possible difference in the carbon chain distribution of their products, with the products produced in Europe more likely to have a distribution skewed towards the shorter chain length components compared to a more Gaussian distribution in products in the United States. This is a possible explanation for the findings. Other explanations include different volatilities or accumulation potential for the different components and differences in metabolism for the different components. It is not possible to determine which of these, or other, possibilities accounts for the findings.

Table 3.47 Concentrations of chlorinated paraffins (unspecified chain length) in pooled samples from in and around Sweden (Jansson et al., 1993)

Sample	Number of samples	Location/date	lipid content	Concentration* (µg/kg lipid)
Whitefish muscle	35	Lake Storvindeln, Lapland, 1986	0.66%	1,000
Arctic char muscle	15	Lake Vättern, Central Sweden, 1987	5.3%	570
Herring muscle	100	Bothnian Sea, 1986	5.4%	1,400
Herring muscle	60	Baltic proper, 1987	4.4%	1,500
Herring muscle	100	Skagerrak, 1987	3.2%	1,600
Ringed seal blubber	7	Kongsfjorden, Svalbard, 1981	88%	130
Grey seal blubber	8	Baltic Sea, 1979-85	74%	280
Rabbit muscle	15	Revingehed, Skåne, 1986	1.1%	2,900
Moose muscle	13	Grimsö, Västtmanland, 1985-86	2.0%	4,400
Reindeer suet	31	Ottsjö, Jämtland, 1986	56%	140
Osprey muscle	35	Sweden, 1982-1986	4.0%	530

*   Refers to chlorinated paraffins with 6-16 chlorine atoms and so may contain chlorinated paraffins other than C_{14-17}.

Tomy et al. (1998) report the results of Metcalfe-Smith et al. (1995), who found that levels of C_{14}-C_{17} chlorinated paraffins were below the detection limit (<3.5 mg/kg) in Zebra Mussel from the St. Lawrence River, Canada, taken downstream from a chlorinated paraffin manufacturing plant.

Recent data on the levels of medium-chain chlorinated paraffin in beluga whale (*Delphinapterus leucas*), rainbow trout (*Oncorhynchus mykiss*) and carp (*Cyprinus carpio*) from Canada have been reported (Bennie et al., 2000). For the whale, 37 blubber samples and 6 liver samples from 25 individuals were analysed for C_{14-17} chlorinated paraffins and the samples were taken from dead animals from the St. Lawrence River between 1987 and 1991. The fish samples were all taken from Lake Ontario in 1996 and 3 carp and 10 trout were analysed (whole body homogenates). The levels are shown in **Table 3.48**. The authors indicated that method used (involving low resolution mass spectrometry) may be more subject to analytical interferences from other organohalogen compounds than some of the methods used in other analyses (for example the authors indicate that analytical interferences may explain why their data for short-chain chlorinated paraffins in Beluga whale samples obtained using this method were one or two orders of magnitude higher than those obtained by other workers using high resolution mass spectrometry on the same samples). Therefore the results of this study should be treated with caution.

Table 3.48 Levels of medium-chain chlorinated paraffins in biota from Canada (Bennie et al., 2000)

Species	Sample	Lipid content	Concentration of medium-chain chlorinated paraffin (mg/kg wet wt.)
Beluga whale (*Delphinapterus leucas*)	Blubber samples from 15 females taken from mid depth of the subcutaneous fat	81-91% range 86.2% mean	1.78-79.0 range 20.5 mean
	Blubber samples from 10 males taken from mid depth of the subcutaneous fat	68-96% range 83.5% mean	15.8-80.0 range 39.1 mean
	Liver samples from 3 females	11-32% range	0.55-20.9 range

Table 3.48 continued overleaf

Table 3.48 continued   Levels of medium-chain chlorinated paraffins in biota from Canada (Bennie et al., 2000)

Species	Sample	Lipid content	Concentration of medium-chain chlorinated paraffin (mg/kg wet wt.)
	Liver samples from 3 males	20-52% range	2.74-5.82 range
Carp (*Cyprinus carpio*)	Whole body homogenates from 3 individuals	12-19% range 16% mean	0.276-0.563 range 0.393 mean
Trout (*Oncorhynchus mykiss*)	Whole body homogenates from 10 individuals	18-30% range 24% mean	0.257-4.39 range 1.23 mean

3.1.5.3   Comparison of predicted and measured levels

Little information appears to be available on the levels of medium-chain chlorinated paraffins alone in biota samples. Most samples have been analysed for a range of chlorinated paraffins that includes the medium-chain ones combined with other types. This means that the levels found of total (e.g. C_{10-20}) chlorinated paraffins cannot be compared directly with the predicted concentrations in fish and food.

A monitoring survey has recently been completed within the United Kingdom, looking specifically at the levels of the medium-chain (and short-chain) chlorinated paraffins in biota samples collected near to possible sources of release. The results of this survey are summarised in **Table 3.41**. In this survey, the levels found in aquatic organisms were in the range <0.1-5.2 mg/kg wet weight (with the highest levels being tentatively identified as short-chain chlorinated paraffin) which is slightly lower than, but in reasonable agreement with, the predictions. Further, the survey also included monitoring of earthworms from soil where sewage sludge containing medium-chain chlorinated paraffins had been applied. The levels found in the earthworms were in the range <0.1-1.7 mg/kg wet weight, which is in reasonable agreement with the levels predicted. However, it should be noted that the method used could not unambiguously determine the exact identity (e.g. medium-chain or short-chain) of the chlorinated paraffin present in all of these samples.

The predicted concentrations will be used in the risk assessment.

3.2   EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT) ASSESSMENT

3.2.1   Aquatic compartment

3.2.1.1   Toxicity to fish

The toxicity of medium-chain chlorinated paraffins to fish is summarised in **Table 3.49.**

Lindén et al. (1979) studied the toxicity of three medium-chain chlorinated paraffins to the Bleak (*Alburnus alburnus*) in brackish water. The tests were carried out under static conditions without aeration at 10°C. Acetone was used as cosolvent (up to 500 µl/l). The water used for the test was taken from a nearby bay and had a pH of 7.8, a salinity of 7‰ and a dissolved oxygen concentration of 5 mg/l at the end of the test. Based on the concentrations of test substance initially added, the 96-hour LC$_{50}$'s were determined as >10,000 mg/l for a C$_{14-17}$, 52% chlorinated paraffin, >5,000 mg/l for a C$_{14-17}$, 50% chlorinated paraffin, and >5,000 mg/l for a C$_{15.5}$, 40% Cl chlorinated paraffin (the C$_{15.5}$ probably refers to the mean carbon chain length in the commercial medium-chain chlorinated paraffin).

Bengtsson et al. (1979) also studied the toxicity of a medium-chain chlorinated paraffin to Bleaks (*Alburnus alburnus*) as part of a bioaccumulation study. The chlorinated paraffin tested was a C$_{14-17}$, 50% wt. Cl substance. The tests were performed at 10°C using a semi-static procedure in which the test solutions containing 125 µg/l of the substance were renewed every two to three days over the 14-day exposure period. The water used in the experiment was Baltic Sea water with a salinity of 7‰, and acetone was present in all aquaria, including controls at a concentration of 0.1 ml/l. The fish used in the experiment had an average weight of 4.5 g and were not fed during the exposure period. Six groups of 15 fish were used for both the exposure and control solutions. No mortality or effect on behaviour was seen in fish exposed to the medium-chain chlorinated paraffin during the test.

Hoechst AG (1976 and 1977) reported the results of acute toxicity tests using several medium-chain chlorinated paraffins with Golden Orfe (*Leuciscus idus*). Few details of the tests are available and so it is not possible to validate these data. The results are reported in **Table 3.49** as supporting information.

The toxicity of a C$_{14-17}$, 52% wt. Cl paraffin to Rainbow Trout (*Oncorhynchus mykiss*) has been studied over 60 days in a GLP study (Madeley et al., 1983b). The substance tested was a commercial product mixed with a n-pentadecane-8-^{14}C that had been chlorinated to a similar degree. Two concentrations were tested; 1.05 mg/l and 4.5 mg/l, both based on mean measured concentrations over the 60 day period and 30 fish (approximate weight/fish = 2 g at start of test) were used per concentration. Acetone (500 ppm v/v - this concentration was required to maintain the test substance in suspension) was used as cosolvent and a flow-through system was used for the test.

Table 3.49 Toxicity to fish

Species	Substance tested	Comments	Result	Reference
Alburnus alburnus (bleak)	$C_{15.5}$, 40% Cl	Nominal concentration; acetone cosolvent (0.5 ml/l); static test	96h-LC_{50} >5,000 mg/l	Lindén et al. (1979)
	C_{14-17}, 50% Cl	Nominal concentration; acetone cosolvent (0.5 ml/l); static test	96h-LC_{50} >5,000 mg/l	Lindén et al. (1979)
	C_{14-17}, 52% Cl	Nominal concentration; acetone cosolvent (0.5 ml/l); static test	96h-LC_{50} >10,000 mg/l	Lindén et al. (1979)
	C_{14-17}, 50% Cl	Nominal concentration; brackish water; acetone cosolvent (0.1 mg/l); semi-static limit test	Not toxic at 0.125 mg/l over 14 days	Bengtsson et al. (1979)
Leuciscus idus (golden orfe)	C_{14-17}, 41% Cl (Chlorparaffin 40 fl.nv)	Substance added directly to test medium	Harmful threshold (48 hour) = 400 mg/l	Hoechst AG (1976)
	C_{14-17}, 41% Cl* (Hordalub 70 VT)		Harmful threshold (48 hour) = >500 mg/l	Hoechst AG (1977)
	C_{14-17}, 49% Cl (Hordalub 80 EM)		Harmful threshold (48 hour) = >500 mg/l	Hoechst AG (1977)
Oncorhynchus mykiss (rainbow trout)	C_{14-17}, 52% Cl, mixed with a n-pentadecane-8-^{14}C, 51% Cl	Acetone cosolvent (500 ppm v/v); measured concentrations; flow-through system;	No adverse effects at 4.5 mg/l over 60 days	Madeley et al. (1983b)
Oryzias latipes (Japanese medaka)	$C_{14}H_{23.3}Cl_{6.7}$, 55% Cl, ^{14}C-labelled	Static test; measured concentrations	No adverse effects on embryos or larvae at up to 1.6 mg/l over 20 days	Fisk et al., 1999
	$C_{14}H_{24.9}Cl_{5.1}$, 48% Cl	Static test; concentrations estimated from measurements with ^{14}C-$C_{14}H_{23.3}Cl_{6.7}$	No adverse effects on embryos or larvae at up to 3.4 mg/l over 20 days	Fisk et al., 1999

*   Preparation containing chlorinated paraffin and PEG also.

The other test conditions were pH=7.4-8.6, dissolved oxygen=9.4-11.4, temperature=12±1°C and water hardness=42-71 mg/l as $CaCO_3$. As well as mortality in the test, the 'normal' behaviour of the fish was qualitatively assessed (by comparison with controls) in terms of a) swimming behaviour; b) general behaviour of individuals (e.g. intense activity, sluggishness, quiescence, position in test vessel); c) response to presence of food; d) skin pigmentation changes. During the test, an insignificant number of fish died (2 fish escaped from the tanks - one from the acetone control and one from the 4.5 mg/l treatment; one death occurred in the 4.5 mg/l treatment). Further, overall no significant difference in the behaviour of the exposed fish compared with the control populations was seen. On days 5, 8 and 9, a few individuals in the 4.5 mg/l treatments showed a sluggish response to the presence of food but this was transient and disappeared after day 9 and was not considered treatment related. The report also gave information on the fish growth (weights and length) during the study. Although the data was not analysed statistically in the report, it did show that little or no effect on growth (compared with controls) occurred during the experiment (mean weights at end of study were 9.46 g in controls, 9.23 g in acetone control, 8.76 g in 1 mg/l exposure group and 8.41 g in 5.6 mg/l exposure group; mean length at end of study were 84.2 mm in controls, 81.2 mm in acetone controls, 82.0 mm in 1 mg/l exposure group and 78.0 mm in 5.6 mg/l exposure group). Overall, little or no effect was seen on fish exposed for 60 days at 4.5 mg/l.

A toxicity test using embryos of Japanese medaka (*Oryzias latipes*) is also available (Fisk et al., 1999). This study used a series of chlorinated paraffins with single carbon chain lengths and known chlorine contents. Two C_{14}-compounds were synthesised. The first compound was synthesised by the chlorination of 1,13-tetradecadiene, and so the positions of the chlorine atoms along the molecule were generally known. The composition of this product was:

Average formula $C_{14}H_{24.9}Cl_{5.1}$ 48% wt. Cl consisting of;

> 10.5% 1,2,13,14-tetrachlorotetradecane (42.3% wt. Cl)
> 74.3% x,1,2,13,14-pentachlorotetradecane (47.7% wt. Cl)
> 14.2% x,y,1,2,13,14-hexachlorotetradecane (52.6% wt. Cl)
> 1.0% x,y,z,1,2,13,14-heptachlorotetradecane (56.4% wt. Cl)
> where x, y and z are unidentified positions on the carbon chain.

The second compound was synthesised by the free radical chlorination of 1-^{14}C-tetradecane, and resulted in a more complex mixture. The composition of this product was:

Average formula [14]C-$C_{14}H_{23.3}Cl_{6.7}$ 55% wt. Cl consisting of;

> 0.2% $C_{14}H_{26}Cl_4$ (42.3% wt. Cl)
> 4.4% $C_{14}H_{25}Cl_5$ (47.7% wt. Cl)
> 34% $C_{14}H_{24}Cl_6$ (52.6% wt. Cl)
> 45% $C_{14}H_{23}Cl_7$ (56.4% wt. Cl)
> 14% $C_{14}H_{22}Cl_8$ (59.9% wt. Cl)
> 1.9% $C_{14}H_{21}Cl_9$ (62.8% wt. Cl)

In the experiment, fertilised eggs from the fish were individually exposed to the test substance in 1.8 ml vials with teflon-lined caps. The chlorinated paraffins were added to the vials by firstly dissolving the substance in a mixture of dichloromethane and hexane and then adding the required amount of solution to the vial and allowing the solvent to evaporate for 24 hours. Then 1 ml of the medaka rearing solution was added to the vial and the mixture was sonicated for 30 minutes before the fertilised egg was added. The vials were then sealed and incubated at 25°C for the test period (20 days). The concentrations of chlorinated paraffin tested were based on their estimated water solubility, along with concentrations of 1/100, 1/10, 10· and 100· the

estimated water solubility. Separate experiments were used to determine the extent of the adsorption of the ^{14}C-labelled chlorinated paraffin onto the glass vials and these data were used to determine the amount of chlorinated paraffin that was needed in order to achieve the desired test concentration in the test medium. Sets of 10 vials/eggs were used for each test concentration, and 1 control group of 10 vials/eggs was established for every 5 treatments.

The analytical methodology used was only sufficiently sensitive enough to determine the concentrations of the ^{14}C-labelled compound. Therefore, the actual concentration of the unlabelled 48% wt. Cl substance in the test media was estimated from the measurements with the ^{14}C-labelled substance, along with knowledge of the amounts added to the vials. Similarly, the concentration of the chlorinated paraffin present in the eggs and larvae could only be determined with the ^{14}C-labelled substance. The measured concentrations of the ^{14}C-labelled chlorinated paraffin in the test media were found to be close to the desired concentration in the low concentration vials, but were lower than expected in the high test concentration vials, possibly due to increased adsorption onto the glass vial. The measured concentrations for the ^{14}C-labelled chlorinated paraffins are shown in **Table 3.50**. The estimated concentrations for the C_{14}, 48% wt. Cl substance were 2.9, 25, 250, 880 and 3,400 µg/l.

No significant deaths or recognisable lesions occurred in the eggs, and no effects were seen in the larvae, at any of the concentrations of the two C_{14}-chlorinated paraffins tested. However, the hatching success in the exposed and control vials were low and variable, and in almost all cases unhatched eggs were still alive on the last observation day (day 20). Further observation on day 40 indicated that the majority of eggs had hatched by this time. The average hatching time in this study was >15 days, which was longer than normal for this species (11-13 days). It was thought that the variable hatching rate was unlikely to be related to the chlorinated paraffin exposure.

Larvae and eggs from the same treatment concentration were found to have similar concentrations of the ^{14}C-chlorinated paraffin, suggesting that the substance could diffuse through the egg shell. With the exception of the very highest exposure concentration, the concentration in larvae increased in proportion with the water concentration. The measured concentrations are shown in **Table 3.50**.

Similar experiments were carried out with short-chain length chlorinated paraffins (C_{10}-, C_{11}- and C_{12}-). In these experiments, toxic effects were seen in the eggs and larvae that were consistent with a narcotic mode of action. In addition, much higher uptake by the eggs and larvae was seen than in the experiments with the C_{14}- chlorinated paraffin. It was concluded that in these experiments, the C_{14}-chlorinated paraffins did not reach the narcotic tissue concentration (estimated to be 2-8 µmol/g) in the eggs or larvae.

Table 3.50 Exposure concentrations and uptake in Medaka eggs and larvae of ^{14}C-C_{14}, 55% wt. Cl chlorinated paraffin

Nominal water concentration (µg/l)	Measured water concentration (µg/l)	Measured concentration in eggs (mg/kg)	Measured concentration in larvae (mg/kg)	Larvae BCF
0.5	1.4	0.94	0.24	170
5.0	12	8.4	8.2	680
50	120	63	45	380
500	420	110	84	200
5,000	1,600	72	51	32

This study is similar in some ways to the OECD 210 fish early life-stage test, but falls short of the current guidelines in some areas as follows:

- this study was carried out for approximately 3 days post-hatch, but the OECD guideline recommends a test duration of 30 days post-hatch for *Oryzias latipes*;

- the test was carried out as a static test in sealed vials - no indication was given as to whether the dissolved oxygen level was maintained at a suitable level throughout the test period;

- the rate of hatching was slow in controls and so it is difficult to determine if any effects were seen on this endpoint; and

- the number of eggs/test concentration was only 10 compared with at least 60 recommended in the OECD guidelines.

The effects of the same two medium-chain chlorinated paraffins as above on behaviour and liver and thyroid histology in juvenile rainbow trout (*Oncorhynchus mykiss*) have been studied through dietary exposure (Cooley et al., 2001). The food used in the test was commercial fish food that was spiked with a known concentration of each chlorinated paraffin. The fish food consisted of 41% protein, 14% lipid and 3% fibre. In the test, juvenile rainbow trout (initial weight ~2 g) were exposed to one of three concentrations of each chlorinated paraffin for either 21 or 85 days. The food was spiked by suspending a known amount of each chlorinated paraffin in 100 ml of hexane and 50 g of fish food and slowly evaporating the solvent. The spiked food was then air-dried for 24 hours and stored at 10°C. The control food was prepared in the same way without the addition of chlorinated paraffin. The daily feeding rate was equivalent to 1.5% of the mean weight of the fish. If food had not been consumed within 5 minutes of its introduction, the aquarium was checked periodically over the next two hours to see if the food had been consumed; any unconsumed food was removed after this two-hour period.

Each treatment group consisted of 10 fish housed in either 10, 20 or 40 l glass aquaria supplied with dechlorinated tap water (using a flow-through system) at 11°C. Three control groups were also run. After 21 days exposure the trout from the two highest exposure groups for each chlorinated paraffin (and two control groups) were subject to histological examination (five fish per treatment) and analysis of the chlorinated paraffin concentration (five fish per treatment). Three fish were also sacrificed from each low exposure group and the remaining control group (but were not analysed) and the remaining fish in the low exposure groups were exposed for a further 64 days. On day 85 the remaining fish were subject to histological examination (three fish per treatment) and analysis of the chlorinated paraffin concentration (three fish per treatment). The concentrations used in the test and the effects seen are summarised in **Table 3.51**.

No effects were seen in the test on the mean weights of fish or on liver somatic indices when compared to controls, and no treatment-related mortalities were seen in the test. The fish exposed to the lowest concentrations of each medium-chain chlorinated paraffin were considered to show normal behaviour when compared to the control fish, however abnormal behaviour was seen in the fish exposed to the higher concentration of each medium-chain chlorinated paraffin. This abnormal behaviour included development of dark colouration, lack of response to tapping, spinal curvature, little activity and poor feeding.

Qualitative histological examination of the livers and thyroid after 21 days exposure was carried out only for the middle exposure groups for each chlorinated paraffin tested. These examinations indicated that a number of alterations had occurred on exposure to both chlorinated paraffins. Both treatments showed fish with livers displaying mild to moderate hepatocyte necrosis and moderate to severe depletion of glycogen/lipids. No lesions or abnormalities were seen in the

thyroids of fish exposed to the middle concentration of either of the medium-chain chlorinated paraffins tested. Qualitative histological examinations were not carried out for the high exposure groups owing to the erratic feeding seen.

Table 3.51 Effects of dietary exposure to medium-chain chlorinated paraffins on juvenile rainbow trout (Cooley et al., 2001)

Chlorinated paraffin	Exposure period (days)	Concentration in food (mg/kg)	Summary of effects seen
$C_{14}H_{24.9}Cl_{5.1}$ 48% wt. Cl	85	0.082	Normal behaviour.
	21	0.78	Normal behaviour. Livers displaying mild hepatocyte necrosis and moderate to severe depletion of glycogen/lipids. No effects on thyroid.
	21	2.9	Abnormal behaviour from day 3 onwards.
^{14}C-$C_{14}H_{23.3}Cl_{6.7}$ 55% wt. Cl	85	5.7	Normal behaviour.
	21	29	Abnormal behaviour from day 2 onwards. Livers displaying mild to moderate hepatocyte necrosis and moderate to severe depletion of glycogen/lipids. No effects on thyroid.
	21	78	Abnormal behaviour from day 3 onwards.

In addition to the qualitative histological examinations, quantitative histomorphological measurements were also carried out on livers and thyroid of the exposed fish in the middle exposure group after 21 days, and also the low exposure group after 85 days. The parameters investigated included hepatocyte nuclear diameter, hepatocyte volume index, nucleus:cytoplasm area ratio and thyroid epithelium cell height. After 21 days' exposure to the middle concentration, no significant differences (p=0.05) were seen in the hepatocyte nuclear diameters in fish exposed to either medium-chain chlorinated paraffin when compared with the control fish. The mean hepatocyte volume index was found to be significantly (p=0.05) reduced when compared with controls in fish exposed to the middle concentration of the C_{14} 48% wt. Cl only. No significant differences in any of the other endpoints studied (index nucleus:cytoplasm area ratio and thyroid epithelium cell heights) were seen for the middle concentrations of the other short-chain chlorinated paraffins tested).

For the low dose treatments at 85 days, no significant differences were seen in any of the above parameters for the exposed fish compared with control fish at the p=0.05 level.

It is possible that the effects seen in this study could be explained solely by the reduced feeding rate of the fish in the study. The control food was prepared in an identical manner to the spiked food (minus the addition of medium-chain chlorinated paraffin) and the control group was used as the comparison for all the effects seen. It is therefore clear that feeding was reduced in a manner related to the medium-chain chlorinated paraffin treatment rather than as an artefact of the food preparation method. The effects seen were therefore most probably related to the medium-chain chlorinated paraffin treatments. It is not possible to distinguish whether the effect was direct (i.e. toxic effects from ingestion of the medium-chain chlorinated paraffin including effects on feeding rate) or indirect (i.e. toxic effects resulting from reduced ingestion of food containing the medium-chain chlorinated paraffin for whatever reason (e.g. avoidance/unpalitability of treated food)).

3.2.1.2   Toxicity to aquatic invertebrates

The toxicity of medium-chain chlorinated paraffins to invertebrates is summarised in **Table 3.52**.

3.2.1.2.1   Daphnia magna

The acute toxicity of a medium-chain chlorinated paraffin to *Daphnia magna* has been studied using OECD method 202, art 1 (GLP study) (Thompson et al., 1996). The substance tested was a commercially produced C_{14-17}, 52% wt. Cl product (containing 0.3% epoxy soya bean oil stabiliser) that was mixed with radiolabelled n-pentadecane-8-^{14}C, 51% Cl. The daphnids used in the test were <24 hours old and the test was carried out using 250 ml beakers (5 daphnids/beaker with 4 replicates/concentration) covered with loose fitting glass lids. Stock solutions of the test substance were made up in acetone and each test solution was prepared by adding 0.2 ml of the appropriate stock solution to 2 litres of water.

Each test solution contained 0.1 ml/l of acetone as cosolvent. A solvent control (containing acetone at 0.1 ml/l) and control solution was also tested. The nominal chlorinated paraffin concentrations tested were0.0032, 0.0056, 0.01, 0.018, 0.032, 0.056 and 0.1 mg/l. The actual concentration of test substance was determined by radiochemical methods. The measured concentrations at the start of the test were found to be in the range 91-116% of the nominal value, but these had fallen to between 41-79% of the nominal value by the end of the test. The mean measured values over the test period were 73-95% of the nominal.

Table 3.52 Toxicity to aquatic invertebrates and algae

Species	Substance tested	Comments	Result	Reference
Water flea (*Daphnia magna*)	C_{14-17}, 52% wt. Cl (containing 0.3% epoxy soya bean oil stabiliser), mixed with n-pentadecane-8-^{14}C 51% wt. Cl	OECD 202 method Static test system	48h-EC_{50} = 7.7 µg/l (nominal) 48h-EC_{50} = 5.9 µg/l (measured)	Thompson et al. (1996)
	C_{14-17}, 52% wt. Cl	OECD 202 – dilutions of water soluble fractions tested Static test system	48h-EC_0 = 140 µg/l (measured) 48h-EC_{25} = 339-423 µg/l (measured)	Frank (1993); Frank and Steinhäuser (1994)
	C_{14-17}, 52% wt. Cl	OECD 202 method Static test system	48h-NOEC < 0.0065 mg/l (nominal) (see Table 3.52 for further details)	Thompson (2004)
	C_{14-17}, 52% wt. Cl	OECD 202 – water soluble fractions tested Static test system	48h-NOEC <0.10 mg/l (nominal) (see Table 3.52 for further details)	Thompson (2004)
	C_{14-17}, 52% wt. Cl (containing 0.3% epoxy soya bean oil stabiliser), mixed with n-pentadecane-8-^{14}C 51% wt. Cl	OECD 202 method. Semi-static test system – acetone as cosolvent	21-day NOEC = 10 µg/l (measured) 21-day LOEC = 18 µg/l (measured)	Thompson et al. (1997b)
	C_{14-17}, 52% wt. Cl	OECD 202 method Dilutions of water soluble fraction tested Semi-static test system	21d-NOEC = 12.6-15.6 µg/l (measured) 21d-LOEC = 25.3-31.3 µg/l (measured)	Frank (1993); Frank and Steinhäuser (1994).
	C_{14-17}, 52% wt. Cl	OECD 202 method. Dilutions of water soluble fraction tested Semi-static test system	21-day NOEC = 0.18 vol. % (dilution of water soluble fraction) ~ 4-8 µg/l (measured approx.)	TNO (1993).
Crustacean (*Gammarus pulex*)	C_{14-17}, 52% wt. Cl	Static test system	96h-LC_{50} > 1.0 mg/l	Thompson and Gore (1999)
Harpacticoid (*Nitocra spinipes*)	C_{14-17}, 45% wt. Cl	Static test system	96h-LC_{50} = 9 mg/l	Tarkpea et al. (1981); as quoted in WHO (1996)
	C_{14-17}, 52% wt. Cl	Static test system	96h-LC_{50} = >10,000 mg/l	

Table 3.52 continued overleaf

Table 3.52 continued Toxicity to aquatic invertebrates and algae

Species	Substance tested	Comments	Result	Reference
Mussel (*Mytilus edulis*)	C14-17, 52% wt. Cl, mixed with n-pentadecane-8-14C 51% wt. Cl	Flow-through system	60-day NOEC = 0.22 mg/l (measured concentration)	Madeley and Thompson (1983)
Alga (*Selenastrum capricornutum*)	C14-17, 52% wt. Cl (containing 0.3% epoxy soya bean oil stabiliser), mixed with n-pentadecane-8-14C 51% wt. Cl	OECD 201	96h-NOECbiomass = 0.1 mg/l 96h-EC50(biomass) = >3.2 mg/l 72h-NOECgrowth rate = 0.049 mg/l 72h-EC50(growth rate) = >3.2 mg/l (nominal concentrations)	Thompson et al. (1997a)

At 24 hours, no immobilisation of the *Daphnia* was seen at concentrations of 0.01 mg/l (nominal) and below, and the immobilisation at the higher concentrations did not exceed 40%. At 48 hours, no immobilisation was seen at 0.0032 mg/l (nominal) and complete immobilisation was seen at concentrations of 0.056 mg/l (nominal) and above. The 48-hour EC50 was determined as 0.0077 mg/l based on nominal concentrations or 0.0059 mg/l based on the mean measured concentrations. It was also noted that a number of animals exposed at each test concentration displayed a red colouration on parts of the exoskeleton. The significance of this effect is uncertain (Thompson et al., 1996).

The effects of a medium-chain chlorinated paraffin on reproduction of *Daphnia magna* have been studied over 21 days using the OECD 202 method (GLP study) (Thompson et al., 1997b). The study was carried out using a static-renewal procedure (renewal 3 times/week) using 10 replicates for each test concentration, with each replicate containing 1 organism. The test was carried out at 19.5-20.3^{o}C at a pH of 7.41-8.13 and the dissolved oxygen concentration was maintained at 6.2-9.2 mg/l. The substance tested was the same as in the acute toxicity study above. In the test, acetone (0.025 ml/l) was used as cosolvent. The nominal concentrations tested were 0.0056, 0.01, 0.018, 0.032, 0.056 and 0.1 mg/l. The concentrations were measured at the start and end of each renewal period and were 78-94% of nominal at the start and 7.3-61% of nominal at the end of each renewal period. The overall mean concentrations were 50-60% of the nominal concentration i.e. mean measured concentrations were 0.0037, 0.0050, 0.010, 0.018, 0.032 and 0.065 mg/l. For the parent mortality end-point the following LC50 values were obtained based on measured concentrations: 3-day LC50 = >0.065 mg/l; 4-day LC50 = 0.046 mg/l; 7-day LC50 = 0.028 mg/l; 14-day LC50 = 0.027 mg/l and 21-day LC50 = 0.025 mg/l.

For the reproduction endpoints, the number of live offspring in the control was significantly less (p=0.05) than seen in the acetone control and so the test substance treatments were compared with the acetone control only. A significant decrease in the number of live offspring was seen at measured concentrations at or above 0.018 mg/l. Also, at higher concentrations the release of first offspring was delayed (e.g. at 0.032 mg/l (measured) first offspring were produced on day 11 compared with day 8 at lower concentrations and in controls). The NOEC for reproduction was therefore 0.010 mg/l (measured) and the LOEC was 0.018 mg/l (measured).

The mean length of the parent animals was found to be significantly (p=0.05) reduced compared to solvent controls at measured concentrations of 0.018 mg/l and above. The NOEC for this endpoint was therefore 0.010 mg/l (measured) and the LOEC was 0.018 mg/l (measured) (Thompson et al., 1997b).

Another study has looked at the toxicity of a medium-chain chlorinated paraffin to *Daphnia magna* over short and long term exposures (Frank, 1993; Frank and Steinhäuser, 1994). The chlorinated paraffin used in these studies was a commercial C_{14-17} product with a 52% by weight chlorine content. In the test, stock solutions of the chlorinated paraffins were made up in water to give nominal concentrations of either 100 mg/l or 10 g/l. The 100 mg/l solution was sonicated for 1 hour and then left to stand in the dark for 48 hours before use. The 10 g/l solution also stood for 48 hours in the dark before use, but this time without sonication. After this period, both solutions were filtered firstly with glass filters and then with membrane filters to remove undissolved test substance (microscopic and spectroscopic investigations of the filtered solutions gave no indication of the presence of droplets) to give the respective water soluble fractions. The concentrations of medium-chain chlorinated paraffin in the water soluble fractions were then determined by AOX (adsorbable organic halogen) analysis (detection limit of 10 μg/l Cl was equivalent to around 20 μg/l of the chlorinated paraffin). This analysis showed that the concentration of chlorinated paraffin present in the water soluble fraction was around 404-500 μg/l for the 10 g/l nominal solution and 71-142 μg/l for the 100 mg/l stock solution. The

results for the 10 g/l nominal solution are considered more reliable as the concentrations found in the 100 mg/l nominal stock solution were close to the detection limit for the method. Experiments were carried out to show that in the test vessels, although the concentration present fell over time, it remained within 80% of the initial concentration over 2-3 days. This time period was used in the long-term test as the renewal period for the solutions (semi-static method).

Acute (48-hour) toxicity tests were carried out using dilutions of the two prepared water soluble fractions. The method used was DIN 38 412, Teil 11, which is equivalent to OECD 202. In the tests using the water soluble fraction from the 100 mg/l nominal solutions no toxicity was seen at concentrations up to the undiluted stock solution (i.e. no effects up to around 71-142 µg/l). In experiments using the water soluble fraction from the 10 g/l stock solution, an EC0 of 140 µg/l (also reported as 100-110 µg/l in the paper) and an EC_{25} of 423 µg/l (also reported as 420-470 µg/l in the paper) was determined (maximum mortality seen was 25%) (Frank, 1993). The latter results for the 10 g/l stock solution were reported by Frank and Steinhäuser (1994) as EC0 = 140 µg/l and EC25 = 339 µg/l, and it was noted that some of the *Daphnia* were floating on the surface of the test solution. In the later study (Frank and Steinhäuser, 1994), the results of further acute toxicity studies were reported using the same test method. In this case an EC50 of 37 µg/l and an EC0 of 9 µg/l were determined using the water soluble fraction from the 100 mg/l stock solution and no toxic effects were seen in tests with the water soluble fraction from the 10 g/l stock solution (approximately EC0 ≥525 µg/l). The authors noted that the effects seen in the acute tests showed poor reproducibility, probably because effects were seen only around the water solubility limit of the substance. However, the authors thought that the possibility of undissolved droplets affecting the results could be ruled out, as floating *Daphnia* were only sporadically observed in the test. Nevertheless, the results of these studies should be treated with caution, as the effects were mainly seen in the saturated solutions only.

Long-term (21-day) reproduction studies were also performed using dilutions of the water soluble fractions of the two stock solutions (dilutions used 1:2 to 1:32). In these experiments, the test medium was changed 3 times/week and 10 animals per concentration were used. The tests were carried out at $20^{o}C$ and a pH 7.79-8.44. Two end-points were determined in the study: effects on parent mortality and effects on reproduction (number of offspring/adult).

Parent mortality in the controls was 0%. Elevated parent mortality was seen in the exposed populations and all the organisms exposed to the highest dilutions (1:2 dilution of the 100 mg/l stock solution or 1:2 and 1:4 dilution of the 10 g/l stock solution) died during the test. Further details of the dose-response seen in this study have been provided by UBA (2001). In the experiments using the 100 mg/l stock solution the mortality seen in the exposed populations was 0% at 1:32 dilution, 0% at 1:16 dilution, 20% at 1:8 dilution, 90% at 1:4 dilution and 100% at 1:2 dilution. In the experiments using the 10 g/l stock solution the mortality seen in the exposed populations was 0% at 1:32 dilution, 30% at 1:16 dilution, 70% at 1:8 dilution and 100% at lower dilutions. Based on the known measured concentrations in the stock solutions and the dilution rates used the NOEC for mortality was determined as around 4.4-8.9 µg/l (i.e. 1:16 dilution) for the 100 mg/l nominal stock solution experiments and 12.6-15.6 µg/l (i.e.1:32 dilution) for the 10 g/l nominal stock solution experiments. The corresponding LOECs were 8.9-17.8 µg/l (100 mg/l nominal stock) and 25.3-31.3 µg/l (10 g/l nominal stock).

For the reproduction end point the average number of young/adult in controls was 82.1 (variability 25.2%) in the 100 mg/l nominal stock solution series of experiments and 74 (variability 17%) in the 10 g/l nominal stock solution experiments. A significant reduction in the number of young/adult was seen in some of the exposed organisms. Further details of the dose-response seen in this study have been provided by UBA (2001). In the experiments using the 100 mg/l stock solution the average number of young/adult was 82 in the 1:32 dilution, 89 in the 1:16

dilution, 80 in the 1:8 dilution, 15 in the 1:4 dilution and 0 in the 1:2 dilution (all parents died). Similarly in the experiments using the 10 g/l stock solution the average number of young/adult was 74 in the 1:32 dilution, 64 in the 1:16 dilution., 43 in the 1:8 dilution and 0 in the 1:4 and 1:2 dilutions (all parents died). The NOEC for this effect were determined as 8.9-17.8 µg/l (i.e. 1:8 dilution) for the 100 mg/l nominal stock experiments and 12.6-15.6 µg/l (i.e. 1:32 dilution) for the 10 g/l nominal stock solution experiments. The LOECs for this endpoint were 17.8-35.5 µg/l (100 mg/l nominal stock) and 25.3-31.3 µg/l (10 g/l nominal stock).

As mentioned above, the measured concentrations in the 10 g/l nominal stock solution are considered to be more reliable than those in the 100 mg/l nominal stock solution and so the overall NOEC for this study is taken to be 12.6-15.6 µg/l (Frank, 1993). The same results (with minor differences to some of the reported (no) effect concentrations) were reported by Frank and Steinhäuser (1994). In addition, a limit test using the water soluble fraction from a 1 mg/l nominal stock solution was also tested. This showed no effects on parent mortality or reproduction in the test (Frank and Steinhäuser, 1994).

A third 21-day *Daphnia magna* reproduction study (OECD 202) has been reported by TNO (1993). The test substance was a C_{14-17}, 52% wt. Cl product and a semi-static test procedure (replacement 3 times per week) was used, with 4 replicates, each containing 10 daphnids, per test concentration. The test solutions were prepared by stirring 20 g of the test substance in 2 litres of heated water (60^oC) with stirring and then filtration through a 0.8 µm and 0.2 µm filter to give a saturated solution (water soluble fraction). From this solution, dilutions of 0.18, 0.32, 0.56, 1.0, 1.8 and 3.2 volume (vol.) % were tested. The test solutions (0.18, 1.0 and 3.2 vol. % only) were analysed directly, both before and after renewal, for the presence of the chlorinated paraffin by a total extractable organic halogen (EOX) method. The EOX concentrations in the 1.0 vol. % and 3.2 vol. % test solutions were similar and corresponded to the concentration present in a saturated solution prepared by a column technique. This indicated that the solubility limit of the chlorinated paraffin in the test system was in the region of 36 µg/l. The test was carried out at 20 ± 1^oC and solutions were gently aerated from day 9 onwards. The pH of the test water varied between 7.7 and 8.3, the dissolved oxygen concentration was >7.0 mg/l and the hardness was 214 mg/l as $CaCO_3$. All test solutions were reported to be completely clear throughout the test.

No mortality was seen in the control populations. A significant (p=0.01) effect on *Daphnia* survival was seen at the 1.0, 1.8 and 3.2 vol. % solutions, with no significant effects seen in the 0.56, 0.32 and 0.18 vol. % tests concentrations. Thus, the NOEC and LOEC for this endpoint were estimated at 0.56 vol. % and 1.0 vol. % respectively. A 21-day LC50 for this endpoint of 1.48 vol. % was estimated. Observations of the effects on size and condition of the animals (swimming behaviour, colour etc.) indicated that no significant effects were occurring at the 0.18, 0.32 and 0.56 vol. % concentrations. The NOEC and LOEC for these endpoints were thus estimated at 0.56 vol. % and 1.0 vol. % respectively. For the reproduction endpoints, no reduction in reproduction in terms of cumulative number of young per living female were seen at the 0.18, 0.32 and 0.56 vol. % concentrations, but an increase over controls in the numbers of dead young and aborted eggs were seen in the 0.32 and 0.56 vol. % exposure groups. Thus, the NOEC and LOEC for reproduction were estimated as 0.18 vol. % and 0.32 vol. % respectively. The approximate 21-day LC50 for the reproductive endpoints was around 1.86 vol. % (TNO, 1993). The analytical results obtained using the EOX method are too erratic to allow precise determinations of the actual exposure concentrations in the test, however, the EOX concentrations found in the 0.18 vol. % (i.e. overall NOEC) solution were generally around 2-4 µg/l. This is equivalent to an approximate chlorinated paraffin concentration of around 4-8 µg/l, which agrees well with the NOEC results from the other tests.

Studies to investigate the possible effects of the use of a carrier solvent on the acute toxicity of medium-chain chlorinated paraffins to *Daphnia magna* have recently been carried out (Thompson, 2004). The substance tested was a C$_{14-17}$, 52% wt. chlorinated paraffin (samples from both EU and United States suppliers were tested) and tests were carried out using acetone and dimethylformamide (DMF) as carrier solvents and also with water-accommodated fractions. In the experiments with carrier solvents, stock solutions of the test substance (1,000 mg/l) were prepared in either DMF or acetone and aliquots of these were added to dilution water and stirred for twenty-five (DMF) or forty (acetone) minutes prior to the start of the test. The concentrations tested (nominal values) were 0.0065, 0.013, 0.025, 0.05 and 1.0 mg/l. The concentration of carrier solvent was 0.1 mg/l in all test solutions, and a solvent control was also run.

For the tests using water-accommodated fractions, solutions corresponding to initial loading rates of around 0.14, 0.36, 1.2, 3.2 and 10.5 mg/l for the EU test substance and 0.10, 0.35, 0.13, 3.2 and 10.2 mg/l for the United States test substance were prepared by adding the test substance directly to the surface of a glass slide and immersing this slide in a glass vessel containing either 1 or 5 litres of dilution water. The dilution water containing the slide was then stirred for twenty two hours. After stirring the vessels were allowed to settle for 40 minutes and then the appropriate amount of dilution water was decanted into the test vessels for the toxicity tests. No visible undissolved phase was noted in the test water (the initial 100 ml of decanted water was discarded in case there was a film of undissolved material on the surface).

In all cases the toxicity tests were carried in duplicate (five *Daphnia magna* per replicate; the *Daphnia* were <24 hours old at the start of the test) at 20°C for 48 hours. The pH of the test solutions were in the range 7.8 to 8.1. The animals were not fed during the test and the solutions were not aerated (the dissolved oxygen concentration was between 8.8 and 9.4 mg/l throughout the test). During the test, any animals floating on the surface were noted and were re-submerged using drops of test solution. The results of the test are summarised in **Table 3.53**. No effects were seen in the control and solvent control exposures. In the experiments with both acetone and DMF as carrier solvent, ≥90% immobilisation was seen at all medium-chain chlorinated paraffin levels tested and it was not possible to determine the NOECs or EC50s in the various test systems. However, as a similar response was seen in the experiments with both acetone and DMF, it is reasonable to conclude that toxicity of medium-chain chlorinated paraffins is similar in the two carrier solvent systems used. Similarly, there appeared to be no differences in the toxicity between the EU and the United States samples of medium-chain chlorinated paraffins used.

In the tests using the water-accommodated fractions, >50% effects were seen at nominal concentrations at and above 0.35-0.36 mg/l. The sample from the United States appeared to show a lower toxicity than that from the EU, but it was concluded that further work would be needed to confirm that this was a real difference. A number of floating *Daphnia* were noted in some of the treatments, indicating the possible presence (and the physical effect) of undissolved test substance in the treatments.

It should be noted that the actual water solubility of medium-chain chlorinated paraffins is around 0.027 mg/l and that the higher concentrations tested in the experiments with carrier solvents were in excess of this solubility value. Therefore it is possible that some undissolved test substance may have been present in some of the test solutions used. However, adverse effects were seen even at the lowest concentrations tested, and the results obtained in these tests are generally consistent with the 48-hour EC50 of 0.0059 mg/l determined by Thompson et al. (1996). Similarly, when considering the results of the tests with water-accommodated fractions, it is likely that the actual dissolved test concentration present would be much lower than indicated by the nominal loading rate. Taken altogether the results of this series of tests show

that medium-chain chlorinated paraffin are toxic to *Daphnia magna* at concentrations close to or below the water solubility using a variety of test systems.

Table 5.53 Comparison of acute toxicity to Daphnia magna using different test systems (Thompson, 2004)

Test system	Nominal concentration (mg/l)		% Immobilisation after 48 hours (% Flotation)	
			EU sample	United States sample
Acetone carrier solvent	Solvent control		0	0
	0.0065		100 (20)	90
	0.013		100	100
	0.025		100	100
	0.05		100	100
	0.1		100	100
DMF carrier solvent	Solvent control		0	0
	0.0065		100	100
	0.013		100	100
	0.025		100	100
	0.05		100	100
	0.1		100	100 (40)
Water-accommodated fraction	Control		0	0
	0.14[a]	0.10[b]	90 (20)	20 (60)
	0.36[a]	0.35[b]	90 (60)	60 (50)
	1.2[a]	1.2[b]	100	70 (70)
	3.2[a]	3.2[b]	100	100
	10.5[a]	10.2[b]	100 (20)	100

The results from the available studies with *Daphnia magna* are discussed further in Section 3.2.1.2.3.

3.2.1.2.2   Other species

The results of tests with the brackish water harpacticoid *Nitocra spinipes* have been reported (Tarkpea et al., 1981; as quoted in WHO, 1996). The results reported were a 96-hour LC50 of 9 mg/l for a C_{14-17}, 45% wt. Cl compound and a 96-hour LC50 of >10,000 mg/l for a C_{14-17}, 52% wt. Cl compound. No other details of the test were reported by WHO (1996), but the test method was probably the same as reported by Tarkpea et al. (1986), where a static method was employed using water of salinity 7‰ at a temperature of 20-22°C without aeration, probably using acetone as cosolvent.

The toxicity of a medium-chain chlorinated paraffin to common mussel (*Mytilus edulis*) has been determined over 60 days. A flow-through test system with filtered natural seawater (salinity 35‰, pH 8.1-8.3, dissolved oxygen 6.15-8.0 mg/l) at 15°C was employed. Acetone, at a concentration of 0.5 ml/l, was present in the test. The chlorinated paraffin used was a C_{14-17}, 52% wt. Cl commercial substance, mixed with a small amount of a radiolabelled chlorinated paraffin (n-pentadecane-8-^{14}C, 51% wt. Cl). Two chlorinated paraffin concentrations were tested and the mean measured concentrations were determined as 0.22 and 3.8 mg/l over the 60 day period (by ^{14}C measurements). The test solution at the higher concentration tested was reported to be cloudy in appearance, possibly indicating the presence of undissolved test substance. No significant mortality was seen at either of the two test concentrations. Non-quantitative visual observation indicated that the filtering activity was reduced in the 3.8 mg/l treatment but was

generally normal at 0.22 mg/l. The solubility limit for the substance in the test system was reported to be <3.8 mg/l and so the effects on filtering activity at the higher concentration could have been due to the presence of undissolved test substance rather than a true toxic effect. No effects on mean shell length were seen in either of the two exposure concentrations when compared to the control populations (data on tissue weights were not reported) (Madeley and Thompson, 1983).

The acute toxicity of a C_{14-17}, 52% wt. Cl substance has been tested using the freshwater crustacean *Gammarus pulex*. The medium-chain chlorinated paraffin used was dissolved in acetone and then added to beakers containing *Gammarus* to give nominal concentrations of 0.1, 0.32 and 1.0 mg/l. A control and solvent control (containing 0.1 ml/l acetone) were also run. The test was carried out for 96 hours at 15°C, with the solutions being renewed after 48 hours. The water used in the study had a hardness of 220 mg/l as $CaCO_3$ and had a pH of 8.0-9.2. No mortalities of the *Gammarus* were seen in any of the test substance solutions or control. One animal died in the solvent control. Therefore, no significant toxic effects were seen with the medium-chain chlorinated paraffin over the concentration range tested. This contrasted markedly to the situation when *Daphnia magna* were exposed using the same test system at 20°C over 48 hours, where complete immobilisation was seen at the lowest test concentration (0.1 mg/l) (Thompson and Gore, 1999).

3.2.1.2.3   Discussion of invertebrate results

From the available invertebrate toxicity data, it appears that medium-chain chlorinated paraffins are toxic to *Daphnia*. No toxicity has been seen in the available experiments with fish (see Section 3.2.1.1), other invertebrates or algae (see Section 3.2.1.3). Thus the toxicity profile for the C_{14-17} chlorinated paraffins appears to be different from that of the short-chain (C_{10-13}) chlorinated paraffins, where long-term toxicity was seen in algae, fish and mussels (see the assessment of that substance for further details).

The experiments carried out by Frank (1993), Frank and Steinhäuser (1994), TNO (1993) and the water-accommodated fraction experiments of Thompson (2004) essentially created a saturated solution of the medium-chain chlorinated paraffin and tested dilutions of this on *Daphnia*. Thus if the original medium-chain chlorinated paraffin tested had a small amount of the C_{10-13} chlorinated paraffin present as an impurity, this would also have been present in the test solution at a saturated concentration (a large excess of chlorinated paraffin was used to make up the test solution) which may account for the toxicity seen in the experiment, and also the much lower toxicity seen when a small excess of the chlorinated paraffin was used to make up the water soluble fraction (e.g. the 1 mg/l nominal stock solution in the Frank (1993) and Frank and Steinhäuser (1994) study). [Industry has indicated verbally that the test material used in early studies in Germany may have contained up to 10% C_{10-13} chlorinated paraffin – current production contains <1% (personal communication).] However, the method used to make up the test solutions in the Thompson et al. (1997b) study (and also the carrier solvent experiments of Thompson (2004)) would mean that the substance in solution represented the composition of the original test substance. Thus, in these experiments, if a small percentage of the C_{10-13} chlorinated paraffin was present in the test substance, it would still only contribute a similarly small percentage of the total chlorinated paraffin present in the test solution and would be unlikely to account for all the toxicity seen in the test (for instance the long-term NOEC for a C_{10-13} chlorinated paraffin is around 5 μg/l and so would have to be present at around 50% of the commercial medium-chain chlorinated paraffin tested in this study in order to account for the toxicity seen here). From the available acute and long-term studies on *Daphnia*, it has to be

concluded that the effects seen are likely to be due to the C_{14-17} chlorinated paraffin tested, but any C_{10-13} chlorinated paraffin present would contribute to this toxicity.

Another possible explanation for the toxicity seen purely with *Daphnia* is that a significant part of their exposure comes from adsorption on the food used in the study. This was postulated by Frank (1993) as an explanation for the toxicity seen in that series of tests. The *Daphnia* in these tests were fed with live algae (*Scenedesmus subspicatus*) at a rate of 0.1-0.2 mg C/*Daphnia*/day. However, the later paper by Frank and Steinhäuser (1994) found that the adsorption of the chlorinated paraffin to the food (algae) in the test was small and probably would not be able to account for the toxicity seen.

It should also be noted that feeding was also carried out in the other long-term tests available. In the Thompson et al. (1997b) series of experiments with *Daphnia*, a daily diet of algae (*Chlorella vulgaris*) and a commercially available microencapsulated diet were used, and the TNO (1993) *Daphnia* studies used a daily diet of algae (*Chlorella*) and yeast. In the long-term fish study, daily feeding of 2% body weight of a commercial trout food was used (Madeley et al., 1983) and in the long-term study with mussels, the organisms were continuously fed with algae (*Platymonas suecica*) dosed by peristaltic pump (around $1 \cdot 10^9$ cells were added each day). Thus, although uptake via food could be an explanation for the particular toxicity to *Daphnia* of this substance in some of the tests, it is likely that such uptake would have also occurred in the fish and mussel tests. This again indicates that *Daphnia* appear to be particularly sensitive to medium-chain chlorinated paraffins. In addition, the acute toxicity of medium-chain chlorinated paraffins to *Daphnia* has been demonstrated in several studies where feeding is not carried out during the exposure.

A further explanation for the toxicity seen with *Daphnia* could be due to a physical effect due to the adsorption of the test substance onto *Daphnia*. This is more likely to be the case in the acute studies, where higher test concentrations are used. Although this remains a possibility for the effects seen in the acute and long-term studies, direct toxic effects of the chlorinated paraffins themselves cannot be ruled out in the studies.

There is a potential conflict between the acute toxicity data for *Daphnia* and the results obtained in the longer term tests as one study (Thompson et al., 1996) gave a 48-hour EC50 of 5.9 µg/l which is lower than the NOEC seen in the long-term test. The reason for this discrepancy is unknown, and several other studies indicate that the acute EC_{50} is higher than found in this study (e.g. effects were seen with saturated solutions only in the experiments of Frank (1993) and Frank and Steinhäuser (1994), and a 72h-LC50 of >65 µg/l was determined during the Thompson et al. (1997b) study). It is understood that work has been undertaken by the Chlorinated Paraffins Industry Association (CPIA, 2000) in the United States to investigate the reproducibility of the acute *Daphnia* toxicity tests using a variety of different administration methods. Only a few details of these tests were made available to the rapporteur. Preliminary results from the tests (the analytical verification of the test concentrations had not been completed) indicated that when the tests were carried out with acetone as cosolvent the EC50 was around 14 µg/l, but when dimethylformamide was used as cosolvent or no cosolvent was used, the EC50 was >100 µg/l. However, more recent work by Thompson (2004) has shown that the cosolvent/carrier solvent used has little impact on the acute toxicity to *Daphnia,* and the results obtained in this study were reasonably consistent with the results from Thompson et al. (1996).

The lack of feeding in the acute toxicity tests (resulting in the *Daphnia* being more susceptible to toxic effects) has been put forward as a possible explanation for the apparent discrepancy between the available acute toxicity data and the long-term toxicity data (where feeding is

carried out). For example, Thompson et al. (1997b) carried out a preliminary investigation into this during the range finding test for the definitive 21-day *Daphnia* reproduction test. In this investigation *Daphnia* (<48 hours) were exposed to nominal medium-chain chlorinated paraffin concentrations of 0.018 and 0.032 mg/l for up to nine days. During the test, five out of the ten *Daphnia* in each treatment group were fed using the same regime as used in the chronic test (see Section 3.2.1.2.1) and five were not fed. After three days exposure, all of the unfed animals at both exposure concentrations had died, whereas all the fed animals in the 0.018 mg/l in the treatment group and four out of the five fed animals in the 0.032 mg/l treatment group survived until the end of the nine-day exposure period and produced offspring. It was concluded that the presence of food decreased the sensitivity of the *Daphnia*, either directly by improving the nutritional status of the animals, or indirectly by increasing the rate at which the test substance concentration declined (as a result of adsorption), between solution renewals.

For the current risk assessment, the long-term NOEC of 10 µg/l determined for *Daphnia* in the Thompson et al. (1997b) study will be considered to be reliable and will be used in the PNEC determination. The NOECs obtained from the two other *Daphnia* studies using the water soluble fraction give very similar results to this value. This value was obtained in a test where the *Daphnia* were fed (and is based on measured exposure concentrations) and so is considered most relevant for use in the risk assessment. Medium-chain chlorinated paraffins have been shown to be toxic to *Daphnia* at concentrations around, or below, this value in acute tests where no feeding was carried out, and it is possible that the lack of feeding may increase the susceptibility of *Daphnia* to medium-chain chlorinated paraffins. However, as organisms in the environment will be feeding, it is considered most relevant to base the PNEC on a study were feeding occurred.

3.2.1.3   Toxicity to algae

The toxicity of medium-chain chlorinated paraffins to algae is summarised in **Table 3.52**.

The toxicity of a C_{14-17}, 52% wt. Cl paraffin to the green alga *Selenastrum capricornutum* has been determined using OECD method 201 (GLP study) (Thompson et al., 1997a). The test substance was a commercial product containing 0.3% epoxy soya bean oil stabiliser and was mixed with a small amount of radiolabelled n-pentadecane-8-^{14}C (51% chlorinated). Stock solutions of the test substance were prepared in acetone and each test solution was prepared by addition of 0.1 ml of the appropriate stock solution to 1 litre of culture medium. The nominal chlorinated paraffin concentrations tested were 0.10, 0.18, 0.32, 0.56, 1.0, 1.8 and 3.2 mg/l. Control and solvent control (containing 0.1 ml/l acetone) exposures were also carried out. Visual inspection of the test solutions indicated that the 0.10, 0.18, 0.32 and 0.56 mg/l test solutions were clear and colourless, whereas the 1.0, 1.8 and 3.2 mg/l test solutions contained a transparent, faint, white homogeneous suspension. The initial cell density used in each test was 1×10^4 cells/ml and 6 replicates for solvent control and 3 replicates for control and each test concentration were used. Radiochemical analysis was used to verify the exposure concentrations (detection limit for the method = 0.025 mg/l). The concentrations measured at the start of the test ranged from 75-120% of the nominal. The concentrations in solutions without the presence of algae were found to reduce to <4-8% of the nominal value after 96 hours. The overall mean measured concentrations in these solutions were found to be between 38 and 49% of the nominal over the 96 hour period. No measurements were carried out in the test vessels containing algae at 96 hours.

It was not possible to estimate the EC50 (biomass) after 4 days exposure as the maximum inhibition seen was 18% compared with controls. A significant (p=0.05) inhibition in growth was

seen at a nominal concentration of 0.18 mg/l, but no effects were seen at 0.10 mg/l. Similar results were seen after 3 days exposure, with a small but statistically significant inhibition of growth at concentrations of 0.1-0.18 mg/l (nominal), but there was no significant effect at the two highest concentrations tested (1.8 and 3.2 mg/l). It was suggested that the low level of effects seen over a wide range of exposure concentrations and the lack of concentration-related response indicate that the effects seen may have been due to undissolved test substance present as a dispersion. Based on the biomass data, the NOEC = 0.1 mg/l (nominal), LOEC = 0.18 mg/l (nominal) and the EC50 is >3.2 mg/l (nominal). A mean measured concentration of 1.2 mg/l was found in the 3.2 mg/l (nominal) test solution.

Effects on the algal growth rate were determined over 72 hours. No effects were seen at the two highest test concentrations (1.8 and 3.2 mg/l nominal), but small but statistically significant reductions in growth rate (up to 3% reduction) were seen at lower concentrations. The LOEC for this endpoint was 0.18 mg/l nominal and the NOEC was 0.1 mg/l nominal. Analysis of the growth data over 96 hours showed a statistically significant difference between the solvent control and all test substance concentrations. However, because of a marked decline in the growth rate of all control and test substance treatments between days 3 and 4, these statistics were not considered reliable. This is supported by the fact that the growth rate determined after 96 hours in the test substance treatments was not significantly different from the control.

At the start of the test, the pH was 7.4-7.5, but had reached 10.0-10.3 by the end of the test. The shift in pH was thought to be a function of the high growth rates observed in the test (e.g. the mean solvent control cell density increased by a factor of 566 over the 4 day period). Overall, very little effect on algal growth was observed in the test. The maximum inhibition in the growth rate seen was 3%, and the maximum inhibition of biomass was 18%. No clear dose-response curve was determined. The NOEC from the test is around 0.1 mg/l (nominal), but it should be noted that no statistically significant effects were seen at some higher concentrations. The low levels of inhibition seen mean that it is not possible to derive an EC50 from the test. Although there is some uncertainty in this test over the actual exposure concentrations, particularly with regard to the dissolved fraction (stable emulsions appear to have been present at the high exposure concentrations), and hence the true NOEC value, it is clear that little or no toxic effect was seen on the algal growth in the test.

3.2.1.4 Microorganisms

The toxicity of medium-chain chlorinated paraffins to anaerobic bacteria from a domestic waste water treatment plant has been studied using the ETAD fermentation tube method (Hoechst AG, 1976 and 1977). The full details of the test are not available and so it is not possible to fully validate the results. The reported results are shown in **Table 3.54**.

The toxicity of a C_{14-17}, 52% wt. Cl chlorinated paraffin has been tested in a 3-hour respiration inhibition test (unpublished study). The chlorinated paraffin was emulsified in water using 0.5 g/l nonylphenol ethoxylate surfactant and then incubated for 3 hours with activated sludge from a municipal sewage treatment plant. No effect on respiration was seen up to the highest concentration tested (2,000 mg/l) (Hoechst AG; as reported in BUA, 1992).

Table 3.54 Results of microorganism toxicity tests

Substance	Comments	Result	Reference
C_{14-17}, 41% Cl*	Anaerobic bacteria: ETAD fermentation tube method	Harmful threshold (24 hour) = 2,500 mg/l	Hoechst AG (1977)
C_{14-17}, 41% Cl	Anaerobic bacteria: ETAD fermentation tube method	Harmful threshold (24 hour) = 800 mg/l	Hoechst AG (1976)
C_{14-17}, 52% Cl	Mixed bacterial culture: respiration inhibition test	3-hour EC0 >2,000 mg/l	Hoechst AG

*   Preparation containing the chlorinated paraffin and possibly PEG also.

3.2.1.5   Sediment organisms

Industry has recently carried out two prolonged toxicity studies on sediment organisms. The results are discussed in the following Sections.

3.2.1.5.1   *Chironomus riparius*

A prolonged toxicity study with spiked sediment has been carried out with the midge *Chironomus riparius* (Thompson et al., 2001c). The test protocol was based on the OECD 218 draft guideline (February 2000 version). The substance used in the test was a commercial C_{14-17}, 52% wt. Cl substance containing no stabilisers (the substance was reported to have a C_{14-17} content of 99.06% with 0.67% of C_{10-13} chain length substances) that was mixed with a small amount of a radiolabelled n-pentadecane-8-^{14}C, 51% wt. Cl substance (radiochemical purity >96.6%).

The sediment used in the test was an artificial sediment consisting of 10% sphagnum moss peat, 70% quartz sand, 20% kaolinite clay and <0.1% calcium carbonate. The sediment had a mean organic carbon content of 4.9% and a pH of 6.0. The sediment was spiked with the test substance by firstly mixing a solution of the test substance in acetone with the dry sand component of the sediment and allowing the acetone to evaporate overnight under an air stream. Finally the treated sand was mixed into the other components of the sediment for 16 hours. A solvent control and control sediment were prepared in a similar way.

In the test, groups of midge larvae (<48 hours post hatch) were exposed to a series of 6 concentrations of the chlorinated paraffin, plus a control and solvent control sediment, for 28 days at 20°C using a static system. The test vessels were 600 ml beakers containing 60 g of sediment (providing a sediment depth of approximately 12-15 mm) and dilution water to give a total volume of 300 ml. Gentle aeration was provided to the water phase during the test. The dissolved oxygen concentration in the overlying water was in the range 7.3 to 8.6 mg/l throughout the test. The sediment-water system was allowed to equilibrate for 8 days prior to the start of the experiment. At the start of the test 15 larvae were added to each test vessel, with 3 replicate vessels being used for each treatment. Feeding (fish food) was carried out daily at a rate of 0.25 mg per animal per day for the first seven days and then 0.5 mg per animal per day. The test substance was not added to the food. The number of emerged adults was counted daily.

The concentration of the test substance in the sediment phase was determined at the start of the equilibrium period (day -8), the day before the test began (day -1) and at the end of the test (day 28). Analysis was by a radiochemical method. The measured concentrations were 93-95% of the nominal values at day -8, 86-93% of nominal at day -1 and 71-86% of nominal at day 28.

The mean measured values between day -1 and day 28 are shown in **Table 3.55** and are taken to represent the actual exposure during the test.

Table 3.55 Toxicity of a C$_{14-17}$, 52% wt. Cl substance to *Chironomus riparius*

Exposure concentrations (mg/kg dry wt.)		Emergence			Sex ratio of emerged adults (proportion of males)
Nominal	Mean measured	Time to first emergence	Mean emergence time	Mean number emerged/replicate after 28 days	
Control	0	16.7 days	19.2 days	14.7	55%
Solvent control	0	16.0 days	19.1 days	12.3	53%
44	36	15.7 days	18.3 days	12.0	43%
140	110	16.0 days	18.7 days	13.0	52%
440	370	16.0 days	19.2 days	13.3	50%
1,400	1,200	16.0 days	19.2 days	13.0	55%
4,400	3,800	16.0 days	18.9 days	13.7	42%
14,000	13,000	18.3 days	20.8 days	9.7*	40%

*   Significantly different (p=0.05) from pooled control and solvent control group (there were no significant differences when compared to the solvent control group alone).

The biological data from the study are summarised in **Table 3.55**. The time to first emergence was 16.7 days and 16.0 days in the controls and solvent controls respectively, which is normal for this type of test. No statistically significant differences (p=0.05) were found between the time to first emergence in the treatment groups when compared to either the control or solvent control group. Therefore the NOEC for time to first emergence is $\geq$13,000 mg/kg dry wt.

The mean emergence time in the control and solvent control groups was 19.2 and 19.1 days respectively. There were no statistically significant differences in mean emergence time at any treatment level when compared with the control or solvent control populations. Therefore the NOEC for mean emergence time (development rate) is $\geq$13,000 mg/kg dry wt.

The adult emergence in the control and solvent controls after 28 days was 98% and 82% respectively. The mean number of adults emerged in the treatments were not statistically significantly (p=0.05) different from the solvent control group at any concentration, but when compared with the control group, a statistically significant reduction in the mean number of adults emerged was seen at the highest concentration tested (13,000 mg/kg dry wt.). Since no statistically significant differences were found in the mean number of adults emerged in the control and solvent control groups, the emergence in the treatments was also compared with the pooled control groups. This again showed a statistically significant difference in the mean number of adults emerged in the 13,000 dry wt. treatment group. Thus the NOEC for number of adults emerged is 3,800 mg/kg dry wt. and the LOEC is 13,000 mg kg dry wt. (this NOEC and LOEC should be considered as borderline as no effects were seen at the highest concentration tested when compared to the solvent control group alone).

The sex ratio, expressed as the percentage males of the emerged adults, was determined to be 55% in the control population and 53% in the solvent control population. No statistically significant differences (p=0.05) in the sex ratios of the treatment groups were found when compared with the control or solvent control groups. Therefore the NOEC for sex ratio is $\geq$13,000 mg/kg dry wt.

The overall NOEC from this study is 3,800 mg/kg dry wt. using the default water content for sediment given in the TGD; this is equivalent to a NOEC of 1,460 mg/kg on a wet wt. basis.

3.2.1.5.2   *Lumbriculus variegatus*

A prolonged toxicity test using spiked sediment has been carried out with the oligochaete *Lumbriculus variegatus* using a static system at 20°C (Thompson et al., 2001d). The substance tested was the same C_{14-17}, 52% wt. Cl substance mixed with a radiolabelled n-pentadecane as used in the midge study discussed in Section 3.2.1.5.1. The test method was based on that described by Phipps et al. (1993).

An artificial sediment was used in the test, comprising 10% sphagnum moss peat, 70% quartz sand, 20% kaolinite clay and <0.1% calcium carbonate. The pH of the sediment was 6.0 and the organic carbon content was 4.9%. The test sediments were made up by adding the test substance to the sand phase as a solution in acetone, evaporating the acetone overnight and mixing the spiked sand with the rest of the sediment for 16 hours. A solvent control and control sediment were also prepared.

The organisms used in the test were adults approximately 20 to 40 mm in length. The tests were carried out in 600 ml beakers containing 40 g dry sediment (giving a sediment depth of 12 to 13 mm) and dilution water was added to provide a total volume of 300 ml. Six replicate vessels, each containing 10 organisms, were used for each treatment level. The water was aerated gently throughout the test and the dissolved oxygen concentration was maintained at 7.7-8.7 mg/l. The spiked sediment-water system was equilibrated for seven days prior to addition of the organisms at the start of the test. Around 90 mg of fish food was also present in the sediment during this equilibration period to allow the food to reach equilibrium with the medium-chain chlorinated paraffin in the sediment. This was the only food supplied for the first seven days of the test, after which the organisms were fed uncontaminated fish food for 18 days at a rate of 5 mg/kg/day (incorporation of the entire food supply was not feasible (based on earlier trials) because it would have resulted in an excessive oxygen demand (and possibly excessive ammonia loading) in the sediment). Overall, the contaminated food present at the start of the test amounted to 50% of the total food supplied to the organisms during the test. The total exposure period was 28 days. Observations for abnormal behaviour and appearance of the worms were made two times per week during the experiment.

The sediment concentrations of the test substance were measured by a radiochemical method at the start of the equilibration period (day -7), at the start of the test (day 0) and at the end of the test (day 28). The measured values were 93-95% of the nominal concentration at day -7 and day 0, and were 84-89% of the nominal value at day 28, indicating that the exposure concentrations had been well maintained throughout the test. The mean measured concentrations over the exposure period (day 0 to day 28) are shown in **Table 3.56**.

Table 3.56 Toxicity of a C_{14-17}, 52% wt. Cl substance to *Lumbriculus variegatus*

Exposure concentrations (mg/kg dry wt.)		Mean number of worms/replicate at day 28	Mean total dry wt. of worms/replicate at day 28 (mg)	Mean dry weight/worm at day 28 (mg)
Nominal	Mean measured			
Control	0	28.2±3.2	39.1±7.7	1.40±0.33
Solvent control	0	27.3±2.7	34.5±4.1	1.27±0.18
44	39	24.8±4.4	28.1±3.7	1.16±0.22
140	130	25.7±1.8	30.8±6.4	1.22±0.31
440	410	19.0±2.4**	19.5±3.8**	1.02±0.09
1,400	1,300	13.7±1.6**	15.4±1.8**	1.13±0.09
4,400	4,000	14.7±4.1**	17.1±8.0**	1.18±0.56
14,000	13,000	14.5±2.1**	14.2±2.9**	0.99±0.18

**   Significantly different from solvent control group (p=0.01).

The biological data determined in the study are summarised in **Table 3.55**. Two main endpoints were determined: mortality/reproduction as determined by the total number of worms present at the end of the study (it is not possible to distinguish adult and young organisms in this test and so the total number of worms at the end of the study is a combination of the mortality rate and the reproductive success of adults during the test); and growth as determined by weight of worms.

At the end of the study the number of worms in the control and solvent control groups had increased by a factor of 2.7 and 2.8 respectively, which was considered to be satisfactory. A statistically significant (p=0.01) reduction in the mean final number of worms/replicate was seen at exposure concentrations of 410 mg/kg dry weight and above when compared to the solvent control or the control groups. Therefore the NOEC for mortality/reproduction is 130 mg/kg dry wt.

The mean total weight of worms/replicate was 39.1 mg dry wt. in the control group and 34.5 mg dry wt. in the solvent control group. A statistically significant (p=0.01) reduction in the mean total weight of worms/replicate was seen at exposure concentrations of 410 mg/kg dry wt. and above. Therefore the NOEC for total weight of worms is 130 mg /kg dry wt. When the data for dry wt. per worm are considered, no statistically significant differences were seen between the control or solvent control groups and the treatment groups. This indicates that the effects on total weight of worms are mainly due the number of worms present, rather than the size of the worms.

Overall, the NOEC from this study is 130 mg/kg wet wt. Using the default water content for sediment given in the TGD, this is equivalent to a NOEC of 50 mg/kg on a wet wt. basis.

3.2.1.5.3   *Hyalella azteca*

A prolonged sediment toxicity test using spiked sediment has recently been carried out with the amphipod *Hyalella azteca* using a semi-static system (Thompson et al., 2002). The substance used in the test was a mixture of a commercial medium-chain chlorinated paraffin product (C_{14-17}, 52.5% wt. Cl) mixed with a small amount of a radiolabelled chlorinated n-pentadecane-8-[14]C (51% wt. Cl). The ratio of unlabelled product:radiolabelled product used was ≥14:1.

The dilution/overlying water used in the experiment was UV-sterilised and filtered dechlorinated tap water. The sediment used in the test was an artificial sediment consisting of 10% Sphagnum

moss peat, 70% quartz sand, 20% Kaolinite clay and <0.5% calcium carbonate. The sediment had an organic carbon content of 5% and a pH of around 6.0. The test substance was added to the sediment as a solution in acetone. The acetone solution (10 ml for each treatment) was applied to the surface of approximately 70 g of quartz sand and the acetone was then allowed to evaporate overnight and the dry spiked sand was then mixed with the remaining sediment components and wetted with an equal volume of dilution water. The spiked sediment was then mixed for 24 hours and then 75 g dry weight of sediment was added into each test vessel and dilution water was added to give a total volume of 300 ml. The test vessels used consisted of 600 ml beakers and had a total depth of sediment of 18 mm. The system was allowed to equilibrate for 7 days at 23°C prior to the addition of the test organisms. In all, five nominal concentrations (38, 75, 150, 300 and 600 mg/kg dry weight), a control and solvent control were run. Six replicates were carried out for each treatment group. Ten juvenile *Hyalella azteca* (~7-day-old) were used in each replicate.

Food (tropical fish flake and macerated, pre-conditioned Maple leaves, both applied as slurries) were added to the test system at two or three daily intervals. The food was not contaminated with the test substance, but the first two additions of food to the test system were made three and one days prior to the addition of the test organisms, and so would have had time to equilibrate to some extent with the test substance present in the sediment-water system.

The overlying water in the test system was gently aerated throughout the study and was partially replaced with fresh, uncontaminated, water at approximately weekly intervals during the test. Around 150 ml of water was replaced on each occasion. The concentration of the test substance was measured in the sediment phase by radiochemical analysis at the start of the 7-day equilibration period prior to addition of the test organisms and at the start and end of the 28-day exposure period of the test organisms. The concentrations present at the start of the equilibration period were 80-99% of the nominal values, the concentrations at the start of the exposure period were 85-97% of the nominal values and the concentrations at the end of the 29-day exposure period were 78-90% of nominal. As the concentration in the sediment was found to decline only slightly during the test, this indicated that the semi-static method used (weekly water replacement) resulted in only minor loss of test substance from the system over the 28-day test period, and the results of the test were expressed as the arithmetic mean concentration during the exposure period. The overlying water characteristics throughout the test were dissolved oxygen 7.7-8.4 mg/l, pH 7.0-7.6, hardness 41-42 mg CaCO$_3$/l and temperature 22.4-23.2^{o}C.

The endpoints investigated in the study included survival, growth (dry weight) and sexual development of females (proportion of gravid females). The results are summarised in **Table 3.57**.

Table 3.57 Toxicity of a C$_{14-17}$, 52.5% wt. Cl substance to *Hyalella azteca*

Exposure concentrations (mg/kg dry wt.)		Survival of amphipods at day 28	Mean dry wt. of amphipods (mg/individual)		Mean proportion of gravid females/replicate (fraction of total female survivors/replicate)
Nominal	Mean measured		Males	Females	
Control	0	100%	0.699±0.078	0.651±0.083	0.861±0.164
Solvent control	0	87%	0.559±0.127	0.626±0.122	0.705±0.081
38	32	92%	0.555±0.208	0.542±0.084	0.632±0.168
75	61	97%	0.705±0.139	0.496±0.107	0.688±0.081
150	130	85%	0.500±0.252	0.520±0.225	0.500±0.316

Table 3.57 continued overleaf

Table 3.57 continued Toxicity of a C$_{14-17}$, 52.5% wt. Cl substance to *Hyalella azteca*

Exposure concentrations (mg/kg dry wt.)		Survival of amphipods at day 28	Mean dry wt. of amphipods (mg/individual)		Mean proportion of gravid females/replicate (fraction of total female survivors/replicate)
Nominal	Mean measured		Males	Females	
300	270	78%	0.601±0.203	0.444[b]±0.152	0.528±0.452
600	470	50%[a]	0.452±0.196	0.323[a, b]±0.184	0.407[a]±0.136

a)   Significantly different from solvent control group (p=0.05).
b)   Significantly different from pooled control and solvent control group (p=0.05).

No statistically significant differences (p=0.05) were observed between the control and solvent control groups for any endpoint investigated. For the survival endpoint, a statistically significant reduction in survival was seen at 470 mg/kg dry weight when compared with the solvent control or control group. The survival seen in the other treatment groups was not significantly different from the control group. Thus the NOEC for survival was determined to be 270 mg/kg dry weight.

The growth data were analysed separately for the male and female amphipods. For the males, no statistically significant difference (p=0.05) was seen in the mean dry weight of survivors in any treatment group when compared with either the control or solvent control group. However, for the female survivors, a statistically significant reduction in mean weight was seen at a concentration of 470 g/kg dry weight when compared with the control or solvent control population and a statistically significant reduction in mean weight compared to the control population (and also the pooled control and solvent control population) was also seen at 270 mg/kg dry weight. Thus the NOEC for growth was determined to be 130 mg/kg dry weight.

For the sexual development endpoint, there was a statistically significant (p=0.05) reduction in the proportion of gravid females in the 470 mg/kg dry weight treatment group when compared with the solvent control or the control population. The NOEC for this endpoint was determined to be 270 mg/kg dry weight. The report indicated that there is, however, little information in the literature on the factors that might affect the proportion of gravid females within this type of experiment; in particular the ratio of males to females may be expected to have an influence on this endpoint. Since in this study the initial proportion of males to females varied between replicates and treatments (the test organisms were randomly assigned to the various treatments), and was also affected by the mortalities seen in the study, the actual significance of these findings on sexual development are uncertain.

Overall, the lowest NOEC determined in this study was 130 mg/kg dry weight for growth of females over 28 days. Using the default water content for sediment given in the TGD, this is equivalent to a NOEC of 50 mg/kg on a wet wt. basis.

3.2.1.6   Predicted no effect concentration (PNEC) for the aquatic compartment

3.2.1.6.1   Surface water

There is a complete 'base set' of acute toxicity data for medium-chain chlorinated paraffins. There are reported long-term no observed effect concentrations (NOECs) for fish, *Daphnia*, mussels and algae. From the available database, effects have so far almost exclusively been observed on *Daphnia*. No effects on other organisms have been seen in short term tests; this

includes tests with other aquatic invertebrates. *Daphnia* are also the only species to show effects below the solubility in long term tests; these effects include mortality as well as effects on reproduction. Although it is possible that, at least in some of the acute toxicity tests, the effects seen with *Daphnia* were due to physical adsorption of the substance onto the test organism, direct toxic effects of the medium-chain chlorinated paraffins themselves cannot be ruled out with the current database. Effects were seen on algal biomass and growth at concentrations above solubility, and a NOEC determined which is an order of magnitude greater than that for *Daphnia*. Two 60-day tests are available, with fish and mussels, at test concentrations significantly higher than the solubility. Measurements show that in both these tests the substance was accumulated in the organism. Fish showed no effects on mortality, growth or behaviour at 1 and 4.5 mg/l. Mussels showed some effect on filtration rate at the higher exposure concentration, so the NOEC is taken as 0.22 mg/l. These long-term studies with fish and mussels, although showing little or no effect over extended time periods, do not necessarily cover possible effects on several life stages (i.e. only adults were exposed and reproductive endpoints were not covered). A 20-day embryo-larval fish test is available which covers some reproductive endpoints. However, although no effects were seen with medium chain chlorinated paraffins, the method was deficient in some aspects when compared to the current test guidelines for such a study.

Using the available data for medium-chain chlorinated paraffins a PNEC of 0.2 µg/l could be derived based on the NOEC of 10 µg/l from the long-term *Daphnia* study, using an assessment factor of 50 (as two NOECs are available, including the most sensitive species from the short-term studies). In this case it could be possible to refine the PNEC further if a fully valid long-term fish test is carried out covering all the relevant endpoints. However, there is a considerable body of information available for other chlorinated paraffins (e.g. short-chain) that indicates that invertebrates, and *Daphnia* in particular, are more sensitive to long-term exposure to chlorinated paraffins than fish. This information is summarised below.

For short-chain chlorinated paraffins standard long-term toxicity tests have been carried out for both fish and *Daphnia* (ECB, 2000). Here the 21-day NOEC for *Daphnia* was 5 µg/l, and this compared with a NOEC of 280 µg/l in a standard 32-day fish early lifestage study using sheepshead minnow (*Cyrpinodon variegatus*). The most sensitive endpoint found in the fish early life stage study was growth of the fish. No effects on survival and hatchability were seen in the study (concentrations up to 621 µg/l were tested). In addition, two other long-term fish tests have been carried out for short-chain chlorinated paraffins that are directly comparable to those carried out for medium-chain chlorinated paraffins. These are a 60-day study with rainbow trout (*Oncorhynchus mykiss*) where an LC50 of 340 µg/l was determined for short-chain chlorinated paraffins for survival (no effects on mortality or growth were seen in the equivalent test for medium-chain chlorinated paraffins at up to 4,500 µg/l) and a 20-day embryo-larval study with *Oryzias latipes* where NOECs of 9.6-62 µg/l were determined for four short-chain chlorinated paraffins (no effects were seen at the highest concentrations tested (1,600 or 3,400 µg/l) for two medium-chain chlorinated paraffins in the equivalent test). Although, as indicated in Section 3.2.1.1, the reliability of the test with *Oryzias latipes* can be questioned, when all the available fish toxicity data are considered together it can be concluded that the NOEC from a standard fish early lifestage test for medium chain chlorinated paraffins is unlikely to be lower than the lowest long-term NOEC already available for *Daphnia magna*. The comparison of the results obtained for short- and medium-chain chlorinated paraffins in the various long-term tests is summarised in **Table 3.58**.

Table 3.58 Comparison of long-term toxicity values for short- and medium-chain chlorinated paraffins

Study type	NOEC value for short-chain chlorinated paraffins	NOEC value for medium-chain chlorinated paraffins
21-day *Daphnia* reproduction study	NOEC = 5 μg/l	NOEC = 10 μg/l
32-day fish early life stage study with *Cyprinodon variegatus*	280 μg/l	No data
60-day study with *Oncorhynchus mykiss*	LC_{50} = 340 μg/l	No effects at up to 4,500 μg/l
20-day embryo-larval study with *Oryzias latipes*	NOEC = 9.6-62 μg/l (four substances tested)	No effects at up to 1,600 or 3,400 μg/l (two substances tested)

Using the quantitative structure-activity relationship (QSAR) given in the Technical Guidance Document, a long-term NOEC for fish of around 1-1.3 μg/l and a long-term NOEC for *Daphnia magna* of 0.25-0.32 μg/l can be estimated (based on a molecular weight of 400-500 g/mole for a 52% wt. Cl chlorinated paraffin and a log Kow of 7). Thus, QSAR estimates predict that *Daphnia magna* are likely to be more sensitive than fish to medium-chain chlorinated paraffins. It should be noted that the NOEC predicted here is lower than that found experimentally and may reflect the fact that that the actual bioconcentration of medium-chain chlorinated paraffins is lower than would be predicted for a substance of log Kow of 7 (the measured fish BCF is 1,087 l/kg compared to the value of 45,710 l/kg estimated for a substance with a log Kow of 7 using the methodology outlined in the Technical Guidance Document (see Section 3.1.1.5.1)). Therefore the reliability of these estimates is uncertain.

It is therefore unlikely that the NOEC from a standard fish early lifestage study for medium-chain chlorinated paraffins would be lower than the NOEC obtained from the 21-day study with *Daphnia magna.* Therefore it is proposed that an assessment factor of 10 is applied to the NOEC from the study with *Daphnia magna* on the basis that this is the most sensitive species. Thus the $PNEC_{water}$ will be taken to be 1 μg/l in the risk assessment. This value is used in the risk characterisation.

3.2.1.6.2   Sewage treatment processes

There are toxicity data available for the effects of medium-chain chlorinated paraffins on bacteria. In these experiments, the lowest threshold concentration reported to cause effects (approximates to a NOEC/LOEC) was 800 mg/l. The Technical Guidance Document suggests that an assessment factor of 10 can be applied to the NOEC or EC_{10} from a test using mixed bacterial populations. Therefore, the PNEC for waste water treatment plants can be estimated at 80 mg/l.

3.2.1.6.3   Sediment

A PNEC for sediment can be estimated using the equilibrium partitioning method as follows:

$$PNEC_{sed} = \frac{K_{susp-water} \times PNEC_{water} \times 1000}{RHO_{susp}}$$

where $K_{susp-water}$ = suspended matter – water partition coefficient = 14,721 m³/m³
             RHO_{susp} = bulk density of suspended matter = 1,150 kg/m³

Using a PNEC$_{water}$ of 1 µg/l the PNEC$_{sed}$ = 12.8 mg/kg wet wt. However, the ingestion of sediment-bound substance by the exposed organisms may not be sufficiently explained by this relationship for substances with a log Kow >5. The Technical Guidance Document suggests that in such cases, the PEC/PNEC ratio derived by the equilibrium partitioning method should be increased by a factor of 10.

Sediment toxicity data are also available for medium-chain chlorinated paraffins. The lowest NOEC from three prolonged toxicity studies is 50 mg/kg wet wt., obtained both in a study with *Lumbriculus variegatus* and a study with *Hyalella azteca.* An assessment factor of 10 is appropriate for this data set. Thus the PNEC$_{sed}$ = 5 mg/kg wet wt.

As this PNEC is derived from actual sediment data using a sediment with a similar organic carbon content to the TGD default value (4.9%-5.0% compared with the TGD default of 5%), there is no need to normalise the value to the default organic carbon content and there is no need to increase the resulting PEC/PNEC ratios by a factor of 10 to take into account direct ingestion, i.e. the organisms in the test would have been exposed via both pore water and sediment-bound substance and so if direct ingestion was important it would be already taken account of in the toxicity results obtained. The studies from which the PNEC were derived were carried out in such a way that the organisms were provided with food during at least part of the test that did not contain chlorinated paraffin, and so could possibly have reduced the potential exposure via the ingestion route. However, the results obtained are consistent with this route of exposure being of only minor importance[11].

The PNEC obtained using the equilibrium partitioning approach agrees with the PNEC obtained from the sediment toxicity data directly to within a factor of 2.6. At least some of the difference between the two values could be explained by the fact that the NOECs underlying both PNEC determinations depend to some extent on the actual concentrations and concentration intervals used in the various tests. Taking this into account it can be concluded that there is good agreement between the PNECs obtained by the two methods (a similarly good agreement between the two methods is also found for the PNECs derived for the terrestrial compartment (see Section 3.2.2.4). This suggests that the toxicity seen for medium-chain chlorinated paraffins in sediment is consistent with exposure being mainly via the pore water.

The PNEC$_{sed}$ of 5 mg/kg wet wt. derived from the available experimental data will be considered in the risk characterisation.

3.2.2   Terrestrial compartment

Industry has recently carried out three prolonged toxicity studies on terrestrial organisms. The results are discussed in the following Sections.

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[11] Some EU member states, notably Germany, have argued that the available sediment tests carried out with medium-chain chlorinated paraffins have not fully taken into account the possibility of increased exposure from the ingestion of contaminated food over the entire test period. Although it is recognised that the tests have been carried out using the best available methods at the time, it is therefore possible that this could have lead to an underestimatation of the actual toxicity of medium-chain chlorinated paraffins. It is not currently possible to determine unambiguously whether or not this was the case.

3.2.2.1 Toxicity to microorganisms

The toxicity of a C_{14-17}, 52.5% wt. Cl substance to soil microorganisms has been studied in the OECD 216 Soil Microorganisms, Nitrogen Transformation Test (Thompson, 2002). The soil used in the test was a natural soil and had a pH of 6.5, a 1.4% organic carbon content and a maximum water holding capacity of 50.5%. Fourteen days before the test, the soil moisture content was adjusted to 22.7% (~45% of the maximum water holding capacity) and the soil was incubated in the dark at 20 ± 2^oC prior to the start of the test. The soil moisture content remained at this level throughout the test. At the start of the test, the soil samples were treated with the test material using quartz sand as carrier. The test substance was added to sand as an acetone solution and, once the acetone had evaporated, the sand was thoroughly mixed into the soil samples. At the same time lucerne meal (5 g/kg) was added into the soil. The concentrations tested were 25, 50,100, 200 and 400 mg/kg dry weight plus a control and each treatment was carried out in triplicate (each replicate used 300 g dry weight of soil). The addition of sand and lucerne meal to the soil were calculated to increase the soil organic carbon content to 1.6%. A known inhibitor of nitrogen transformation in soil (2-chloro-6-(trichloromethyl)-pyridine) was used as a reference substance in the test. The soil samples were incubated at 20 ± 2^oC in the dark for 28 days. Nitrate production was determined after 28 days incubation.

The nitrate increase over 28 days in the amended (lucerne meal) control was approximately twice that seen in the unamended (no lucerne meal) control and was considered satisfactory (the increase in the unamended control was thought to be due to nitrification of the organic nitrogen components of the natural soil organic matter). In the soils treated with the medium-chain chlorinated paraffin, the increase in nitrate concentration seen during the test was greater than or equal to that in the amended control at 25, 50, 100 and 200 mg/kg dry weight. The increase in nitrate at the highest concentration tested (400 mg/kg dry weight) was slightly lower than the amended control (87% of the control value) but this decrease was not statistically significant (P=0.05).

The positive control substance was found to cause no inhibition of nitrate production at 0.5 mg/kg dry weight, 35% inhibition at 3.2 mg/kg dry weight and 29% inhibition at 20 mg/kg dry weight.

The variation in the increase in nitrate concentration between replicate control samples was <15% at 28 days (the mean and standard deviation was 29.2±1.81 mg/kg dry weight) indicating a valid test. The NOEC from this test is therefore ≥400 mg/kg dry weight.

3.2.2.2 Plants

The toxicity of a C_{14-17}, 52% wt. Cl substance to wheat (*Triticum aestivum*; monocotyledon), oilseed rape (*Brassica napus*; dicotyledon) and mung bean (*Phaseolus aureus*; dicotyledonous legume) has been studied using OECD guideline 208 (the protocol is based on the July 2000 proposal for revision of the guideline) (Thompson et al., 2001a). The substance used in the test was a commercial product that contained no stabilisers. The C_{14-17} content of the product was 99.06%, with only trace amounts (0.67%) of C_{10-13} congeners present. The nominal concentrations tested were 50, 158, 500, 1,580 and 5,000 mg/kg dry wt. A small amount of ^{14}C-labelled n-pentadecane, 51% wt. Cl substance (radiochemical purity >96.6%) was mixed with the test substance at the lowest, middle and highest concentrations tested to allow radiochemical analysis of the concentrations present in the soil and plants to be determined during the study.

The soil used in the test was a commercial formulation consisting of 50% sterilised Surrey loam and 50% gravel (4 mm) with appropriate nutrient additions. The test soils were prepared by firstly adding a solution of the test substance in acetone to dry silver sand (sieved to 1 mm) and allowing the acetone to evaporate overnight under an air stream. Secondly, this spiked sand was mixed with the soil (10% sand:90% soil) to give the desired nominal test concentrations. Control and solvent control soils were prepared in a similar way. The soil had an organic carbon content of 2.3%.

For each treatment, 4 replicate pots were prepared, each containing 9 seeds at the start of the test. On day 7 a preliminary assessment of germination was undertaken and after a further 7 days a definitive assessment of germination was carried out and the seedlings were randomly thinned to 5 seedlings/replicate where possible. On day 28 of the study, plants were cropped at soil level and the total fresh weight of the shoots from each replicate was determined. A visual assessment of the condition of the plants was made on day 14 and day 28 of the test. The tests were carried out in glass houses and the overall temperature range during the study was 16 to 31.8^{o}C.

The concentrations of test substance in the solvent controls and the low, middle and highest test concentration were determined at the start and end of the test using a radiochemical method. The results of these analyses were variable due to difficulties in obtaining representative small subsamples of soil as a result of the relatively large proportion of soil particles >2 mm present in the soils. The results, however, were generally close to the nominal values (e.g. the mean measured values (on a dry wt. basis) were 49 mg/kg, 520 mg/kg. and 5,800 mg/kg for the nominal 50 mg/kg, 500 mg/kg and 5,000 mg/kg treatments respectively) and so the results were expressed in terms of the nominal concentrations.

The endpoints determined in the study were seed germination and emergence, vegetative growth (dry shoot weight), and visual condition of the seedlings. The results of the study are shown in **Table 3.59**. All seedlings in the treatments appeared normal (as compared to the control groups) throughout the test.

For wheat, no statistically significant (p=0.05) differences were found in emergence of seedlings or growth of seedlings at any treatment level when compared with control and solvent control populations. The NOEC for this species was therefore ≥5,000 mg/kg dry weight.

For oilseed rape, the emergence in the control and solvent control groups was 39% and 50% respectively. These values are below the recommended minimum emergence rate of 65% in the test guideline. The emergence in the treatment groups ranged from 42% to 58%, and was greater than the solvent control group at the highest concentration tested. There was no statistically significant (p=0.05) differences in growth of seedlings at any treatment level when compared to the control and solvent control populations. The test report indicates that the low emergence seen was not considered to have affected the validity of the results and so the NOEC is tentatively given as ≥5,000 mg/kg dry weight for this species.

Table 3.59 Effects of a C14-17, 52% wt. Cl substance on emergence and plant growth

Treatment	Wheat		Oilseed rape		Mungbean	
	Emergence[a]	Growth[b]	Emergence[a]	Growth[b]	Emergence[a]	Growth[b]
Control	81%	0.45±0.02 g	39%	1.16±0.24 g	92%	1.08±0.19 g
Solvent control	78%	0.45±0.06 g	50%	0.88±0.18 g	92%	0.91±0.18 g
50 mg/kg dry wt.	83%	0.44±0.08 g	47%	0.94±0.27 g	86%	0.92±0.14 g

Table 3.59 continued overleaf

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Table 3.59 continued Effects of a C_{14-17}, 52% wt. Cl substance on emergence and plant growth

Treatment	Wheat		Oilseed rape		Mungbean	
	Emergence[a]	Growth[b]	Emergence[a]	Growth[b]	Emergence[a]	Growth[b]
158 mg/kg dry wt.	92%	0.45±0.07 g	53%	0.97±0.16 g	97%	0.96±0.04 g
500 mg/kg dry wt.	75%	0.44±0.07g	58%	0.89±0.15 g	97%	0.90±0.03 g
1,580 mg/kg dry wt.	94%	0.43±0.05 g	42%	1.25±0.42 g	97%	0.83±0.14 g
5,000 mg/kg dry wt.	78%	0.39±0.06 g	56%	0.98±0.29 g	94%	0.75±0.07 g

a)   Emergence determined as percentage of emerged plants on day 14.
b)   Growth determined as mean shoot dry weight per plant.

For mungbean, no statistically significant (p=0.05) effects were seen in emergence rate between the treatment groups and the control and solvent control groups. For growth, no statistically significant effects (p=0.05) were seen between treatment groups and the solvent control group but a statistically significant reduction in growth was seen at the highest two concentrations tested when compared with the control group. The growth in the solvent control group was less than found in the control group, but this difference was not statistically significant and so the data for the control and solvent control groups were pooled. When compared with this pooled control group, no statistically significant effects were seen in growth at any treatment level. Thus the NOEC for this species is ≥5,000 mg/kg dry wt.

Overall, no statistically significant effects were seen with any species in this study. The low emergence rate for oilseed rape means that the results obtained for this species are not fully valid and so should be treated with caution. However, even so, it is clear that little or no effect was occurring in the treatments with this species.

3.2.2.3   Toxicity to earthworms

The toxicity of a medium-chain chlorinated paraffin has been studied in a reproduction test using earthworms (*Eisenia fetida*) (Thompson et al., 2001b). The test guideline used was based on the draft OECD guideline (2000 version) for the reproduction test, along with OECD 207 guideline for the acute toxicity to earthworms. The substance tested was a commercial C_{14-17}, 52% wt. Cl substance containing no stabilisers. The substance had a C_{14-17} content of 99.06% and a C_{10-13} content of 0.67%. The nominal concentrations tested were 100, 320, 1,000, 3,200 and 10,000 mg/kg dry weight. The substance was mixed with n-pentadecane-8-^{14}C (radiochemical purity >96.6%) at the lowest, middle and highest concentrations tested, to facilitate radiochemical analysis of the exposure concentrations.

The soil used in the test was an artificial soil consisting of 10% sphagnum moss peat, 70% quartz sand, 20% kaolinite clay and 0.25% calcium carbonate. The soil had an organic carbon content of 4.7% and a pH of 6.66-7.09. Before use, distilled water was added to the dry soil to provide a soil wet:dry ratio of 1.35.

The test concentrations were made up by firstly adding the chlorinated paraffin as a solution in acetone to a portion of the soil and allowing the solvent to evaporate overnight under a stream of compressed air. This soil was then mixed with the rest of the test soil to give the desired nominal concentrations. A solvent control soil was prepared in the same way. The tests were carried out in beakers containing 500 g of soil. Four replicate beakers were used for each treatment level,

with each replicate containing 10 worms. The test was carried out at 20°C. A cereal-based food was added to the test to the soil surface at weekly intervals at approximately 1.25 g dry weight/week. The test substance was not added to the food. The vessels were weighed every 7 days to determine the amount of water evaporated and this amount of water was then added to maintain the desired soil moisture content.

Adult worms (300-400 mg wet wt.) were used at the start of the test. On day 28, all remaining parent (adult) worms were counted and removed from the test vessels and the total wet weight of worms was determined. After removal of the adult worms, each test vessel was incubated for a further 28 days to allow hatching of any egg cocoons produced by the parent worms. At the end of this time period, the number of offspring (juveniles) present was determined.

The soil concentrations in the lowest, middle and highest treatments were determined on days 0, 28 and 56 of the experiment using a radiochemical technique. The mean measured concentrations were 84-95% of nominal at day 0, 74-90% of nominal at day 28 and 64-92% of nominal at day 56. The results indicate that there may have been a decline in the exposure concentration, particularly at the lower concentrations, during the test. As the test measured primarily survival and reproductive output of parent worms exposed during the first 28 days of the experiment, the mean measured concentrations over the first 28 days of the test were thought to best represent the exposure of these animals. These concentrations are shown in **Table 3.60**. The measured concentrations over the day 0 to day 28 period were, on average, 87% of the nominal concentration. This value was used to correct the nominal concentrations of 320 mg/kg dry wt. and 3,200 mg/kg dry wt., for which no analysis was undertaken, to give 'equivalent measured concentrations' of 280 and 2,800 mg/kg dry wt. respectively.

The survival, growth and reproduction results of the study are shown in **Table 3.60**. Parent survival was 100% in solvent control and control groups. Parent survival in the treatment groups was found to be statistically significantly reduced (p=0.05) at the highest concentration tested. Thus the $NOEC_{survival}$ = 2,800 mg/kg dry wt.

Growth of the parent organisms was determined as the percentage weight gain over days 0 to 28. The mean weight gain in the control and solvent control groups was 19%, however, there was a relatively large variability between replicates, reflecting the fact that the worms used in the study were adults at the start of the test and their weight would be expected to be influenced by their recent reproductive output. A dose-responsive reduction in weight gain was seen in the treatment groups. This reduction was statistically significant (p=0.01) at 2,800 mg/kg dry wt. and 9,300 mg/kg dry wt., where the weight/worm had decreased in all replicates. Thus the $NOEC_{growth}$ = 900 mg/kg dry wt.

Reproduction of the earthworms was investigated in terms of number of live offspring (the number of remaining full and empty cocoons was also determined but this did not provide any relevant data). In determining the number of offspring produced, no correction was made for parent mortality. This data showed that a dose-related decrease in the number of live offspring occurred, with this decrease being statistically significant (p=0.01) at concentrations of 900 mg/kg dry weight and above. The $NOEC_{reproduction}$ = 280 mg/kg dry weight.

Thus the overall NOEC from this study is 280 mg/kg dry weight. Using the default water contents for soil recommended in the TGD, this is equivalent to 248 mg/kg on a wet weight basis.

Table 3.60 Toxicity of a 52% wt. Cl medium-chain chlorinated paraffin to earthworm

Exposure concentration (mg/kg dry wt.)		Parent survival	Change in weight of parents	Number of live offspring
Nominal	Measured[a]			
Control	0	100%	19%	34.2±13.8
Solvent control	0	100%	19%	41.5±12.8
100	79	100%	18%	32.3±5.9
320	280[b]	100%	10%	26.3±11.1
1,000	900	100%	6%	14.5±7.7**
3,200	2,800[b]	97.5%	-15%**	1.5±1.7**
10,000	9,300	85%*	-34%**	0**

*   Value significantly different from the solvent control population (p=0.05).
**   Value significantly different from the solvent control population (p=0.01).
a)   Mean measured concentration over days 0 to day 28 of the exposure.
b)   No actual measurements were carried out for these treatments. The concentrations represent 'Equivalent measured concentration'
         using the mean % of nominal (87%) determined in the other treatments.

3.2.2.4   Predicted no effect concentration (PNEC) for the terrestrial compartment

A $PNEC_{soil}$ may be estimated using the equilibrium partitioning method as follows:

$$PNEC_{soil} = \frac{K_{soil-water} \times PNEC_{water} \times 1000}{RHO_{soil}}$$

where $K_{soil-water}$ = soil – water partition coefficient = 17,666 m^3/m^3
                    RHO_{soil} = bulk density of soil = 1,700 kg/m^3

Using a $PNEC_{water}$ of 1 μg/l the $PNEC_{soil}$ is estimated as 10.4 mg/kg wet wt. However, the ingestion of soil-bound substance by soil dwelling organisms may not be sufficiently explained by this relationship for substances with log Kow >5. The TGD suggests that the PEC/PNEC ratio derived by the equilibrium partitioning method should be increased by a factor of 10 to take account of this.

Terrestrial toxicity data are also available for microorganisms, plants and earthworms. The lowest NOEC from the studies is 248 mg/kg wet wt. for the earthworm. According to the TGD an assessment factor of 10 is appropriate for this data set, giving a $PNEC_{soil}$ of 24.8 mg/kg wet wt.

The TGD indicates that for soil organisms, the NOEC should be normalised to the standard organic matter or organic carbon content used in the TGD (2% organic carbon content). The organic carbon content of the soil used in the earthworm study was 4.7%, and so this would lead to a $NOEC_{standard}$ of 106 mg/kg wet wt. and a $PNEC_{soil(standard)}$ of 10.6 mg/kg wet wt.

It should be noted that such a normalisation is only valid if the majority of the exposure of the organism occurs via the soil pore water. For substances with high log Kow values such as medium-chain chlorinated paraffins it is possible that direct ingestion of soil-bound substance may become an important route of exposure. However, a limited amount of uptake data was obtained as part of the toxicity study with earthworms. This is discussed in detail in Section 3.1.1.5.2, and the data are best explained in terms of the uptake (and hence exposure) occurring mainly via the soil pore water. Furthermore, the $PNEC_{soil(standard)}$ of 10.6 mg/kg wet wt.

is in excellent agreement with the PNEC$_{soil}$ value of 10.4 mg/kg wet weight estimated above by the equilibrium partitioning method (this method assumes that the toxicity is expressed mainly via the pore water). Therefore, as a realistic worst case approach the PNEC$_{soil(standard)}$ of 10.6 g/kg wet wt. will be taken forward to the risk characterisation.

3.2.3   Atmosphere

No data are available on possible effects of the substance on the atmosphere. However, given the low volatility of the substance, neither biotic nor abiotic effects are likely.

Chlorinated paraffins, particularly the short-chain ones, have been raised as a possible concern with regards to long-range atmospheric transport and subsequent bioaccumulation in remote regions. This issue is currently being discussed within the appropriate international fora, but no agreement has yet been reached. The potential for long-range transport (and subsequent accumulation) of the medium-chain chlorinated paraffins appears to be less than that for the short-chain. This is because the medium-chain chlorinated paraffins generally have lower vapour pressures, and are likely to adsorb more strongly to soil and sediment. However, the substance is a complex mixture with components exhibiting a range of physico-chemical properties. Some components of the commercial products might have properties that may mean that long-range transport via the atmosphere is a possibility. This issue should be considered further in the appropriate international fora.

3.2.4   Non-compartmental specific effects relevant for the food chain

3.2.4.1   Bioaccumulation

The high log Kow values reported for medium-chain chlorinated paraffins indicate a high potential for bioaccumulation. The available measured bioconcentration factors with aquatic organisms generally shows lower accumulation than would be expected based on the log Kow, but there are uncertainties over the actual exposure concentrations in some of these studies. Studies with fish and with worms in sediment and soil show some uptake of the medium-chain chlorinated paraffins into the organisms. A recent study measured a bioconcentration factor for fish of 1,087 l/kg and this value is considered reliable and has been used in the assessment. Uptake in mammals is also evident through the diet, although the concentrations reached within the animal do not appear to exceed those in the diet. There is some evidence that the bioaccumulative properties of medium-chain chlorinated paraffins may depend on carbon chain length and degree of chlorination (lower accumulation potential for highly chlorinated, longer-chain length components), but the available information indicates that at least some components of the commercial products have the potential to be taken up by organisms from surface water, sediment or soil pore water or diet.

In addition to bioconcentration, the Technical Guidance Document also provides methods to take into account biomagnification in the assessment of secondary poisoning. The method requires a biomagnification factor (BMF) for fish, preferably expressed on a lipid normalised basis. The available data for medium-chain chlorinated paraffins is summarised in Section 3.1.1.5.3. For the risk assessment, a lipid normalised BMF of between 1 and 3 has been considered in the risk assessment for the fish food chain.

3.2.4.2   Avian toxicity

The toxicity of a C_{14-17}, 52% wt. Cl chlorinated paraffin has been determined using mallard ducks (*Anas platyrhynchos*) and ring-necked pheasants (*Phasanius colchius*). In the first part of the test, single oral doses of 10,280 mg/kg body weight for the mallard and 24,606 mg/kg body weight for pheasant were administered (the chlorinated paraffin was administered neat as the undiluted liquid; controls were given an equal volume of water) to groups of 5 males and 5 females, and the birds were observed for 14 days. No mortality or abnormal clinical symptoms were observed during the 14-day period (Madeley and Birtley, 1980).

In the second test, groups of one-day old male and female mallards and pheasants were administered the chlorinated paraffin in their diet for 5 days, with a further 3 days observation period. The dietary doses used were 1,000 or 24,063 mg/kg feed, and the chlorinated paraffin was dissolved in a fixed volume of corn oil before mixing in with the food. Control groups received feed mixed with corn oil alone. All test animals were found to remain in good health throughout the experiment and no mortalities were seen. In the mallard, depressed food intake was seen at the 24,063 mg/kg feed dose, but this did not lead to a significant effect on weight gain. No effects were seen with the pheasant. No abnormalities were observed on autopsy (Madeley and Birtley, 1980).

Madeley and Birtley (1980) also analysed the distribution of the chlorinated paraffin within the bodies of adult mallards given a single oral dose of 10,000 mg/kg body weight and pheasant chicks given a dietary dose of 1,000 mg/kg feed for 5 days. Three days after the last treatment, elevated levels of the chlorinated paraffin were found in fat (both intestinal and subcutaneous), gut and heart (67, 15 and 7 mg/kg wet weight respectively) in the duck and very low levels in all tissues tested in the pheasant (although the test animals were too young to show any fat for analysis). High levels of the chlorinated paraffin (115 mg/kg wet weight) were found in feathers from the mallard. This may indicate a major sink for the substance, with contamination of the feathers occurring via the preen gland, but the measured level could also be an artefact as a result of contamination from gloves, etc., during handling of the birds.

3.2.4.3   Mammalian toxicity

The mammalian toxicity data is reviewed in detail in Section 4. The relevant repeated-dose end-points for secondary poisoning can be summarised as follows:

> NOAEL = 5 mg/kg food in diet (or 0.4 mg/kg body weight/day) in a 90-day feeding study with rats
>
> NOAEL = 10 mg/kg body weight/day in a 90-day feeding study with dogs
>
> NOAEL = 100 mg/kg food in diet (or 8 mg/kg body weight/day) in reproductive studies with rats

The main effects seen in repeated dose studies are on the liver, thyroid and kidneys. The NOAEL for effects on kidneys (inner medullary tubular dilatation and 'chronic nephritis') was 0.4 mg/kg body weight/day in a 90-day study. The changes seen at the next exposure level (4 mg/kg body weight or 50 mg/kg food in diet) were slight and increased only marginally in severity at higher levels, indicating a shallow dose-response curve.

In reproductive studies, effects were seen on neonatal offspring exposed via the lactating mother. The NOAEL for these effects was 100 mg/kg food in diet as a maternal dose.

Using the conversion factors given in the Technical Guidance Document, a dose of 10 mg/kg body weight is equivalent to a dose of 100-200 mg/kg food.

3.2.4.4   Predicted no effect concentration (PNEC) for secondary poisoning

The Technical Guidance Document recommends that the NOAEL from dietary toxicity tests with fish-eating birds or mammals are used to determine the $PNEC_{oral}$. The most relevant study for medium-chain chlorinated paraffins is the dietary study with the mallard. No significant effects were seen in this study, other than a slight depression of food intake at the high dose level of 24,063 mg/kg food.

The Technical Guidance Document suggests that an assessment factor of 3,000 should be applied to the LC_{50} from a 5-day avian study. However, no effects were seen in the available study with two avian species and so it is not appropriate to apply this factor to the NOAEL from the study.

The $PNEC_{oral}$ will be derived from the available mammalian data. From the available data, the NOAEL of around 5 mg/kg food could be used to derive a PNEC, along with an assessment factor of 30 (as recommended in the Technical Guidance Document; although the result is from a 90-day study, data are also from both repeated dose and reproductive studies). This gives a PNEC of 0.17 mg/kg food. It should be noted that the dose-response curve for the effects seen in this study was shallow, and that the effects seen at the next highest concentration tested (50 mg/kg food) were slight (based on this concentration a PNEC of 1.7 mg/kg food could be derived). However, the current Human Health assessment considers the NOAEL of 5 mg/kg food to be an appropriate endpoint from this study and so the PNEC of 0.17 mg/kg food derived from this NOAEL will be used in the risk characterisation for secondary poisoning. However, a second PNEC of 1.7 mg/kg food (based on the slight effects seen in the study) will also be considered in the risk characterisation to investigate the significance of the shallow dose-response curve.

When considering the above PNECs, it should also be noted that some effects on fish have been seen in feeding studies with medium-chain chlorinated paraffins at concentrations of around 0.78 mg/kg food and above (see Section 3.2.1.1). This provides some further support for the use of the PNEC of 0.17 mg/kg food derived above.

The Technical Guidance Document also indicates that a correction factor of 3 can be applied if the laboratory food used is grain (the factor accounts for the difference in calorific content of the diet of the laboratory animals and the diet of fish-eating birds or mammals). However, the Technical Guidance Document also indicates that the use of such a factor is open to debate and, since in this study details of the actual diet used are not available, the factor is not applied.

3.3   RISK CHARACTERISATION

3.3.1   Aquatic compartment (incl. sediment)

The PEC/PNEC ratios for the PVC applications given for surface water and sediment are based on a 45% wt. Cl substance. The corresponding PECs for a 52% wt. Cl substance are shown in Appendix G. These are generally similar, but slightly lower than those determined for the 45% wt. Cl substance.

3.3.1.1   Water

The $PNEC_{water}$ has been estimated as 1 µg/l. The resulting PEC/PNEC ratios for the various scenarios considered in this assessment are shown in **Table 3.61**.

The results are reported using the measured regional concentration of 0.1 µg/l as the background concentration. This is considered to be a more representative value than the predicted regional concentration of 0.389 µg/l or 0.682-0.745 µg/l when the 'waste remaining in the environment' is included.

Recent measurements in the United Kingdom indicate that the concentrations at some sites may be lower than predicted, at around 0.1 µg/l at most (see Section 3.1.2.3). The survey analysed spot water samples taken from downstream of a range of industries where medium-chain chlorinated paraffins were thought to be being used. However, as these results only provide a snapshot of the concentration of the time of sampling and could be influenced by the type of activity being carried out at that time, they cannot be considered to be representative of the possible local concentrations of medium-chain chlorinated paraffins that may occur throughout the EU.

The local calculations for PVC are based on a 45% wt. Cl product. The equivalent PECs based on a less volatile 52% wt. Cl product are given in Appendix G and are in the range 0.15-0.99 µg/l. This gives PEC/PNEC ratios in the range 0.15-0.99.

For formulation of metal cutting fluids it was reported in Section 3.1.1.2.5 that at well controlled formulation sites, oil capture and recovery systems will be used prior to discharge of effluent to the sewage treatment plant. The equipment used is designed to lower the dissolved oil concentration to 5 mg/l or less. In this case the release from the site would make only a minor contribution to the PEC_{local} for water, which is dominated by the regional background concentration.

It should also be noted that for some uses, particularly in metal cutting/working fluids, there is an increasing trend in the amounts of medium chain chlorinated paraffins used, which could result in an increase in the $PEC_{regional}$. This is considered further in Appendix E and, as a worst case could increase the calculated $PEC_{regional}$ to around 0.71 µg/l.

Table 3.61 Estimated PEC/PNEC ratios for surface water

Scenario	Step	Using measured regional concentration of 0.1 µg/l	
		PEC (µg/l)	PEC/PNEC
Production	Site A	0.11	0.11
	Site B	0.19	0.19
	Site C	0.27	0.27
	Site D	0.10	0.10
Use in PVC – plastisol coating	Compounding - O	0.15	0.15
	Conversion – O	0.44	0.44
	Compounding/conversion – O	0.49	0.49
Use in PVC – extrusion/other	Compounding - O	0.27	0.27
	Compounding – PO	1.03	1.03
	Compounding – C	0.18	0.18
	Conversion – O	0.62	0.62
	Conversion – PO	0.66	0.66
	Conversion – C	0.57	0.57
	Compounding/conversion – O	0.79	0.79
	Compounding/conversion – PO	1.59	1.59
	Compounding/conversion – C	0.65	0.65
Use in plastics/ rubber	Compounding	0.19	0.19
	Conversion	0.39	0.39
	Compounding/conversion	0.48	0.48
Use in sealants	Formulation and use	negligible[b]	<1
Use in paints	Formulation	0.38	0.38
	Industrial application	0.21	0.21
	Domestic application	0.10	0.10
Use in metal cutting/ working fluids	Formulation	1.64	1.64
	Use in oil-based fluids (large)	0.71	0.71
	Use in oil-based fluids (small)	0.66	0.66
	Use in emulsifiable fluids	0.15	0.15
	Use in emulsifiable fluids – intermittent release	46.6	46.6
Use in leather fat liquors	Formulation	0.29	0.29
	Use – complete processing of raw hides	1.77	1.77
	Use – processing of wet blue	6.79	6.79

Table 3.61 continued overleaf

Table 3.61 continued Estimated PEC/PNEC ratios for surface water

Scenario	Step	Using measured regional concentration of 0.1 µg/l	
		PEC (µg/l)	PEC/PNEC
Use in carbonless copy paper	Paper recycling	0.43c	0.43
Regional sources		0.1	0.10

a) For the intermittent scenario an assessment factor can be applied to the acute EC_{50}. However, from the available data set this would result in a lower PNEC than that derived from the long-term data. The PEC is greater than the EC_{50} determined in acute and long-term invertebrate studies.
b) Process makes no significant contribution to levels in water.
c) Primary treatment (sludge to landfill) followed by biological waste water treatment (sludge to soil)
O Open systems;
PO Partially open systems;
C Closed systems (as defined in UCD, 1998).

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 conclusion currently applies to the assessment of local releases from production sites, some PVC compounding and/or conversion sites, plastics/rubber compounding sites, formulation and use of sealants, formulation and use in paints, use in metal cutting/working fluids (except where spent emulsifiable fluid is discharged to waste water), formulation of leather fat liquors, recycling of carbonless copy paper and from regional sources.

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

The PECs derived are based, as far as possible, on release information relevant to the industry. These indicate that risk reduction measures may be required for the following areas:

- Use in the production of PVC in some processes (particularly where compounding or compounding and conversion are carried out in partially open systems).
- Formulation of metal cutting fluids, and use in emulsifiable metal cutting/working fluids where the spent fluid is discharged to waste water.
- Use in leather fat liquors.

When the possible effects of the proposed risk reduction measures on short chain chlorinated paraffins on the consumption and use of medium chain chlorinated paraffins are taken into account, the PEC/PNEC ratios also indicate that a risk from use in oil-based metal cutting fluids may also need to be considered if the typical concentration of medium-chain chlorinated paraffins present in the fluid is increased to around 10% (see Appendix E).

3.3.1.2   Sediment

There are three toxicity studies available on sediment-dwelling organisms. A $PNEC_{sed}$ for the sediment compartment of 5 mg/kg wet wt. has been estimated using these data and an assessment factor of 10. The resulting PEC/PNEC ratios for medium-chain chlorinated paraffins are shown in **Table 3.62**.

Table 3.62 Estimated PEC/PNEC ratios for sediment

Scenario	Step	Using measured regional concentrations	
		PEC (mg/kg wet wt.)	PEC/PNEC
Production	Site A	1.41	0.28
	Site B	2.44	0.49
	Site C	3.46	0.69
	Site D	1.28	0.26
Use in PVC – plastisol coating	Compounding - O	1.88	0.38
	Conversion – O	5.68	1.14
	Compounding/conversion - O	6.27	1.25
Use in PVC – extrusion/other	Compounding - O	3.46	0.69
	Compounding – PO	13.2	2.64
	Compounding – C	2.30	0.46
	Conversion – O	7.94	1.59
	Conversion – PO	8.45	1.69
	Conversion – C	7.30	1.46
	Compounding/conversion – O	10.1	2.02
	Compounding/conversion - PO	20.4	4.08
	Compounding/conversion - C	8.32	1.66
Use in plastics/rubber	Compounding	2.38	0.48
	Conversion	4.99	1.00
	Compounding/conversion	6.14	1.23
Use in sealants	Formulation and use	negligible[b]	<1
Use in paints	Formulation	4.86	0.97
	Industrial application	2.69	0.54
	Domestic application	1.28	0.26
Use in metal cutting/working fluids	Formulation	21.0	4.20
	Use in oil-based fluids (large)	9.09	1.82
	Use in oil-based fluids (small)	8.45	1.69
	Use in emulsifiable fluids	1.92	0.38
	Use in emulsifiable fluids – intermittent release	[597 or 11.7][a]	[119 or 2.34][a]
Use in leather fat liquors	Formulation	3.71	0.74
	Use – complete processing of raw hides	22.7	4.54
	Use – processing of wet blue	86.9	17.4
Use in carbonless copy paper	Paper recycling	5.50[c]	1.10

Table 3.62 continued overleaf

Table 3.62 continued Estimated PEC/PNEC ratios for sediment

Scenario	Step	Using measured regional concentrations	
		PEC (mg/kg wet wt.)	PEC/PNEC
Regional sources		0.7	0.14

a)   [ ] Intermittent release scenario - it is not clear how this is dealt with in the TGD for sediment.
b)   Process makes no significant contribution to levels in sediment.
c)   Primary treatment (sludge to landfill) followed by biological waste water treatment (sludge to soil).
O   Open systems;
PO   Partially open systems;
C   Closed systems (as defined in UCD, 1998).

The results are reported using the regional concentrations based on the measured concentrations in surface water and sediment (0.1 µg/l and 0.7 mg/kg wet wt. respectively). The local calculations for PVC are based on a 45% wt. Cl product. The equivalent PECs based on a less volatile 52% wt. Cl product are given in Appendix G and are in the range 1.9-12.7 mg/kg wet wt. This gives PEC/PNEC ratios in the range 0.38-2.54.

The PEC/PNEC ratios indicate a risk to the environment from PVC compounding and conversion processes, conversion processes for plastics/rubber, formulation of metal cutting/working fluids, use of oil-based metal cutting/working fluids, use of emulsifiable metal cutting/working fluids where intermittent release to drain occurs, use in leather fat liquors and recycling of carbonless copy paper.

In general the most recent monitoring data for sediment is consistent with the predicted local concentrations. Indeed, there are several areas in the United Kingdom with measured sediment levels are >5 mg/kg wet wt., indicating that risk reduction measures are required from some uses of medium-chain chlorinated paraffins.

For formulation of metal cutting fluids it was reported in Section 3.1.1.2.5 that at well controlled formulation sites, oil capture and recovery systems will be used prior to discharge of effluent to the sewage treatment plant. The equipment used is designed to lower the dissolved oil concentration to 5 mg/l or less. In this case the release from the site would make only a minor contribution to the PEC_{local} for sediment, which is dominated by the regional concentrations.

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 conclusion currently applies to the assessment of local release from production sites, some use in PVC (compounding in open and closed systems), some uses in plastics/rubber (compounding), formulation and use of sealants, formulation and use in paints, use in emulsifiable metal cutting/working fluids (except where intermittent disposal to drain occurs), formulation of leather fat liquors and from regional sources.

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

Risk reduction measures are required for local release from the following sources:

- Use in PVC: plastisol coating – conversion sites or sites carrying out both compounding and conversion.

- Use in PVC: extrusion/other – compounding sites using partially open processes or sites carrying out both compounding and conversion using open, partially open or closed processes.

- Use in PVC: extrusion/other – conversion sites using open, partially open or closed processes.

- Use in plastics/rubber: sites carrying out conversion or both compounding and conversion.

- 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 at sites with intermittent release (disposal) to sewer/drain.

- Use in leather fat liquors: use at sites carrying out processing of hides/leather.

- Use in carbonless copy paper: sites carrying out paper recycling.

This conclusion is supported by the more recent monitoring data from the United Kingdom, which found measured concentrations of medium-chain chlorinated paraffins at several locations close to industry in the United Kingdom.

3.3.1.3   Sewage treatment processes

A PNEC of 80 mg/l has been estimated for sewage treatment microorganisms. The resulting PEC/PNEC ratios for the various scenarios are shown in **Table 3.63**.

Table 3.63 Estimated PEC/PNEC ratios for waste water treatment plants

Scenario	Step	$C_{effluent}$ (µg/l)	PEC/PNEC
Use in PVC – plastisol coating	Compounding - O	0.88	$1.1 \cdot 10^{-5}$
	Conversion – O	6.48	$8.1 \cdot 10^{-5}$
	Compounding/conversion – O	7.35	$9.2 \cdot 10^{-5}$
Use in PVC – extrusion/other	Compounding - O	3.22	$4.0 \cdot 10^{-5}$
	Compounding – PO	17.5	$2.2 \cdot 10^{-4}$
	Compounding – C	1.49	$1.9 \cdot 10^{-5}$
	Conversion – O	9.80	$1.2 \cdot 10^{-4}$
	Conversion – PO	10.50	$1.3 \cdot 10^{-4}$
	Conversion – C	8.93	$1.1 \cdot 10^{-4}$
	Compounding/conversion – O	13.0	$1.6 \cdot 10^{-4}$
	Compounding/conversion – PO	28.0	$3.5 \cdot 10^{-4}$
	Compounding/conversion – C	10.4	$1.3 \cdot 10^{-4}$

Table 3.63 continued overleaf

Table 3.63 continued Estimated PEC/PNEC ratios for waste water treatment plants

Scenario	Step	Ceffluent (µg/l)	PEC/PNEC
Use in plastics/rubber	Compounding	1.63	$2.0 \cdot 10^{-5}$
	Conversion	5.43	$6.8 \cdot 10^{-5}$
	Compounding/conversion	7.07	$8.8 \cdot 10^{-5}$
Use in sealants	Formulation and use	negligible[a]	<<1
Use in paints	Formulation	5.25	$6.6 \cdot 10^{-5}$
	Industrial application	2.07	$2.6 \cdot 10^{-5}$
	Domestic application	$1.05 \cdot 10^{-5}$	$1.3 \cdot 10^{-10}$
Use in metal cutting/working fluids	Formulation	29.1	$3.6 \cdot 10^{-4}$
	Use in oil-based fluids (large)	11.6	$1.5 \cdot 10^{-4}$
	Use in oil-based fluids (small)	10.5	$1.3 \cdot 10^{-4}$
	Use in emulsifiable fluids	0.88	$1.1 \cdot 10^{-5}$
	Use in emulsifiable fluids – intermittent release	875	0.011
Use in leather fat liquors	Formulation	3.5	$4.4 \cdot 10^{-5}$
	Use – complete processing of raw hides	31.5	$3.9 \cdot 10^{-4}$
	Use – processing of wet blue	126	$1.6 \cdot 10^{-3}$
Use in carbonless copy paper	Paper recycling	6.2	$7.8 \cdot 10^{-5}$

a)   Process makes no significant contribution to the levels in waste water.
O   Open systems;
PO   Partially open systems;
C   Closed systems (as defined in UCD, 1998).

For the four production sites for which information is available, the $C_{effluent}$ is in the range 0.12-5.3 µg/l at sites where biological treatment is carried out. These concentrations also result in PEC/PNEC <1. The risk to waste water treatment plants from the production and use of medium-chain chlorinated paraffins is therefore low.

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 waste water treatment plants from all sources.

3.3.2   **Terrestrial compartment**

Soil organisms could be exposed to medium-chain chlorinated paraffins following application of sewage sludge to agricultural soils. A PNEC$_{soil}$ of 10.6 mg/kg wet wt. has been derived. The resulting PEC/PNEC ratios obtained for agricultural soil are shown in **Table 3.64**.

The results are reported using the measured concentration of 0.088 mg/kg wet wt. to represent the regional concentration in all soil types (natural soil (which acts as the background to the local calculations in agricultural soil) and agricultural soil). Similar to the situation with surface water, the measured regional soil concentration is considered to be representative of the situation throughout the EU. However, in the case of soil, the database available is smaller than in the case with surface water, and so the measured soil data needs to be used with caution. The predicted regional concentration in agricultural soil is 50.4-55.8 mg/kg wet wt. and the predicted regional concentration in natural soil is 1.1 mg/kg wet wt. It should be noted that the predicted concentrations are much higher than the levels that have so far been measured in the environment, and indicates that there are some uncertainties in the levels predicted. These could arise from overestimation of the actual emissions to soil, or an underestimation of the removal (biodegradation) rate in soil. This latter point is considered in detail in Section 3.1.3.3 and Appendix H and the overall uncertainties in the assessment are discussed in Section 3.3.5.

Emissions of particulates containing medium-chain chlorinated paraffins (from weathering of PVC for example) could add to the burden in soil, particularly the urban/industrial soil compartment. There are currently no agreed methods within the Technical Guidance Document for assessing these emissions, but tentative calculations indicate that the resulting regional concentration in industrial/urban soil could be of the order of 147-173 mg/kg wet wt.

There are large uncertainties inherent in these estimates, particularly over the actual (bio) availability of the substance, and the actual residence time of the substance in the soil compartment (the predicted regional concentration in soil is very sensitive to the removal rate assumed in the calculation (see Section 3.1.3.3 and Appendix H). For example if a half-life of 2 years in soil is assumed (as suggested by the analysis in Appendix H) this predicted regional concentration would be reduced to 0.7-0.8 mg/kg wet weight). No monitoring data are currently available that could be considered representative of this scenario. If these emissions do lead to actual exposure of the urban/industrial soil compartment to levels similar to those predicted, then the PEC/PNEC ratio would be >1 in the worst case calculation.

Table 3.64 Estimated PEC/PNEC ratios for agricultural soil (30 day average)

Scenario	Step	Using measured regional concentrations	
		PEC (mg/kg wet wt.)	PEC/PNEC
Production	4 Sites	negligible[c]	<1
Use in PVC – plastisol coating	Compounding - O	0.51	0.05
	Conversion – O	3.21	0.30
	Compounding/conversion – O	3.64	0.34
Use in PVC – extrusion/other	Compounding - O	1.64	0.15
	Compounding – PO	8.53	0.80
	Compounding – C	0.81	0.08
	Conversion – O	4.82	0.45
	Conversion – PO	5.16	0.49
	Conversion – C	4.40	0.42
	Compounding/conversion – O	6.37	0.60
	Compounding/conversion – PO	13.6	1.28
	Compounding/conversion – C	5.12	0.48

Table 3.64 continued overleaf

Table 3.64 continued   Estimated PEC/PNEC ratios for agricultural soil (30 day average)

Scenario	Step	Using measured regional concentrations	
		PEC (mg/kg wet wt.)	PEC/PNEC
Use in plastics/rubber	Compounding	0.87	0.08
	Conversion	2.71	0.26
	Compounding/conversion	3.5	0.33
Use in sealants	Formulation and use	negligible[c]	<1
Use in paints	Formulation	2.62	0.25
	Industrial application	1.08	0.10
	Domestic application	negligible[c]	<1
Use in metal cutting/working fluids	Formulation	14.1	1.33
	Use in oil-based fluids (large)	5.66	0.53
	Use in oil-based fluids (small)	5.15	0.48
	Use in emulsifiable fluids	0.51	0.05
	Use in emulsifiable fluids – intermittent release	46[a]	4.34[a]
Use in leather fat liquors	Formulation	1.78	0.17
	Use – complete processing of raw hides	15.3	1.44
	Use – processing of wet blue	60.8	5.74
Use in carbonless copy paper	Paper recycling	3.02[b]	0.28[b]
Regional sources		0.088	0.008

a) Assumes dilution of sewage sludge at WWTP before application to soil (see Section 3.1.3.1).
b) Primary treatment (sludge to landfill) followed by biological waste water treatment (sludge to soil)
c) Process makes no significant contribution to levels in soil.
O   Open systems;
PO   Partially open systems;
C   Closed systems (as defined in UCD, 1998).

In summary, when the measured regional soil concentration is used, the PEC/PNEC ratios for local scenarios are >1 for use in PVC (extrusion/other for compounding/conversion in partially open systems), formulation of metal cutting/working fluids, use of emulsifiable metal cutting/working fluids where intermittent release (disposal) of the fluid to drain occurs and use in leather fat liquors. When the emissions of 'waste remaining in the environment' to urban/industrial soil are considered, the predicted PEC/PNEC ratio would be >1.

It is possible that the PECs could be refined. The concentrations of medium-chain chlorinated paraffins are predicted to build up in soil over time as no biodegradation was assumed in the EUSES model. This results in high concentrations being predicted in soil, particularly in the regional model, but there may also be some impact on the predicted local levels. These predicted regional concentrations have not been confirmed in the available soil monitoring data and so the monitoring data have been used to represent the regional concentrations. A soil degradation study (from which a reliable half-life for degradation (mineralisation) in soil could be derived) could be considered, to define a reliable removal rate for the substance. A relatively crude analysis (see Appendix H) suggests that a degradation half-life of around 2 years in soil would be consistent with the estimated emission rates and the measured regional concentrations in soil.

A degradation half-life of this order would have the effect of reducing the local PECs for soil by around a factor of 2-3. Since the some of the PEC/PNEC ratios are larger than this factor, a soil degradation study on its own would not necessarily be enough to refine the risk characterisation for this compartment. In addition to this, it would also be very difficult to carry out such a study. Thus, although a soil degradation study would provide useful information for the risk assessment, and would potentially allow the local PECs for soil (and any other local concentrations that rely on the soil concentrations such as those for earthworms (for secondary poisoning) and food for human consumption) to be refined, obtaining such information within a reasonable timescale would be problematical, and the results on their own would not necessarily allow the assessment for the soil compartment to be completed. This option is therefore not recommended.

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 conclusion applies to the assessment of local releases from production sites, PVC plastisol coatings compounding, conversion or combined compounding/conversion sites, PVC extrusion/other compounding sites, PVC extrusion/other conversion sites and PVC extrusion/other combined compounding/conversion sites using open or closed processes, plastics/rubber compounding, conversion and combined compounding/conversion sites, formulation and use of sealants, formulation and use of paints, use in oil-based metal cutting/working fluids, use in emulsifiable metal cutting/working fluids (not intermittent release scenario), formulation of leather fat liquors,, recycling of carbonless copy paper and from regional sources on agricultural land.

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

The PEC/PNEC ratios indicate that risk reduction measures are required for local releases from the following sources:

- Use in PVC: extrusion/other - sites carrying out both compounding and conversion using partially open systems.
- Use in metal cutting/working fluids: formulation sites.
- Use in metal cutting/working fluids: use in emulsifiable fluids at sites with intermittent release (disposal) to sewer/drain.
- Use in leather fat liquors: use at sites carrying out processing of hides/leather.

In these cases, the major source of release to soil is predicted to come from the spreading of sewage sludge onto agricultural land.

The regional assessment of 'waste remaining in the environment' also indicates a possible risk to industrial soil. The major source of release to soil in this scenario is direct particulate release to industrial soil. There are many uncertainties inherent in this scenario.

3.3.3   Atmosphere

Neither biotic nor abiotic effects on the atmosphere are likely because of the limited atmospheric release and low volatility of medium-chain chlorinated paraffins.

Chlorinated paraffins, particularly the short-chain ones, have been raised as a possible concern with regards to long-range atmospheric transport and subsequent bioaccumulation in remote regions. This issue is currently being discussed within the appropriate international fora, but no agreement has yet been reached. The potential for long-range transport (and subsequent accumulation) of the medium-chain chlorinated paraffins appears to be less than that for the short-chain. This is because the medium-chain chlorinated paraffins generally have lower vapour pressures, and are likely to adsorb more strongly to soil and sediment. However, the substance is a complex mixture with components exhibiting a range of physico-chemical properties. Some components of the commercial products might have properties that may mean that long-range transport via the atmosphere is a possibility. This issue should be considered further in the appropriate international fora.

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.

3.3.4   Non-compartment specific effects relevant to the food chain (secondary poisoning)

The PNEC for secondary poisoning has been determined as 0.17 mg/kg food. However, it should be noted that the dose-response seen in the study from which this value was derived was very shallow and only relatively minor effects were seen at the next highest concentration tested. Thus, as explained in Section 3.2.4.4, a second PNEC of 1.7 mg/kg food (derived from the LOAEL from this study) will also be considered in the risk characterisation. The estimated PEC/PNEC ratios using a PNEC of 0.17 mg/kg food are shown in **Table 3.65** (the equivalent PEC/PNEC ratios using a PNEC of 1.7 mg/kg food would be ten times lower). 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.

Table 3.65 Estimated concentrations in fish and earthworms for secondary poisoning

| Scenario | Step | Fish[d] (Using measured regional concentrations) | | | | Earthworms | |
| | | TGD method | | Alternate method | | Using measured regional concentrations | |
		PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC
Production	Site A	0.11-0.33	0.64-1.9	0.22-0.44	1.29-2.59	negligible[c]	<1
	Site B	0.15-0.45	0.88-2.6	0.30-0.60	1.76-3.53	negligible[c]	<1
	Site C	0.19-0.57	1.1-3.4	0.38-0.76	2.24-4.47	negligible[c]	<1
	Site D	0.11-0.33	0.59-1.9	0.22-0.44	1.29-2.59	negligible[c]	<1
Use in PVC – plastisol coating	Compounding - O	0.13-0.39	0.76-2.3	0.26-0.52	1.53-3.06	1.7	10.0
	Conversion – O	0.26-0.78	1.5-4.6	0.52-1.04	3.06-6.12	9.3	54.7
	Compounding/conversion - O	0.28-0.84	1.6-4.9	0.56-1.12	3.29-6.59	10.4	61.2
Use in PVC – extrusion/ other	Compounding - O	0.19-0.57	1.1-3.4	0.38-0.76	2.24-4.47	4.8	28.2
	Compounding - PO	0.52-1.56	3.1-9.2	1.04-2.08	6.12-12.2	24.1	142
	Compounding – C	0.14-0.42	0.82-2.5	0.28-0.56	1.65-3.29	2.5	14.7
	Conversion – O	0.34-1.02	2.0-6.0	0.68-1.36	4.00-8.00	13.7	80.6
	Conversion – PO	0.36-1.08	2.1-6.4	0.72-1.44	4.23-8.47	14.7	86.4
	Conversion – C	0.32-0.96	1.9-5.6	0.64-1.28	3.76-7.53	12.6	74.1
	Compounding/conversion – O	0.42-1.26	2.5-7.4	0.84-1.68	4.94-9.88	18.1	106
	Compounding/conversion - PO	0.77-2.31	4.5-13.6	1.54-3.08	9.06-18.1	38.3	225
	Compounding/conversion – C	0.36-1.08	2.1-6.4	0.72-1.44	4.24-8.47	14.6	85.9
Use in plastics/ rubber	Compounding	0.15-0.45	0.88-2.6	0.30-0.60	1.76-3.53	2.7	15.9
	Conversion	0.24-0.72	1.4-4.2	0.48-0.96	2.82-5.65	7.8	45.9
	Compounding/conversion	0.28-0.84	1.7-4.9	0.56-1.12	3.29-6.59	10.0	58.8

Table 3.65 continued overleaf

Table 3.65 continued Estimated concentrations in fish and earthworms for secondary poisoning

Scenario	Step	Fish[d] (Using measured regional concentrations)				Earthworms	
		TGD method		Alternate method		Using measured regional concentrations	
		PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC
Use in sealants	Formulation and use	negligible[c]	<1	negligible[c]	<1	negligible[c]	<1
Use in paints	Formulation	0.23-0.69	1.4-4.1	0.46-0.92	2.71-5.41	7.6	44.7
	Industrial application	0.16-0.48	0.94-2.8	0.23-0.64	1.35-3.76	3.3	19.4
	Domestic application	negligible[c]	<1	negligible[c]	<1	negligible[c]	<1
Use in metal cutting/working fluids	Formulation	0.80-2.4	4.7-14.1	1.60-3.20	9.41-18.8	39.7	234
	Use in oil-based fluids (large)	0.38-1.14	2.2-6.7	0.76-1.52	4.47-8.94	16.1	94.7
	Use in oil-based fluids (small)	0.36-1.08	2.1-6.4	0.72-1.44	4.24-8.47	14.7	86.5
	Use in emulsifiable fluids	0.13-0.39	0.76-2.3	0.26-0.52	1.53-3.06	1.7	10.0
	Use in emulsifiable fluids – intermittent release	0.52-1.56	3.1-9.2	1.04-2.08	6.12-12.2	129[a]	759[a]
Use in leather fat liquors	Formulation	0.19-0.57	1.1-3.4	0.38-0.76	2.24-4.47	5.2	30.6
	Use – complete processing of raw hides	0.86-2.58	5.1-15.2	1.72-3.44	10.1-20.2	43.0	253
	Use – processing of wet blue	3.10-9.30	18.2-54.7	6.20-12.4	36.5-72.9	171	1,006
Use in carbonless copy paper	Paper recycling	0.23[b]-0.69[b]	1.4[b]-4.1[b]	0.46[b]-0.92[b]	2.7[b]-5.4[b]	8.8[b]	51.8[b]

a) assumes dilution of sewage sludge at WWTP before application to soil (see Section 3.1.3.1).
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 using the methods outlined in the Technical Guidance Document, taking into account accumulation through the food chain. The range reflects the range for the BMF (1-3).
O Open systems;
PO Partially open systems;
C Closed systems (as defined in UCD, 1998).

For the aquatic food chain, based on the method recommended in the Technical Guidance Document most of the PEC/PNEC ratios are >1 when the measured regional surface water concentration is used. Similar conclusions are reached when the alternate method for estimating the PECs is considered.

As discussed in Section 3.1.1.5 and Section 3.1.5.1, 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 (see Section 3.1.5.1; although again there would be some uncertainties associated with the modelled results). Even if the BMF were set to 1 (i.e. exposure expected via uptake from water only), most of the scenarios would still lead to a risk for the aquatic food chain.

For the terrestrial food chain, all of the scenarios give PEC/PNEC ratios greater than 1 when the measured regional soil concentration is taken into account (and, unlike the aquatic food chain, the calculations do not involve any biomagnification factor). The PECs for this endpoint are generally much higher than have so far been found in earthworms in the environment, and depend crucially on the predicted soil concentrations. As discussed in Section 3.3.2, the predicted concentrations are dependent on the rate of biodegradation of medium-chain chlorinated paraffins, as well as the estimated emissions via sewage sludge to the soil compartment. Any refinement to this information for the local soil compartment would therefore alter the PECs and PEC/PNEC ratios for this endpoint. Such refinement may include a soil biodegradation test, but as explained in Section 3.3.2, any such test would be difficult to carry out and on its own may not address all the possible concerns identified in the soil compartment.

There is some uncertainty over the PNEC of 0.17 mg/kg food used for the secondary poisoning assessment, due to the shallow dose-response curve seen in the study from which it was derived. However if the next highest dose tested is considered (where slight effects were seen; see Section 3.2.4), this would lead to a PNEC of 1.7 mg/kg food and essentially the same conclusions would be obtained for the earthworm food chain (in this case most, but not all, scenarios considered would still indicate a risk) and would still indicate a risk in some of the fish food chain scenarios where the current PEC/PNEC ratio is ≥10. It should also be noted that many of the PECs for the fish food chain are similar to, or higher than, concentrations in food that have been shown to cause effects in fish (see Cooley et al. (2001) reported in Section 3.2.1.1).

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 formulation and use of sealants and domestic application of paints.

This also applies to the assessment of secondary poisoning via the earthworm food chain for production (sites where no sewage sludge is applied to land), formulation and use of sealants, and domestic application of paints.

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

For the fish food chain this applies to:

- Production sites.

- Use in the production of PVC – plastisol coating.

- Use in the production of PVC – extrusion/other.

- Use in the production of plastic/rubber.

- Formulation of paints and industrial application of paints.

- Formulation and use in metal cutting/working fluids (all types).

- Formulation and use in leather fat liquors.

- Recycling of carbonless copy paper.

The risk reduction measures proposed for the aquatic compartment for some of these applications should also address the possible risks identified here.

For the earthworm foodchain, this conclusion applies to all the uses of medium-chain chlorinated paraffin (with the exception of production (sites where no sewage sludge is applied to land), formulation and use of sealants, and domestic application of paints).

3.3.5 Areas of uncertainty in the environmental risk assessment

As with any 'generic' risk assessment there are uncertainties inherent in the approach taken. For medium-chain chlorinated paraffins these uncertainties are compounded by the fact that the substance is a complex mixture and is difficult to test in many of the standard assays which means that derivation of the physico-chemical properties and other data necessary for the environmental modelling is difficult. In this assessment, a set of data that is considered to be representative of the substance has been chosen, and the effect of variation of these properties on the environmental modelling has been investigated. However, there are still some areas where reliable information is lacking.

One area where this is particularly apparent is in the actual degradation/removal rate in the environment. This is a vital input into the regional (and to a lesser extent) local concentrations, and has a major impact on the predicted concentrations in soil. This is discussed in detail in Appendix H and Section 3.1.3.3.

Another area of uncertainty is over the actual emission estimates. For most of the scenarios considered, the best information available to the specific industries has been used in preference to the default values. However, in many cases, this information was not generated for medium-chain chlorinated paraffins but has been extrapolated from other substances. This necessarily introduces uncertainties into the estimates.

Another area where information is lacking is in the assessment of the 'waste remaining in the environment'. Here, there are no agreed methodologies available in the Technical Guidance Document for estimating PECs for this type of release, and there are uncertainties associated with the actual (bio)availability and environmental behaviour of the substance when released in this form, which is essentially polymer particulates containing the substance.

There are some uncertainties over the assessment of bioaccumulation/biomagnification for medium-chain chlorinated paraffins (as outlined in Section 3.1.1.5.4) and there is a general lack

of experience in the application of the methods given in the Technical Guidance Document to address these uncertainties.

Some concerns have also been raised about the possibility of natural organohalogens or other substances interfering with analytical measurement of environmental concentrations. It should be stressed that analysis of chlorinated paraffins itself is very difficult. The individual chlorinated paraffin peaks do not separate cleanly during the chromatographic process and essentially a broad 'hand-shaped' peak is obtained over quite a wide retention time window. Any other compound, whether naturally occurring or not, that goes through the clean up method in a similar way to the chlorinated paraffin (the clean up method used is usually designed to remove some of the more common organohalogen pollutants such as dioxins, furans, PCBs, etc.) and has a similar chromatographic retention time could cause interference. The susceptibility of the analysis to this type of interference will depend, to some extent, on the specificity of the detection method used (for example Bennie et al. (2000) indicated that their low resolution mass spectrometric method may be more susceptible to such interferences than a high resolution mass spectrometric method). Another method that is sometimes used (as was the case with the Greenpeace breast milk analysis) involves reduction of the chlorinated paraffin to the parent paraffin and analysis of these (the parent paraffins can be readily separated by standard GC methods). This method provides much more information on the actual carbon chain lengths present, but has the potential for interference from both naturally occurring and anthropogenic n-paraffins (it will also still be subject to interference from naturally occurring chlorinated paraffins). The analytical methods used in the various studies are summarised in Appendix D.

If chlorinated paraffins are naturally produced that are identical to the anthropogenic ones then they would of course interfere in any analysis. It is possible that some complex natural organohalogen compounds could also interfere with the analysis, although there is no evidence that this occurs in practice. It is impossible to say categorically that naturally occurring chlorinated paraffins do not exist, although if there is any significant source it is most likely to be found in the marine environment. It is highly unlikely that the concentrations measured in, for example, sediment close to sites of production/use are natural rather than anthropogenic.

In any case, the environmental risk assessment conclusions are based on the calculated PECs based on the industrial use and release of chlorinated paraffins. A natural source would only add to the background (regional) levels. The monitoring data in the assessment have been used to support the PECs, but a risk would still be identified even if the monitoring data did not exist. In other words, even if medium-chain chlorinated paraffins occur naturally there is still a risk from the use of the anthropogenic substance.

3.3.6   Waste disposal

Similar to chlorinated compounds in general, chlorinated paraffins can act as a source of chlorine during incineration processes. This chlorine can then lead to the formation of polychlorinated dioxins and furans, and is a well known problem with incineration.

In most cases, controls are already in place on incinerators to minimise the formation of these dioxins and furans, and so the presence of the chlorinated paraffins should not lead to increased emissions. However, other processes involving chlorinated paraffins may not be so well controlled. One specific example is when metal swarf from metal working is re-melted. In this case the swarf may be contaminated with metal working/cutting fluids containing chlorinated paraffins which could theoretically contribute to the formation of chlorinated dioxins and furans in the process.

In addition CSTEE (2002) indicates that other unsaturated hydrocarbon products, including aromatic products such as polychlorinated biphenyls and polychlorinated naphtalenes can also be formed under certain circumstances, such as under heat or in contact with alkaline substances.

There is insufficient information available on this issue to make an assessment of the significance these processes in terms of a risk for the environment.

4 HUMAN HEALTH

(To be added later)

4.1.1.1 Indirect exposure via the environment

Medium-chain chlorinated paraffins have several uses that could result in releases to air and water. The uptake of medium-chain chlorinated paraffins into organisms, although it does occur, may be less than the very high log Kow values for this group of substances would indicate. The potential for bioaccumulation in the environment appears to decrease with increasing chlorine content in the group. This is discussed further in Section 3.1.1.5.

The EUSES model has been used to estimate various concentrations of medium-chain chlorinated paraffins in food, air and drinking water. These are shown in **Table 4.2**. The calculations have been carried out twice: firstly using the estimated regional background concentrations of 0.388 µg/l for surface water and 50.4 mg/kg wet wt. for agricultural soil; and secondly using 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 **Table 3.24** in Section 3.1.2.3.1 for surface water and **Table 3.37** in Section 3.1.3.2 for soil).

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 3.1.1.5) has been used in the EUSES 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 root crops, 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.

A accumulation factor of 0.034 on a wet weight basis for uptake into above ground parts of plants from soil has been determined for medium-chain chlorinated paraffins (see Section 3.1.1.5.2), showing that the substance can be taken up into plant tissues. Using this factor, and the concentrations of medium-chain chlorinated paraffins estimated to be present in soil (around 1.5-62 mg/kg wet weight for the scenarios considered in Section 3.1.3.1) the estimated concentration in above ground plant parts would be in the range 0.05-2.1 mg/kg wet weight. These data are reasonably consistent with the concentrations predicted by EUSES to occur in leaf crops, but it is not possible to compare these data with the concentrations predicted by EUSES for root crops.

Table 4.1 Estimated concentrations in food for human daily intake

Scenario	Step	Estimated concentration in human intake media						
		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	0.43 (0.11)[b]	negligible[a]	negligible[a]	$1.1 \cdot 10^{-4}$ ($2.6 \cdot 10^{-5}$)[b]	negligible[a]	negligible[a]	negligible[a]
	Site B	0.50 (0.19)[b]	negligible[a]	negligible[a]	$1.2 \cdot 10^{-4}$ ($4.4 \cdot 10^{-5}$)[b]	negligible[a]	negligible[a]	negligible[a]
	Site C	0.57 (0.26)[b]	negligible[a]	negligible[a]	$1.3 \cdot 10^{-4}$ ($6.0 \cdot 10^{-5}$)[b]	negligible[a]	negligible[a]	negligible[a]
	Site D	0.42 (0.11)[b]	negligible[a]	negligible[a]	$1.1 \cdot 10^{-4}$ ($2.5 \cdot 10^{-5}$)[b]	negligible[a]	negligible[a]	negligible[a]
Use in PVC – plastisol coating	Compounding - O	0.46 (0.15)[b]	9.33 (3.13)[b]	0.017 (0.017)[b]	$1.5 \cdot 10^{-4}$ ($4.9 \cdot 10^{-5}$)[b]	0.14 (0.10)[b]	0.044 (0.032)[b]	negligible[a]
	Conversion – O	0.73 (0.42)[b]	25.9 (19.7)[b]	0.23 (0.23)[b]	$4.1 \cdot 10^{-4}$ ($3.1 \cdot 10^{-4}$)[b]	1.32 (1.28)[b]	0.42 (0.40)[b]	$4.5 \cdot 10^{-5}$
	Compounding/conversion - O	0.77 (0.46)[b]	28.5 (22.3)[b]	0.23 (0.23)[b]	$4.5 \cdot 10^{-4}$ ($3.5 \cdot 10^{-4}$)[b]	1.32 (1.29)[b]	0.42 (0.41)[b]	$4.5 \cdot 10^{-5}$
Use in PVC – extrusion/other	Compounding - O	0.58 (0.26)[b]	16.3 (10.1)[b]	0.080 (0.080)[b]	$2.6 \cdot 10^{-4}$ ($1.6 \cdot 10^{-4}$)[b]	0.49 (0.46)[b]	0.16 (0.14)[b]	$1.6 \cdot 10^{-5}$
	Compounding – PO	1.25 (0.94)[b]	58.6 (52.4)	0.36 (0.36)[b]	$9.2 \cdot 10^{-4}$ ($8.2 \cdot 10^{-4}$)[b]	2.11 (2.07)[b]	0.67 (0.65)[b]	$7.2 \cdot 10^{-5}$
	Compounding – C	0.49 (0.18)[b]	11.2 (4.95)[b]	0.046 (0.046)[b]	$1.8 \cdot 10^{-4}$ ($7.8 \cdot 10^{-5}$)[b]	0.30 (0.26)[b]	0.095 (0.083)[b]	$9.2 \cdot 10^{-6}$
	Conversion – O	0.89 (0.57)[b]	35.8 (29.6)[b]	0.34 (0.34)[b]	$5.6 \cdot 10^{-4}$ ($4.6 \cdot 10^{-4}$)[b]	1.93 (1.89)[b]	0.61 (0.60)[b]	$6.7 \cdot 10^{-5}$
	Conversion – PO	0.92 (0.61)[b]	37.9 (31.6)[b]	0.36 (0.36)[b]	$5.9 \cdot 10^{-4}$ ($5.0 \cdot 10^{-4}$)[b]	2.05 (2.02)[b]	0.65 (0.64)[b]	$7.2 \cdot 10^{-5}$
	Conversion – C	0.85 (0.53)[b]	33.2 (27.0)[b]	0.31 (0.31)[b]	$5.2 \cdot 10^{-4}$ ($4.2 \cdot 10^{-4}$)[b]	1.77 (1.73)[b]	0.56 (0.55)[b]	$6.1 \cdot 10^{-5}$
	Compounding/conversion – O	1.04 (0.73)[b]	45.3 (39.1)[b]	0.40 (0.40)[b]	$7.1 \cdot 10^{-4}$ ($6.1 \cdot 10^{-4}$)[b]	2.29 (2.25)[b]	0.72 (0.71)[b]	$8.0 \cdot 10^{-5}$
	Compounding/conversion - PO	1.75 (1.44)[b]	89.7 (83.5)[b]	0.70 (0.70)[b]	$1.4 \cdot 10^{-3}$ ($1.3 \cdot 10^{-4}$)[b]	4.03 (3.99)[b]	1.27 (1.26)[b]	$1.4 \cdot 10^{-4}$
	Compounding/conversion - C	0.92 (0.60)[b]	37.6 (31.4)[b]	0.34 (0.34)[b]	$5.9 \cdot 10^{-4}$ ($4.9 \cdot 10^{-4}$)[b]	1.94 (1.90)[b]	0.61 (0.60)[b]	$6.7 \cdot 10^{-5}$
Use in plastics/rubber	Compounding	0.50 (0.19)[b]	11.6 (5.36)[b]	0.035 (0.035)[b]	$1.8 \cdot 10^{-4}$ ($8.4 \cdot 10^{-5}$)[b]	0.24 (0.20)[b]	0.076 (0.064)[b]	$6.9 \cdot 10^{-6}$
	Conversion	0.68 (0.37)[b]	22.8 (16.6)[b]	0.19 (0.19)[b]	$3.6 \cdot 10^{-4}$ ($2.6 \cdot 10^{-4}$)[b]	1.12 (1.09)[b]	0.36 (0.34)[b]	$3.8 \cdot 10^{-5}$

Table 4.1 continued overleaf

Table 4.1 continued Estimated concentrations in food for human daily intake

Scenario	Step	Estimated concentration in human intake media						
		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)
	Compounding/conversion	0.76 (0.44)[b]	27.7 (21.5)[b]	0.21 (0.21)[b]	$4.3 \cdot 10^{-4}$ $(3.4 \cdot 10^{-4})$[b]	1.24 (1.20)[b]	0.39 (0.38)[b]	$4.2 \cdot 10^{-5}$
Use in sealants	Formulation and use	negligible[a]	negligible[a]	negligible[a]	negligible[a]	negligible[a]	negligible[a]	negligible[a]
Use in paints	Formulation	0.67 (0.36)[b]	22.3 (16.1)[b]	0.074 (0.074)[b]	$3.5 \cdot 10^{-4}$ $(2.5 \cdot 10^{-4})$[b]	0.48 (0.44)[b]	0.15 (0.14)[b]	$1.4 \cdot 10^{-5}$
	Industrial application	0.52 (0.21)[b]	12.9 (6.7)[b]	0.017 (0.017)[b]	$2.0 \cdot 10^{-4}$ $(1.0 \cdot 10^{-4})$[b]	0.15 (0.11)[b]	0.046 (0.034)[b]	negligible[a]
	Domestic application	0.42 (0.11)[b]	6.75 (0.54)[b]	0.017 (0.017)[b]	$1.1 \cdot 10^{-4}$ $(2.5 \cdot 10^{-5})$[b]	0.13 (0.094)[b]	0.042 (0.030)[b]	negligible[a]
Use in metal cutting/working fluids	Formulation	1.80 (1.49)[b]	92.7 (86.5)[b]	0.018 (0.018)[b]	$1.5 \cdot 10^{-3}$ $(1.4 \cdot 10^{-3})$[b]	0.35 (0.31)[b]	0.11 (0.097)[b]	negligible[a]
	Use in oil-based fluids (large)	0.97 (0.66)[b]	40.9 (34.7)[b]	0.017 (0.017)[b]	$6.4 \cdot 10^{-4}$ $(5.4 \cdot 10^{-4})$[b]	0.22 (0.18)[b]	0.069 (0.057)[b]	negligible[a]
	Use in oil-based fluids (small)	0.92 (0.61)[b]	37.8 (31.6)[b]	0.017 (0.017)[b]	$5.9 \cdot 10^{-4}$ $(5.0 \cdot 10^{-4})$[b]	0.21 (0.17)[b]	0.066 (0.054)[b]	negligible[a]
	Use in emulsifiable fluids	0.46 (0.15)[b]	9.33 (3.13)[b]	0.017 (0.017)[b]	$1.5 \cdot 10^{-4}$ $(4.9 \cdot 10^{-5})$[b]	0.14 (0.10)[b]	0.044 (0.032)[b]	negligible[a]
	Use in emulsifiable fluids – intermittent release	1.25[c] (0.94)[b,c]	288[c] (282)[b,c]	0.020[c] (0.019)[b,c]	$4.5 \cdot 10^{-3c}$ $(4.4 \cdot 10^{-3})$[b,c]	0.83[c] (0.79)[b,c]	0.26[c] (0.25)[b,c]	negligible[a]
Use in leather fat liquors	Formulation	0.59 (0.28)[b]	17.2 (11.0)[b]	0.42 (0.42)[b]	$2.7 \cdot 10^{-4}$ $(1.7 \cdot 10^{-4})$[b]	2.3 (2.3)[b]	0.73 (0.72)[b]	$8.3 \cdot 10^{-5}$
	Use – complete processing of raw hides	1.92 (1.6)[b]	99.9 (93.7)[b]	0.018 (0.018)[b]	$1.6 \cdot 10^{-3}$ $(1.5 \cdot 10^{-3})$[b]	0.36 (0.33)[b]	0.12 (0.10)[b]	negligible[a]
	Use – processing of wet blue	6.40 (6.08)[b]	379 (373)[b]	0.020 (0.020)[b]	$6.0 \cdot 10^{-3}$ $(5.9 \cdot 10^{-3})$[b]	1.06 (1.02)[b]	0.34 (0.32)[b]	negligible[a]
Use in carbonless copy paper	Paper recycling	0.67 (0.35)[b]	25.0 (18.8)[b]	0.017 (0.017)[b]	$3.9 \cdot 10^{-4}$ $(2.9 \cdot 10^{-4})$[b]	0.18 (0.14)[b]	0.056 (0.044)[b]	negligible[a]
Regional sources		0.42 (0.11)[b]	309 (0.541)[b]	0.020 (0.017)[b]	$4.9 \cdot 10^{-3}$ $(2.5 \cdot 10^{-5})$[b]	1.99 (0.094)[b]	0.63 (0.030)[b]	$3.4 \cdot 10^{-6}$

a)   The process makes no significant contribution to the concentration in food/air.
b)   Figures in ( ) are recalculated 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 Section 3.1.3.1).
O   Open systems;
PO   Partially open systems; C = Closed systems (as defined in UCD, 1998).

5 RESULTS

5.1 INTRODUCTION

Medium-chain chlorinated paraffins are produced at five sites in the EU. The main area of use is as a secondary plasticiser in PVC, but substantial amounts are also used in other plastics/rubber products, sealants, paints, metal cutting/working fluids, leather fat liquors and carbonless copy paper. They are viscous liquids of very low volatility.

5.2 ENVIRONMENT

Medium-chain chlorinated paraffins have a high acute toxicity towards aquatic organisms, a high fish bioconcentration factor and are poorly degradable. For surface water, the estimated PEC/PNEC ratios are >1 for several of the life-stages of medium-chain chlorinated paraffins, and so a risk to surface water exists from some uses of medium-chain chlorinated paraffins. The risk to surface water from regional sources is low.

The PEC/PNEC ratios obtained for sediment also indicate a risk to the environment from several of the local scenarios considered. The regional PEC/PNEC ratio is currently <1, indicating a low risk to the environment from regional sources.

No risk to the environment is identified from the assessment of waste water treatment plants or the atmosphere.

For the soil compartment the PEC/PNEC ratios are >1 for four of the local scenarios. When the emissions of 'waste remaining in the environment' to urban/industrial soil are considered, the predicted regional PEC/PNEC ratio would be >1 for that type of soil.

For secondary poisoning, almost all uses of medium chain chlorinated paraffins lead to a possible risk of secondary poisoning via the earthworm food chain and many of these uses also indicate a risk via the fish food chain. No risk of secondary poisoning was identified from formulation and use in sealants and domestic application of paints.

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.

A low risk to waste water treatment plants and the atmospheric compartment[12] have been identified from both the production and use of medium-chain chlorinated paraffins.

For surface water, this conclusion currently applies to the assessment of local releases from production sites, some PVC compounding and/or conversion sites, plastics/rubber compounding sites, formulation and use of sealants, formulation and use in paints, use in metal cutting/working fluids (except where spent emulsifiable fluid is discharged to waste water), formulation of leather fat liquors, recycling of carbonless copy paper and from regional sources.

For sediment, this conclusion currently applies to the assessment of local release from production sites, some use in PVC (compounding in open and closed systems), some uses in plastics/rubber (compounding), formulation and use of sealants, formulation and use in paints,

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[12] Some components of the commercial products might have properties that may mean that long-range transport via the atmosphere is a possibility. This issue should be considered further in the appropriate international fora.

use in emulsifiable metal cutting/working fluids (except where intermittent disposal to drain occurs), formulation of leather fat liquors and from regional sources.

For soil, this conclusion applies to the assessment of local releases from production sites, PVC plastisol coatings compounding, conversion or combined compounding/conversion sites, PVC extrusion/other compounding sites, PVC extrusion/other conversion sites and PVC extrusion/other combined compounding/conversion sites using open or closed processes, plastics/rubber compounding, conversion and combined compounding/conversion sites, formulation and use of sealants, formulation and use of paints, use in oil-based metal cutting/working fluids, use in emulsifiable metal cutting/working fluids (not intermittent release scenario), formulation of leather fat liquors,, recycling of carbonless copy paper and from regional sources on agricultural land.

For secondary poisoning via the fish food chain, a low risk was identified from formulation and use of sealants, and domestic application of paints. A low risk of secondary poisoning via the earthworm food chain is also indicated for production (sites where no application of sewage sludge onto land occurs), formulation and use in sealants, and domestic application of paints.

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

For surface water, a risk is identified from the following applications:

- Use in the production of PVC in some processes (particularly where compounding or compounding and conversion is carried out in partially open systems).

- Formulation of metal cutting fluids, and use in emulsifiable metal cutting/working fluids where the spent fluid is discharged to waste water.

- Use in leather fat liquors.

For sediment, a risk is identified from the following applications:

- Use in PVC: plastisol coating – conversion sites or sites carrying out both compounding and conversion.

- Use in PVC: extrusion/other – compounding sites using partially open processes or sites carrying out both compounding and conversion using open, partially open or closed processes.

- Use in PVC: extrusion/other – conversion sites using open, partially open or closed processes.

- Use in plastics/rubber: sites carrying out conversion or both compounding and conversion.

- 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 at sites with intermittent release (disposal) to sewer/drain.

- Use in leather fat liquors: use at sites carrying out processing of hides/leather.

- Use in carbonless copy paper: sites carrying out paper recycling.

For the terrestrial compartment, a risk is identified from:

- Use in PVC: extrusion/other - sites carrying out both compounding and conversion using partially open systems.

- Use in metal cutting/working fluids: formulation sites.

- Use in metal cutting/working fluids: use in emulsifiable fluids at sites with intermittent release (disposal) to sewer/drain.

- Use in leather fat liquors: use at sites carrying out processing of hides/leather.

- Regional assessment of 'waste remaining in the environment'.

For secondary poisoning, a risk is identified from all uses of medium-chain chlorinated paraffins for the earthworm food chain (other than for production (sites where there is no spreading of sewage sludge to land), formulation and use of sealants, and domestic application of paints). The following scenarios also indicate a concern for the fish food chain:

- Production sites.

- Use in the production of PVC - plastisol coating.

- Use in the production of PVC – extrusion/other.

- Use in the production of plastic/rubber.

- Formulation of paints and industrial application of paints.

- Formulation and use in metal cutting/working fluids (all types).

- Formulation and use in leather fat liquors.

- Recycling of carbonless copy paper.

5.3 HUMAN HEALTH

(To be added later)

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ABBREVIATIONS

ADI	Acceptable Daily Intake
AF	Assessment Factor
Ann	Annex
ASTM	American Society for Testing and Materials
ATP	Adaptation to Technical Progress
AUC	Area Under The Curve
B	Bioaccumulation
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
BCF	Bioconcentration Factor
BMC	Benchmark Concentration
BMD	Benchmark Dose
BMF	Biomagnification Factor
BOD	Biochemical Oxygen Demand
bw	body weight / *Bw, bw*
C	Corrosive (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
°C	degrees Celsius (centigrade)
C_{50}	median immobilisation concentration or median inhibitory concentration 1 / *explained by a footnote if necessary*
CA	Chromosome Aberration
CA	Competent Authority
CAS	Chemical Abstract Services
CEC	Commission of the European Communities
CEN	European Standards Organisation / European Committee for Normalisation
CEPE	European Committee for Paints and Inks
CMR	Carcinogenic, Mutagenic and toxic to Reproduction
CNS	Central Nervous System
COD	Chemical Oxygen Demand
CSTEE	Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO)
CT_{50}	Clearance Time, elimination or depuration expressed as half-life
d	Day(s)
d.wt	dry weight / dw
dfi	daily food intake
DG	Directorate General
DIN	Deutsche Industrie Norm (German norm)
DNA	DeoxyriboNucleic Acid
DOC	Dissolved Organic Carbon

DT50	Degradation half-life or period required for 50 percent dissipation / degradation
DT_{50lab}	Period required for 50 percent dissipation under laboratory conditions (define method of estimation)
DT90	Period required for 90 percent dissipation / degradation
$DT_{90field}$	Period required for 90 percent dissipation under field conditions (define method of estimation)
E	Explosive (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
EASE	Estimation and Assessment of Substance Exposure Physico-chemical properties [Model]
EbC50	Effect Concentration measured as 50% reduction in biomass growth in algae tests
EC	European Communities
EC10	Effect Concentration measured as 10% effect
EC50	median Effect Concentration
ECB	European Chemicals Bureau
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECVAM	European Centre for the Validation of Alternative Methods
EDC	Endocrine Disrupting Chemical
EEC	European Economic Communities
EINECS	European Inventory of Existing Commercial Chemical Substances
ELINCS	European List of New Chemical Substances
EN	European Norm
EPA	Environmental Protection Agency (USA)
ErC50	Effect Concentration measured as 50% reduction in growth rate in algae tests
ESD	Emission Scenario Document
EU	European Union
EUSES	European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment]
F(+)	(Highly) flammable (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
FAO	Food and Agriculture Organisation of the United Nations
FELS	Fish Early Life Stage
foc	Organic carbon factor (compartment depending)
G	Gram(s)
GLP	Good Laboratory Practice
h	hour(s)
ha	Hectares/h
HEDSET	EC/OECD Harmonised Electronic Data Set (for data collection of existing substances)
HELCOM	Helsinki Commission -Baltic Marine Environment Protection Commission

HPLC	High Pressure Liquid Chromatography
HPVC	High Production Volume Chemical (> 1000 tonnes/annum)
IARC	International Agency for Research on Cancer
IC	Industrial Category
IC50	median Immobilisation Concentration or median Inhibitory Concentration
ILO	International Labour Organisation
IPCS	International Programme on Chemical Safety
ISO	International Organisation for Standardisation
IUCLID	International Uniform Chemical Information Database (existing substances)
IUPAC	International Union for Pure and Applied Chemistry
JEFCA	Joint FAO/WHO Expert Committee on Food Additives
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
kg	kilogram(s)
Koc	organic carbon normalised distribution coefficient
Kow	octanol/water partition coefficient
Kp	solids-water partition coefficient
kPa	kilo Pascals
l	litre(s)
L(E)C50	median Lethal (Effect) Concentration
LAEL	Lowest Adverse Effect Level
LC50	median Lethal Concentration
LD50	median Lethal Dose
LEV	Local Exhaust Ventilation
LLNA	Local Lymph Node Assay
LOAEL	Lowest Observed Adverse Effect Level
LOEC	Lowest Observed Effect Concentration
LOED	Lowest Observed Effect Dose
LOEL	Lowest Observed Effect Level
log	logarithm to the basis 10
m	Meter
MAC	Maximum Allowable Concentration
MATC	Maximum Acceptable Toxic Concentration
MC	Main Category
mg	Milligram(s)
MITI	Ministry of International Trade and Industry, Japan
MOE	Margin of Exposure
MOS	Margin of Safety

MW	Molecular Weight
N	Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC
NAEL	No Adverse Effect Level
NOAEL	No Observed Adverse Effect Level
NOEL	No Observed Effect Level
NOEC	No Observed Effect Concentration
NTP	National Toxicology Program (USA)
O	Oxidising (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
OC	Organic Carbon content
OECD	Organisation for Economic Cooperation and Development
OEL	Occupational Exposure Limit
OJ	Official Journal
OSPAR	Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic
P	Persistent
PBT	Persistent, Bioaccumulative and Toxic
PBPK	Physiologically Based PharmacoKinetic modelling
PBTK	Physiologically Based ToxicoKinetic modelling
PEC	Predicted Environmental Concentration
pH	logarithm (to the base 10) (of the hydrogen ion concentration $\{H^+\}$
pKa	logarithm (to the base 10) of the acid dissociation constant
pKb	logarithm (to the base 10) of the base dissociation constant
PNEC	Predicted No Effect Concentration
PNEC$_{water}$	Predicted No Effect Concentration in Water
POP	Persistent Organic Pollutant
PPE	Personal Protective Equipment
QSAR	(Quantitative) Structure-Activity Relationship
R phrases	Risk phrases according to Annex III of Directive 67/548/EEC
RAR	Risk Assessment Report
RC	Risk Characterisation
RfC	Reference Concentration
RfD	Reference Dose
RNA	RiboNucleic Acid
RPE	Respiratory Protective Equipment
RWC	Reasonable Worst-Case
S phrases	Safety phrases according to Annex IV of Directive 67/548/EEC

SAR	Structure-Activity Relationships
SBR	Standardised birth ratio
SCE	Sister Chromatic Exchange
SDS	Safety Data Sheet
SETAC	Society of Environmental Toxicology And Chemistry
SNIF	Summary Notification Interchange Format (new substances)
SSD	Species Sensitivity Distribution
STP	Sewage Treatment Plant
T(+)	(Very) Toxic (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
TDI	Tolerable Daily Intake
TG	Test Guideline
TGD	Technical Guidance Document
TNsG	Technical Notes for Guidance (for Biocides)
TNO	The Netherlands Organisation for Applied Scientific Research
ThOD	Theoritical Oxygen Demand
UC	Use Category
UDS	Unscheduled DNA Synthesis
UN	United Nations
UNEP	United Nations Environment Programme
US EPA	Environmental Protection Agency, USA
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products of Biological material
µg	microgram(s)
vB	very Bioaccumulative
VOC	Volatile Organic Compound
vP	very Persistent
vPvB	very Persistent and very Bioaccumulative
v/v	volume per volume ratio
w	gram weight
w/w	weight per weight ratio
WHO	World Health Organisation
WWTP	Waste Water Treatment Plant
Xn	Harmful (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
Xi	Irritant (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)

Appendix A EUSES modelling

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

EUSES Printout	Scenario
USE PATTERN 1	Use in PVC – plastisol applications
formulation	compounding site – open system
processing	conversion site – open system
private use	combined compounding/conversion site – open system
USE PATTERN 2	Use in PVC – extrusion/other
formulation	compounding site – open system
processing	compounding site – partially open system
private use	compounding site – closed system
USE PATTERN 3	Use in PVC – extrusion/other
formulation	conversion site – open system
processing	conversion site – partially open system
private use	conversion site – closed system
USE PATTERN 4	Use in PVC - extrusion other
formulation	combined compounding/conversion site - open system
processing	combined compounding/conversion site - partially open system
private use	combined compounding/conversion site - closed system
USE PATTERN 5	Use in plastics/rubber
formulation	compounding site
processing	conversion site
private use	combined compounding/conversion site
USE PATTERN 6	Use in paints and varnishes
formulation	formulation site
processing	industrial application of paints
private use	domestic application of paints
USE PATTERN 7	Use in metal cutting/working fluids
formulation	formulation site
processing	use in oil-based fluids (large site)
private use	use in emulsifiable fluids
recovery	use in emulsifiable fluids – intermittent release
USE PATTERN 8	Use in metal cutting/working fluids
processing	use in oil-based fluids (small site)
USE PATTERN 9	Use in leather fat liquors
formulation	formulation site
processing	use - complete processing of raw hides
private use	use – processing of 'wet blue'
USE PATTERN 10	Use in carbonless copy paper
recovery	paper recycling

Appendix B Estimated vapour pressures for C_{14-17} chlorinated paraffins

Vapour pressures have been estimated for each combination of number of carbon atoms and number of chlorine atoms for the medium chain-chlorinated paraffins. The results are shown in **Table B1**. The QSAR used is that determined for the short-chain (C_{10-13}) chlorinated paraffins by Drouillard et al. (1998)[13]:

$$\log (\text{vapour pressure}) = -(0.353 \cdot \text{no. of C atoms}) - (0.645 \cdot \text{no. of Cl atoms}) + 4.462$$

where the vapour pressure units are Pa at 25°C.

Table B1 Estimated vapour pressures for medium-chain chlorinated paraffins

No. carbon atoms	No. chlorine atoms	No. hydrogen atoms	Molecular weight	%Cl	Vapour pressure (Pa)
14	1	29	232.5	15.3	0.074989421
14	2	28	267	26.6	0.016982437
14	3	27	301.5	35.3	0.003845918
14	4	26	336	42.3	8.70964E-04
14	5	25	370.5	47.9	1.97242E-04
14	6	24	405	52.6	4.46684E-05
14	7	23	439.5	56.5	1.01158E-05
14	8	22	474	59.9	2.29087E-06
14	9	21	508.5	62.8	5.18800E-07
14	10	20	543	65.4	1.17490E-07
14	11	19	577.5	67.6	2.66073E-08
14	12	18	612	69.6	6.02560E-09
14	13	17	646.5	71.4	1.36458E-09
14	14	16	681	73.0	3.09030E-10
15	1	31	246.5	14.4	0.033265955
15	2	30	281	25.3	0.007533556
15	3	29	315.5	33.8	0.001706082
15	4	28	350	40.6	3.86367E-04
15	5	27	384.5	46.2	8.74984E-05
15	6	26	419	50.8	1.98153E-05
15	7	25	453.5	54.8	4.48745E-06
15	8	24	488	58.2	1.01625E-06
15	9	23	522.5	61.1	2.30144E-07

Table B1 continued overleaf

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[13] Drouillard K. G., Tomy G. T., Muir D. C. G. and Friesen K. J. (1998). Volatility of chlorinated n-alkanes (C_{10-12}): vapour pressures and Henry's Law constants. Environ. Toxicol. Chem., **17**, 1252-1260.

Table B1 continued Estimated vapour pressures for medium-chain chlorinated paraffins

No. carbon atoms	No. chlorine atoms	No. hydrogen atoms	Molecular weight	%Cl	Vapour pressure (Pa)
15	10	22	557	63.7	5.21195E-08
15	11	21	591.5	66.0	1.18032E-08
15	12	20	626	68.1	2.67301E-09
15	13	19	660.5	69.9	6.05341E-10
15	14	18	695	71.5	1.37088E-10
15	15	17	729.5	73.0	3.10456E-11
16	1	33	260.5	13.6	0.014757065
16	2	32	295	24.1	0.00334195
16	3	31	329.5	32.3	7.56833E-04
16	4	30	364	39.0	1.71396E-04
16	5	29	398.5	44.5	3.88150E-05
16	6	28	433	49.2	8.79023E-06
16	7	27	467.5	53.2	1.99067E-06
16	8	26	502	56.6	4.50817E-07
16	9	25	536.5	59.6	1.02094E-07
16	10	24	571	62.2	2.31206E-08
16	11	23	605.5	64.5	5.23600E-09
16	12	22	640	66.6	1.18577E-09
16	13	21	674.5	68.4	2.68534E-10
16	14	20	709	70.1	6.08135E-11
16	15	19	743.5	71.6	1.37721E-11
16	16	18	778	73.0	3.11889E-12
17	1	35	274.5	12.9	0.006546362
17	2	34	309	23.0	0.001482518
17	3	33	343.5	31.0	3.35738E-04
17	4	32	378	37.6	7.60326E-05
17	5	31	412.5	43.0	1.72187E-05
17	6	30	447	47.7	3.89942E-06
17	7	29	481.5	51.6	8.83080E-07
17	8	28	516	55.0	1.99986E-07
17	9	27	550.5	58.0	4.52898E-08
17	10	26	585	60.7	1.02565E-08
17	11	25	619.5	63.0	2.32274E-09
17	12	24	654	65.1	5.26017E-10
17	13	23	688.5	67.0	1.19124E-10

Table B1 continued overleaf

Table B1 continued Estimated vapour pressures for medium-chain chlorinated paraffins

No. carbon atoms	No. chlorine atoms	No. hydrogen atoms	Molecular weight	%Cl	Vapour pressure (Pa)
17	14	22	723	68.7	2.69774E-11
17	15	21	757.5	70.3	6.10942E-12
17	16	20	792	71.7	1.38357E-12
17	17	19	826.5	73.0	3.13329E-13

Appendix C Generic level III fugacity modelling

The potential environmental distribution of medium-chain chlorinated paraffins has been studied using a generic level III fugacity model. The level III model used was a four compartment model (FUGMOD version 1, January 1992) that has been circulated for use within the OECD HPV program. The program also carries out level I and level II modelling of the substance. The model was run using the default settings in the model and the following chemical specific input data:

water solubility	0.027 mg/l
vapour pressure	0.00027 Pa
log Kow	7
degradation half-life in air	48 hours
degradation half-life in other media	very large (e.g. $1 \cdot 10^{11}$ hours)

The level III model was run four times with a nominal release rate of 1,000 kg/hour initially entering the air, soil or water compartments in different proportions.

Fugacity level I, II and III programs for OECD workshop – version 1 – January 1992

Generic parameters

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SIX COMPARTMENT FUGACITY LEVEL I CALCULATION
Properties of MCCPs


Temperature deg C                 25
Molecular mass g/mol              488
Melting point deg C               0
Fugacity ratio                    1.000E+00
Vapor pressure Pa                 .00027
Sub-cooled liquid vapor press Pa  .00027
Solubility g/m3                   .027
Solubility mol/m3                 5.533E-05
Henry's law constant Pa.m3/mol    4.88
Log octanol-water p-coefficient   7
Octanol-water partn-coefficient   1E+07
Organic C-water ptn-coefficient   4100000
Fish-water partition coefficient  500000
Air-water partition coefficient   1.969E-03
Soil-water partition coefficient  196800
Sedt-water partition coefficient  393600
Susp sedt-water partn coeffnt     1230000
Aerosol-air partition coeff       2.222222E+10
Aerosol Z value                   8964843
Aerosol density kg/m3             2000


Amount of chemical moles          204918
Amount of chemical kilograms      100000
Fugacity Pa                       5.517889E-10
Total of VZ products              3.714E+14


Phase properties and compositions
```

Phase	Air	Water	Soil solids	Sedt solids	Susp sedt	Fish
Volume m3	1.000E+14	2.000E+11	9.000E+09	1.000E+08	1.000E+06	2.000E+05
Density kg/m3	1.185413	1000	2400	2400	1500	1000
Depth m	1000	20	.1	.01		
Area m2	1E+11	1E+10	9E+10	1E+10		
Area fraction	1	.1	.9	.1		
Frn org carb			.02	.04	.2	
Z mol/m3.Pa	4.034E-04	2.049E-01	4.033E+04	8.066E+04	2.520E+05	1.025E+05
VZ mol/Pa	4.034E+10	4.098E+10	3.630E+14	8.066E+12	2.520E+11	2.049E+10
Fugacity Pa	5.518E-10	5.518E-10	5.518E-10	5.518E-10	5.518E-10	5.518E-10
Conc mol/m3	2.226E-13	1.131E-10	2.225E-05	4.450E-05	1.391E-04	5.654E-05
Conc g/m3	1.086E-10	5.518E-08	1.086E-02	2.172E-02	6.787E-02	2.759E-02
Conc ug/g	9.164E-08	5.518E-08	4.525E-03	9.049E-03	4.525E-02	2.759E-02
Amount mol	22.26015	22.6143	200272.3	4450.494	139.0779	11.30715
Amount kg	10.86295	11.03578	97732.86	2171.841	67.87003	5.517889
Amount %	1.086295E-02	1.103578E-02	97.73286	2.171841	6.787003E-02	5.517889E-03

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SIX COMPARTMENT FUGACITY LEVEL II CALCULATION  MCCPs


Emission rate of chemical mol/h   2049.18
Emission rate of chemical  kg/h   1000
Fugacity Pa                       1.725E-06
Total of VZ products              3.714E+14
Total amount of chemical mol      6.404954E+08
Total amount of chemical kg       3.125617E+08


Phase properties,compositions and rates


Phase          Air          Water        Soil solids   Sedt solids   Susp sedt     Fish
Adv.flow m3/h  1E+12        2E+08        0             2000
Adv.restime h  100          1000         0             50000
Rct halflife h 48           1E+11        1E+11         1E+11
Rct rate c.h-1 .0144375     6.93E-12     6.93E-12      6.93E-12
Fugacity Pa    1.725E-06    1.725E-06    1.725E-06     1.725E-06     1.725E-06
1.725E-06
Conc mol/m3    6.958E-10    3.534E-07    6.955E-02     1.391E-01     4.347E-01
1.767E-01
Conc g/m3      3.395E-07    1.725E-04    3.394E+01     6.788E+01     2.121E+02
8.623E+01
Conc ug/g      2.864E-04    1.725E-04    1.414E+01     2.828E+01     1.414E+02
8.623E+01
Amount mol     69576.73     70683.66     6.259745E+08  1.391054E+07  434704.5
35341.83
Amount kg      33953.44     34493.63     3.054756E+08  6788346       212135.8
17246.81
Amount %       1.086296E-02 1.103578E-02 97.73287      2.171841      6.787004E-02
5.51789E-03
D rct mol/Pa.h 5.824E+08    2.840E-01    2.515E+03     5.589E+01
D adv mol/Pa.h 4.034E+08    4.098E+07    0.000E+00     1.613E+08
Rct rate mol/h 1004.514     4.898378E-07 4.338004E-03  9.640007E-05
Adv rate mol/h 695.7673     70.68366     0             278.2109
Rct rate kg/h  490.2029     2.390408E-07 2.116946E-03  4.704324E-05
Adv rate kg/h  339.5344     34.49363     0             135.7669
Reaction %     49.02028     2.390408E-08 2.116946E-04  4.704323E-06
Advection %    33.95344     3.449363     0             13.57669


Total reaction D value        5.824E+08
Total advection D value       6.057E+08
Total D value                 1.188E+09


Output by reaction    mol/h 1004.518
Output by advection   mol/h 1044.662
Total output by reaction and advection mol/h  2049.18


Output by reaction    kg/h  490.205
Output by advection   kg/h  509.795
Total output by reaction and advection kg/h    1000


Reaction residence time  h   637614.3
Advection residence time h   613112.6
Overall residence time   h   312561.7


Bulk phase volume fractions and pure phase Z values used in Level III calculation


Phase          Volume fraction     Z  value
Air            1                   4.034E-04
 Aerosol       2.000E-11           8.965E+06

Water          .999994             2.049E-01
 Susp sedt     .000005             2.520E+05
 Fish          .000001             1.025E+05

Soil solids    .5                  4.033E+04
 Soil air      .2                  4.034E-04
 Soil water    .3                  2.049E-01

Sedt solids    .2                  8.066E+04
 Pore water    .8                  2.049E-01
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FOUR COMPARTMENT FUGACITY LEVEL III CALCULATION          MCCPs

Bulk phase properties,compositions and rates


Phase              Air           Water         Soil          Sediment      Total         Fish
Bulk vol m3        1E+14         2E+11         1.8E+10       5E+08
Density kg/m3      1.185413      1000.003      1500.237      1280
Bulk Z value       5.827E-04     1.568E+00     2.016E+04     1.613E+04
1.025E+05
Bulk VZ            5.827E+10     3.135E+11     3.630E+14     8.066E+12     3.714E+14
Emission mol/h     2049.18       0             0             0             2049.18
Emission kg/h      1000          0             0             0             1000
Fugacity Pa        1.045E-06     5.944E-07     1.335E-05     2.321E-06
5.944E-07
Conc mol/m3        6.091E-10     9.319E-07     2.691E-01     3.744E-02
6.091E-02
Conc g/m3          2.972E-07     4.547E-04     1.313E+02     1.827E+01
2.972E+01
Conc ug/g phase    2.507E-04     4.547E-04     8.754E+01     1.427E+01
2.972E+01
Conc ug/g solids   2.286E+03     4.874E+01     1.094E+02     3.806E+01
Amount mol         60905.64      186370.9      4.844276E+09  1.871971E+07  4.863243E+09
Amount kg          29721.95      90948.98      2.364007E+09  9135217       2.373262E+09
Amount %           1.252367E-03  3.832234E-03  99.60999      .3849223
Adv.flow m3/h      1E+12         2E+08         0             10000
D rct mol/Pa.h     8.413E+08     2.173E+00     2.515E+03     5.590E+01
D adv mol/Pa.h     5.827E+08     3.135E+08     0.000E+00     1.613E+08
Rct rate mol/h     879.3252      1.29155E-06   3.357083E-02  1.297276E-04  879.3589
Rct rate kg/h      429.1107      6.302765E-07  1.638257E-02  6.330706E-05  429.1271
Adv rate mol/h     609.0564      186.3709      0             374.3941      1169.821
Adv rate kg/h      297.2195      90.94899      0             182.7043      570.8729
Reaction %         42.91107      6.302766E-08  1.638257E-03  6.330706E-06
Advection %        29.72195      9.094899      0             18.27044


Residence Times h :    Overall   2373263   Reaction   5530442   Advection   4157252


Intermedia Data. Half times   Equiv flows  D values      Rates  of transport
                    h          m3/h         mol/Pa.h       mol/h         kg/h
Air to water        5.700E+02  1.216E+11    7.085E+07     7.405E+01     3.614E+01
Air to soil         8.295E+01  8.355E+11    4.869E+08     5.089E+02     2.483E+02
Water to air        1.289E+04  1.075E+07    1.685E+07     1.002E+01     4.889E+00
Water to sediment   1.724E+02  8.041E+08    1.260E+09     7.493E+02     3.656E+02
Soil to air         2.776E+08  4.493E+01    9.060E+05     1.209E+01     5.901E+00
Soil to water       6.758E+06  1.846E+03    3.722E+07     4.967E+02     2.424E+02
Sediment to water   3.461E+04  1.001E+04    1.613E+08     3.749E+02     1.829E+02
    Transport velocity parameters            m/h           m/year
         1    air side air-water MTC          5             43800
         2    water side air-water MTC        .05           438
         3    rain rate                       .0001         .876
         4    aerosol deposition velocity     6E-10         5.256E-06
         5    soil air phase diffusion MTC    .02           175.2
         6    soil water phase diffusion MTC  .00001        .0876
         7    soil air boundary layer MTC     5             43800
         8    sediment-water diffusion MTC    .0001         .876
         9    sediment deposition velocity    .0000005      .00438
        10    sediment resuspension velocity  .0000002      .001752
        11    soil water runoff rate          .00005        .438
        12    soil solids runoff rate         1E-08         .0000876
Individual process D values
Air-water diffusion (air-side)     2.017E+07      Air-water diffusion (water-side)   1.025E+08
Air-water diffusion (overall)      1.685E+07
Rain dissolution to water          204918         Aerosol deposition to water        5.378906E+07
Rain dissolution to soil           1844262        Aerosol deposition to soil         4.841015E+08
Soil-air diffusion (air-phase)     726152.3       Soil-air diffusion (water-phase)   184426.2
Soil-air diffusion (bndry layer)   1.815381E+08   Soil-air diffusion (overall)       906033.9
Water-sediment diffusion           204918
Water-sediment deposition          1.260246E+09   Sediment-water resuspension        1.613115E+08
Soil-water runoff (water)          922131.1       Soil-water runoff (solids)         3.629508E+07
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FOUR COMPARTMENT FUGACITY LEVEL III CALCULATION          MCCPs

Bulk phase properties,compositions and rates


Phase              Air            Water          Soil           Sediment        Total          Fish
Bulk vol m3        1E+14          2E+11          1.8E+10        5E+08
Density kg/m3       1.185413       1000.003       1500.237       1280
Bulk Z value       5.827E-04      1.568E+00      2.016E+04      1.613E+04
1.025E+05
Bulk VZ            5.827E+10      3.135E+11      3.630E+14      8.066E+12       3.714E+14
Emission mol/h     0              2049.18        0              0               2049.18
Emission kg/h      0              1000           0              0               1000
Fugacity Pa        1.834E-08      2.145E-06      2.343E-07      8.373E-06
2.145E-06
Conc mol/m3        1.069E-11      3.362E-06      4.724E-03      1.351E-01
2.197E-01
Conc g/m3          5.217E-09      1.641E-03      2.305E+00      6.591E+01
1.072E+02
Conc ug/g phase    4.401E-06      1.641E-03      1.536E+00      5.150E+01
1.072E+02
Conc ug/g solids   4.013E+01      1.759E+02      1.921E+00      1.373E+02
Amount mol         1068.986       672364.8       8.502434E+07   6.753454E+07    1.532323E+08
Amount kg          521.6651       328114         4.149188E+07   3.295686E+07    7.477738E+07
Amount %           6.976243E-04   .4387878       55.48721       44.0733
Adv.flow m3/h      1E+12          2E+08          0              10000
D rct mol/Pa.h     8.413E+08      2.173E+00      2.515E+03      5.590E+01
D adv mol/Pa.h     5.827E+08      3.135E+08      0.000E+00      1.613E+08
Rct rate mol/h     15.43348       4.659488E-06   5.892187E-04   4.680144E-04    15.43455
Rct rate kg/h      7.53154        2.27383E-06    2.875387E-04   2.28391E-04     7.532059
Adv rate mol/h     10.68986       672.3648       0              1350.691        2033.746
Adv rate kg/h      5.216651       328.114        0              659.1371        992.4678
Reaction %         .7531541       2.27383E-07    2.875388E-05   2.28391E-05
Advection %        .5216652       32.81141       0              65.91372


Residence Times h :    Overall   74777.38    Reaction   9927880    Advection   75344.88


Intermedia Data. Half times   Equiv flows  D values       Rates  of transport
                      h          m3/h       mol/Pa.h        mol/h        kg/h
Air to water        5.700E+02    1.216E+11    7.085E+07      1.300E+00    6.342E-01
Air to soil         8.295E+01    8.355E+11    4.869E+08      8.931E+00    4.358E+00
Water to air        1.289E+04    1.075E+07    1.685E+07      3.614E+01    1.764E+01
Water to sediment   1.724E+02    8.041E+08    1.260E+09      2.703E+03    1.319E+03
Soil to air         2.776E+08    4.493E+01    9.060E+05      2.122E-01    1.036E-01
Soil to water       6.758E+06    1.846E+03    3.722E+07      8.718E+00    4.255E+00
Sediment to water   3.461E+04    1.001E+04    1.615E+08      1.352E+03    6.600E+02
   Transport velocity parameters              m/h            m/year
       1    air side air-water MTC            5              43800
       2    water side air-water MTC          .05            438
       3    rain rate                         .0001          .876
       4    aerosol deposition velocity       6E-10          5.256E-06
       5    soil air phase diffusion MTC      .02            175.2
       6    soil water phase diffusion MTC    .00001         .0876
       7    soil air boundary layer MTC       5              43800
       8    sediment-water diffusion MTC      .0001          .876
       9    sediment deposition velocity      .0000005       .00438
      10    sediment resuspension velocity    .0000002       .001752
      11    soil water runoff rate            .00005         .438
      12    soil solids runoff rate           1E-08          .0000876
Individual process D values
Air-water diffusion (air-side)      2.017E+07     Air-water diffusion (water-side)   1.025E+08
Air-water diffusion (overall)       1.685E+07
Rain dissolution to water           204918        Aerosol deposition to water        5.378906E+07
Rain dissolution to soil            1844262       Aerosol deposition to soil         4.841015E+08
Soil-air diffusion (air-phase)      726152.3      Soil-air diffusion (water-phase)   184426.2
Soil-air diffusion (bndry layer)    1.815381E+08  Soil-air diffusion (overall)       906033.9
Water-sediment diffusion            204918
Water-sediment deposition           1.260246E+09  Sediment-water resuspension        1.613115E+08
Soil-water runoff (water)           922131.1      Soil-water runoff (solids)         3.629508E+07
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FOUR COMPARTMENT FUGACITY LEVEL III CALCULATION          MCCPs

Bulk phase properties,compositions and rates


Phase             Air           Water          Soil           Sediment       Total          Fish
Bulk vol m3       1E+14         2E+11          1.8E+10        5E+08
Density kg/m3      1.185413      1000.003       1500.237       1280
Bulk Z value      5.827E-04     1.568E+00      2.016E+04      1.613E+04
1.025E+05
Bulk VZ           5.827E+10     3.135E+11      3.630E+14      8.066E+12      3.714E+14
Emission mol/h    0             0              2049.18        0              2049.18
Emission kg/h     0             0              1000           0              1000
Fugacity Pa       4.275E-08     2.108E-06      5.429E-05      8.229E-06
2.108E-06
Conc mol/m3       2.491E-11     3.304E-06      1.095E+00      1.327E-01
2.159E-01
Conc g/m3         1.216E-08     1.612E-03      5.343E+02      6.478E+01
1.054E+02
Conc ug/g phase   1.025E-05     1.612E-03      3.561E+02      5.061E+01
1.054E+02
Conc ug/g solids  9.350E+01     1.728E+02      4.452E+02      1.350E+02
Amount mol        2490.894      660771.1       1.970603E+10   6.637004E+07   1.977307E+10
Amount kg         1215.556      322456.3       9.616545E+09   3.238858E+07   9.649256E+09
Amount %          1.259741E-05  3.341774E-03   99.66099       .3356588
Adv.flow m3/h     1E+12         2E+08          0              10000
D rct mol/Pa.h    8.413E+08     2.173E+00      2.515E+03      5.590E+01
D adv mol/Pa.h    5.827E+08     3.135E+08      0.000E+00      1.613E+08
Rct rate mol/h    35.96229      4.579144E-06   .1365628       4.599444E-04   36.09932
Rct rate kg/h     17.5496       2.234623E-06   6.664265E-02   2.244529E-04   17.61647
Adv rate mol/h    24.90895      660.7712       0              1327.401       2013.081
Adv rate kg/h     12.15557      322.4563       0              647.7716       982.3835
Reaction %        1.75496       2.234622E-07   6.664265E-03   2.244529E-05
Advection %       1.215557      32.24563       0              64.77716


Residence Times h :   Overall  9649256   Reaction   5.477408E+08   Advection   9822291


Intermedia Data. Half times   Equiv flows  D values       Rates  of transport
                    h           m3/h        mol/Pa.h       mol/h        kg/h
Air to water       5.700E+02   1.216E+11    7.085E+07      3.028E+00    1.478E+00
Air to soil        8.295E+01   8.355E+11    4.869E+08      2.081E+01    1.016E+01
Water to air       1.289E+04   1.075E+07    1.685E+07      3.552E+01    1.733E+01
Water to sediment  1.724E+02   8.041E+08    1.260E+09      2.656E+03    1.296E+03
Soil to air        2.776E+08   4.493E+01    9.060E+05      4.919E+01    2.401E+01
Soil to water      6.758E+06   1.846E+03    3.722E+07      2.021E+03    9.861E+02
Sediment to water  3.461E+04   1.001E+04    1.613E+08      1.329E+03    6.486E+02
    Transport velocity parameters            m/h            m/year
        1    air side air-water MTC           5              43800
        2    water side air-water MTC         .05            438
        3    rain rate                        .0001          .876
        4    aerosol deposition velocity      6E-10          5.256E-06
        5    soil air phase diffusion MTC     .02            175.2
        6    soil water phase diffusion MTC   .00001         .0876
        7    soil air boundary layer MTC      5              43800
        8    sediment-water diffusion MTC     .0001          .876
        9    sediment deposition velocity     .0000005       .00438
       10    sediment resuspension velocity   .0000002       .001752
       11    soil water runoff rate           .00005         .438
       12    soil solids runoff rate          1E-08          .0000876
Individual process D values
Air-water diffusion (air-side)      2.017E+07      Air-water diffusion (water-side)  1.025E+08
Air-water diffusion (overall)       1.685E+07
Rain dissolution to water           204918         Aerosol deposition to water       5.378906E+07
Rain dissolution to soil            1844262        Aerosol deposition to soil        4.841015E+08
Soil-air diffusion (air-phase)      726152.3       Soil-air diffusion (water-phase)  184426.2
Soil-air diffusion (bndry layer)    1.815381E+08   Soil-air diffusion (overall)      906033.9
Water-sediment diffusion            204918
Water-sediment deposition           1.260246E+09   Sediment-water resuspension       1.613115E+08
Soil-water runoff (water)           922131.1       Soil-water runoff (solids)        3.629508E+07
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FOUR COMPARTMENT FUGACITY LEVEL III CALCULATION          MCCPs

Bulk phase properties,compositions and rates


Phase               Air            Water          Soil           Sediment       Total          Fish
Bulk vol m3         1E+14          2E+11          1.8E+10        5E+08
Density kg/m3        1.185413       1000.003       1500.237       1280
Bulk Z value        5.827E-04      1.568E+00      2.016E+04      1.613E+04
1.025E+05
Bulk VZ             5.827E+10      3.135E+11      3.630E+14      8.066E+12      3.714E+14
Emission mol/h      1024.59        1024.59        0              0              2049.18
Emission kg/h       500            500            0              0              1000
Fugacity Pa         5.318E-07      1.369E-06      6.791E-06      5.347E-06
1.369E-06
Conc mol/m3         3.099E-10      2.147E-06      1.369E-01      8.625E-02
1.403E-01
Conc g/m3           1.512E-07      1.048E-03      6.682E+01      4.209E+01
6.847E+01
Conc ug/g phase     1.276E-04      1.048E-03      4.454E+01      3.288E+01
6.847E+01
Conc ug/g solids    1.163E+03      1.123E+02      5.568E+01      8.769E+01
Amount mol          30987.31       429367.8       2.46465E+09    4.312713E+07   2.508237E+09
Amount kg           15121.81       209531.5       1.202749E+09   2.104604E+07   1.22402E+09
Amount %            1.235422E-03   1.711831E-02   98.26223       1.71942
Adv.flow m3/h       1E+12          2E+08          0              10000
D rct mol/Pa.h      8.413E+08      2.173E+00      2.515E+03      5.590E+01
D adv mol/Pa.h      5.827E+08      3.135E+08      0.000E+00      1.613E+08
Rct rate mol/h      447.3794       2.975519E-06   1.708003E-02   2.98871E-04    447.3968
Rct rate kg/h       218.3211       1.452053E-06   8.335053E-03   1.45849E-04    218.3296
Adv rate mol/h      309.8731       429.3678       0              862.5425       1601.783
Adv rate kg/h       151.2181       209.5315       0              420.9207       781.6703
Reaction %          21.83212       1.452053E-07   8.335053E-04   1.458491E-05
Advection %         15.12181       20.95315       0              42.09208


Residence Times h :   Overall   1224020   Reaction   5606293   Advection   1565903


Intermedia Data. Half times  Equiv flows  D values      Rates  of transport
                        h        m3/h       mol/Pa.h       mol/h        kg/h
Air to water        5.700E+02    1.216E+11   7.085E+07     3.767E+01    1.839E+01
Air to soil         8.295E+01    8.355E+11   4.869E+08     2.589E+02    1.263E+02
Water to air        1.289E+04    1.075E+07   1.685E+07     2.308E+01    1.126E+01
Water to sediment   1.724E+02    8.041E+08   1.260E+09     1.726E+03    8.424E+02
Soil to air         2.776E+08    4.493E+01   9.060E+05     6.152E+00    3.002E+00
Soil to water       6.758E+06    1.846E+03   3.722E+07     2.527E+02    1.233E+02
Sediment to water   3.461E+04    1.001E+04   1.615E+08     8.636E+02    4.215E+02
   Transport velocity parameters              m/h          m/year
       1    air side air-water MTC            5            43800
       2    water side air-water MTC          .05          438
       3    rain rate                         .0001        .876
       4    aerosol deposition velocity       6E-10        5.256E-06
       5    soil air phase diffusion MTC      .02          175.2
       6    soil water phase diffusion MTC    .00001       .0876
       7    soil air boundary layer MTC       5            43800
       8    sediment-water diffusion MTC      .0001        .876
       9    sediment deposition velocity      .0000005     .00438
      10    sediment resuspension velocity    .0000002     .001752
      11    soil water runoff rate            .00005       .438
      12    soil solids runoff rate           1E-08        .0000876
Individual process D values
Air-water diffusion (air-side)      2.017E+07    Air-water diffusion (water-side)   1.025E+08
Air-water diffusion (overall)       1.685E+07
Rain dissolution to water           204918       Aerosol deposition to water        5.378906E+07
Rain dissolution to soil            1844262      Aerosol deposition to soil         4.841015E+08
Soil-air diffusion (air-phase)      726152.3     Soil-air diffusion (water-phase)   184426.2
Soil-air diffusion (bndry layer)    1.815381E+08 Soil-air diffusion (overall)       906033.9
Water-sediment diffusion            204918
Water-sediment deposition           1.260246E+09 Sediment-water resuspension        1.613115E+08
Soil-water runoff (water)           922131.1     Soil-water runoff (solids)         3.629508E+07
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Appendix D Analytical methods used to determine C_{14-17} chlorinated paraffins in environmental media

Several studies have been undertaken to measure the levels of chlorinated paraffins in water and sediment. However, the analyses are complicated by the fact that there are a wide number of possible chlorinated paraffins (of different carbon chain length, degrees of chlorination and position of the chlorine atoms along the carbon chain) present in any given commercial product. Thus, care has to be taken when comparing the results of one survey with those of another, since different reference compounds may have been used and hence different chemical species may have been measured. The main analytical methods used for determining the concentrations of C_{14-17} chlorinated paraffins in environmental samples are discussed in the following paragraphs. The methods have been referred to by the author names that appear in the sections on environmental levels in the main part of the report. The results from all the methods used are dependent to some extent on the substance(s) used as reference.

Campbell and McConnell, 1980

This method combines solvent extraction/partition, column chromatography and finally TLC with argentation. Quantitation is by visual comparison of the intensity of the TLC 'spot' with those from standards. The intensity of the spot is chlorine dependent and so, in order to err on the high side of the possible concentration, a low chlorine content paraffin e.g. 42-45% wt. Cl, is used as reference. The method is relatively insensitive to chemical structure and cannot distinguish between short-chain (C_{10-13}) and medium-chain (C_{14-20}) chlorinated paraffins. This method, therefore, is likely to detect all medium-chain chlorinated paraffins present in a sample, but may overestimate the concentration.

Murray et al., 1987a and b

This method is based on a gas chromatography/mass spectrometry (GC-MS) method using negative chemical ionisation (NCI). The analysis is carried out by monitoring selected mass ranges of the mass spectrum for ions indicative of chlorinated paraffins. The mass ranges scanned for medium-chain chlorinated paraffins are 399-419, 439-453, and 475-487 amu. The commercial product, Paroil 152 (C_{14-17}, 50-60% Cl), was used as reference material. This method is reasonably specific for medium-chain chlorinated paraffins, but will only identify the components which give rise to ions in the mass spectrometer in the ranges scanned.

Ballschmiter, 1994

This method also uses gas chromatography/mass spectrometry with negative chemical ionisation, and is similar to that of Murray et al. (1987a and b). In this case the following masses were monitored in the mass spectrum: m/z = 402 and 404 ($C_{14}H_{24}Cl_6$, 56% Cl), 416 and 418 ($C_{15}H_{26}Cl_6$, 51% Cl), 436 and 438 ($C_{14}H_{23}Cl_7$, 57%). Again, the method will only detect components that give rise to ions in the mass spectrometer in these ranges. Hordaflex SP (C_{14-17}, 56% Cl) was used as reference. This method was used for the results obtained in 1994 and is reasonably specific for medium-chain chlorinated paraffins. The 1987 data reported for some areas of Germany were apparently obtained using a different analytical method, involving a hydrogenation/dehydrochlorination step (similar to ICI, 1992); however few other details are available.

Jansson et al., 1993

This method is based on GC-MS with NCI. The method does not appear to distinguish between chlorinated paraffins of different chain length and uses Dechlorane as an internal standard and several unspecified commercial chlorinated paraffin products as reference compounds. The method can probably be considered to give an approximation of the concentration of total (i.e. short-, medium and long-chain length) chlorinated paraffins present in a sample.

Environment Agency Japan, 1991

Very few experimental details are given. It is probably based on a GC-MS technique, but no indication is given as to what types of chlorinated paraffin were measured. Again, the method can probably be considered to give an approximation of the concentration of total chlorinated paraffins present in a sample.

ICI, 1992

This method uses on-column reduction of the chlorinated paraffins to the parent hydrocarbon using palladium/hydrogen, followed by quantification using gas chromatography. Calibration uses known mixtures of paraffins or chlorinated paraffins. Preliminary work-up of samples involved separation of water and suspended solids, then extraction and cleanup of each phase followed by gel permeation separation of the chlorinated paraffin components. The method takes no allowance for chlorine content and an average value of 50% is assumed for calibration purposes, thus the method may slightly underestimate the chlorinated paraffin concentration if high chlorine content material is present. This method will, however, unambiguously identify the presence of C_{14-17} chlorinated paraffins, provided any interfering n-paraffins are removed from the sample prior to analysis.

Greenpeace, 1995

The method used is similar to the ICI, 1992 method above. After sample cleanup, the analysis was carried out using on-column reduction to the parent hydrocarbon, followed by GC-MS quantification of the parent hydrocarbon. The masses used for quantification were m/z = 57, 71, 85 and 99. A range of alkanes between C_{10} and C_{24} were used as external standards, with cyclododecane being used as an internal standard. The total chlorinated paraffin contents were calculated as from the measured alkane concentrations assuming an average chlorine content of 50%. The method could distinguish between individual chlorinated paraffins with different carbon chain lengths, thus the concentration of C_{14}, C_{15}, C_{16} and C_{17} chlorinated paraffins could be determined separately. Again, this method may slightly underestimate the chlorinated paraffin concentration if high chlorine content material is present, and may also be subject to interference from other alkanes present in the sample if they were not removed sufficiently in the sample clean-up stage. There is no information available on the efficiency of the sample clean-up steps employed.

As this method was used to determine the levels of medium-chain chlorinated paraffins in breast milk (which is considered in detail in the human health risk assessment) Industry have commissioned an independent critique of this method (A. J. Hanley. 1995 Greenpeace Report on Chloroparaffins in the Environment. LGC (North West) Ltd. Report Number LGCNW4613, May 2002). The report concluded that there was a need for more work to be done on the validation of this analytical method since, although differentiating between various types of chlorinated paraffins, it does not specifically detect chlorinated paraffins and so would be subject to interferences from any alkanes of similar backbone to the chlorinated paraffins present in the

sample. In addition it was concluded that more information was needed on the robustness of the method particularly with regard to the results of method blanks, the lifetime of the catalyst used in the reduction and the effectiveness of the sample clean-up method. This needs to be addressed along with the accuracy and precision of the method in order to fully validate the method. The report also indicated that the relatively limited sample size used in this study makes it difficult to make informed judgements on the levels and occurrence of medium-chain chlorinated paraffins in breast milk samples throughout Europe.

Schmid and Müller, 1995

Analysis was carried out using a GC method with a NCI/mass spectrometer detector. The masses used for quantification were $m/z = 416$ and 430 and $m/z = 465$ and 487. Results were expressed in terms of equivalents to a commercial C_{14-18}, 52% Cl chlorinated paraffin (Witachlor 352), assuming that the masses chosen for detection were representative of the chlorinated paraffins present in the samples and also the commercial chlorinated paraffin used as standard.

Rieger and Ballschmiter, 1995

Sample clean-up using a silica-gel column was employed. Hordaflex 60 (C_{10-13}, 62% Cl) was used as a standard (as only peaks corresponding to C_{10-13} chlorinated paraffins were detected). Analysis was carried out using GC-ECD (electron capture detector) and GC-MS with negative chemical ionisation. The following masses were monitored in the analysis: $m/z = 402$ and 404 ($C_{14}H_{24}Cl_6$); 416 and 418 ($C_{15}H_{26}Cl_6$); 436 and 438 ($C_{14}H_{23}Cl_7$). The method is similar to that used by Ballschmiter (1994) and Murray et al. (1987a and b).

CEFAS, 1999

A gas chromatography-mass spectrometry (GC-MS) method using negative ion chemical ionisation (NCI) was used for the analysis. Several commercial short- and medium-chain commercial products were used for identification and quantification. The ion fragmentation patterns of commercial formulations where highly dependent on the instrumental conditions but featured characteristic ion clusters that allowed some information on carbon-chain length and degree of chlorination to be obtained. This information, along with the retention characteristics of the various formulations, was used as the basis of identification of short- and medium-chain chlorinated paraffins in the environmental samples.

Both short- and medium-chain chlorinated paraffins showed characteristic ion clusters in the m/z range 70-75, corresponding to $Cl_2^{.}$ and $HCl_2^{.}$. The detector response for this mass range was used to estimate the sample concentration. Calibration curves were derived for several short- and medium-chain commercial substances, and that of the commercial substance corresponding most closely to the substances identified in the environment was used for quantification. In cases where the identity of the chlorinated paraffins found in the environment could not be identified reliably, an average response factor for 1 short-chain and 1 medium-chain chlorinated paraffin (with chlorine contents around 52-56% wt. Cl) was used. This was particularly the case with the samples of fish, benthos and earthworms, where the actual identity of the residues present were difficult to assign due to the high concentration of co-extracted lipid-soluble material.

Since accurate calibration of the method is difficult to achieve in the absence of calibration standards for each component of the commercial mixtures, the results obtained can only be considered as estimates of the concentration.

Bennie et al., 2000

Analysis was by low resolution GC-MS with NCI. The MS detector was operated in full-scan mode from m/z=300 to 550. A commercial C_{10-13}, 60% wt. Cl and C_{14-17}, 52% wt. Cl product was used as reference material. Quantitation of the samples was carried out by selected ion monitoring of a limited number of ions from the accumulated full scan (the most abundant ion cluster of the various components was used for quantification and the next most abundant cluster of the various components was used for confirmation). The paper indicates that the method used, as it uses low resolution mass spectrometry, may be more subject to interferences from other substances than some of the other methods.

van Zeijl, 1997

The chlorinated paraffin-containing extracts were fractionated using High Performance Liquid Chromatography (HPLC) with gel permeation columns. The analysis was then carried out on the chlorinated paraffin fractions using GC-MS with electron capture negative ionisation. The following negative ions clusters were monitored in the analyses: m/z –35 and –37 (corresponding to Cl^-); m/z –70 and –72 (corresponding to Cl_2^-) and m/z –71 and –73 (corresponding to HCl_2). There are few details of the compounds used for analytical standards. A range of technical products appear to have been studied and the product whose mass spectra resembled that of the sample most closely appears to have been used for quantification. This appears to have been a C_{22-26}, 42% wt. Cl product as the majority of the chlorinated paraffins found were thought to be long-chain length chlorinated paraffins. The report indicates that the choice of the reference compound was important as the detector responses were found to vary by about 1 order of magnitude between the various products studies.

Metcalf-Smith et al., 1995

The method is similar to Bennie et al., 2000.

Summary

As can be seen from the above discussion, there are potential problems with all the methods used. Most of the methods are likely to provide a rough estimate of the concentration of medium-chain chlorinated paraffin, although some methods may not detect all the medium-chain length chlorinated paraffins present in a sample. The choice of the standard/reference compound used for quantification is important in these analysis, because if the composition of the reference compound is significantly different from that of the substance in the environment, then substantial errors could be introduced into the analysis and also mis-identification of the type of chlorinated paraffin present could occur. Thus the analytical methods should all be treated as giving only approximate concentrations in environmental samples.

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Appendix E Assessment of possible replacement of short-chain chlorinated paraffins with medium-chain chlorinated paraffins

Introduction

The current risk assessment report for short-chain chlorinated paraffins (CAS No: 85535-84-8) recommended that risk reduction measures should be undertaken for two uses. The uses were formulation and use in metal cutting/working fluids and formulation and use in leather treatment (fat liquors).

Draft risk reduction strategies have been developed for these two areas. In both cases marketing and use restrictions were recommended, and it was identified that the medium-chain chlorinated paraffins could be used as an alternative in these applications. This Appendix considers the possible effects of replacement of the short-chain by the medium-chain chlorinated paraffins in these applications.

Quantities and trends

The available data on the amounts of both short-chain and medium-chain chlorinated paraffins used in the EU in these applications are given in **Table E.1**.

Table E.1   Trends in use of chlorinated paraffins in the EU

Use	Year	Quantity of chlorinated paraffin supplied in EU (t/year)		
		Short-chain	Medium-chain	Total
Metal cutting/working fluids	1989	11,300[a]		
	1990	10,050[a]		
	1991	8,350[a]		
	1992	7,300[a]		
	1993	6,150[a]; 7,510[c]		
	1994	9,380[b]; 8,690[c]	2,611[b]	11,301-11,991
	1995	8,502[c]; 8,490[c]	2,765[b]	11,255-11,267
	1996		3,302[b]	
	1997		5,953[b]	
	1998		increased[d]	
Leather treatment (fat liquors)	1994	390[b]	1,614[b] (ca 807)	2,004 (ca 1,000)
	1995		1,270[b] (ca 635)	
	1996	decreased[d]	1,172[b] (ca 586)	decreased[d]
	1997		1,048[b] (ca 524)	
	1998		decreased[d]	

a)   Figures refer to UK, Ireland and continental Western Europe, excluding Italy.
b)   CEFIC data for amounts supplied to the EU. For leather treatment, around 50% of the chlorinated paraffin supplied is exported from the EU after the formulation stage. The figures given in brackets represent the amount of chlorinated paraffin taking into account these exports.
c)   Reported in RPA, 1996 (figures for EU (excluding Luxembourg)).
d)   Figures known but considered as confidential information

Metal working/cutting fluids

The available data indicate that in 1994, a combined total of around 12,000 t/year of short and medium-chain chlorinated paraffins were used in this application in the EU. Before this date, the available information indicates that there was a general decrease in the amounts of chlorinated paraffin used in this application. Since this time, there has been a rapid increase in the amounts of medium-chain chlorinated paraffin used. This increase is most probably due to a move from the short-chain to medium-chain chlorinated paraffins for this application, rather than an increase in the total amounts of chlorinated paraffins used.

The draft risk reduction strategy on short-chain chlorinated paraffins (RPA, 1996) indicates that medium-chain chlorinated paraffins are most likely to be the preferred alternative for neat oil applications. With emulsion-based fluids, the majority of users are expected to move to chlorine-free alternatives, due to concerns over the stability of the fluid, although medium-chain chlorinated paraffins may also be used.

The individual members of Euro Chlor have voluntarily agreed to reduce the use of short-chain chlorinated paraffins in metal cutting fluids to the following timetable: 80% reduction in use (from 1993 levels) by 1997, and elimination in use by year 2000.

The switch to medium-chain chlorinated paraffins as replacements for the short-chain chlorinated paraffin may result in some changes in the fluid formulation for a given application. This arises because the relationship between chlorine content and viscosity is slightly different for the two groups of additives. For a given chlorine content, the medium-chain chlorinated paraffin generally has a higher viscosity than the short-chain chlorinated paraffin. Two important considerations in the formulation of metal cutting/working fluids are viscosity and chlorine content of the fluid. Thus, if short-chain chlorinated paraffins are replaced by medium-chain length chlorinated paraffins two approaches can be taken. Firstly for a given application, a medium-chain chlorinated paraffin of similar chlorine content to, but higher viscosity than, the short-chain chlorinated paraffin can be used. In this case, in order to maintain the viscosity of the final fluid, the base oil may have to be reformulated. The second approach would be to use a medium-chain chlorinated paraffin of similar viscosity (and hence lower chlorine content) as the short-chain chlorinated paraffin. In this case, the chlorine content of the fluid would be lower than the fluid containing short-chain chlorinated paraffin and so the result is that higher concentrations of medium-chain chlorinated paraffins (up to 10% by weight rather than the typical level of 5% by weight) may have to be used in the fluids (RPA, 1996).

In order to take into account the possible replacement of short-chain chlorinated paraffins by medium-chain chlorinated paraffins, it can be assumed as a worst case that the total usage of medium-chain chlorinated paraffins could reach a total of around 12,000 t/year (the sum of medium- and short-chain chlorinated paraffins for this use in 1994). This should represent the likely foreseeable maximum usage of medium-chain chlorinated paraffins in this area as other non-chlorinated alternatives for short-chain chlorinated paraffins may be used, particularly in emulsifiable fluids (RPA, 1996).

In addition, the effects of a possible increase in concentration of the chlorinated paraffin in the fluid from around 5% to 10% will also need to be taken into account.

Leather fat liquors

The draft risk reduction strategy for short-chain chlorinated paraffins (RPA. 1997) indicated that the following substances could possibly be used as alternatives if marketing and use restrictions were applied:

- medium-chain chlorinated paraffins (and also longer chain length chlorinated paraffins);
- animal oils (usually derived from beef tallow);
- vegetable oils (e.g. corn, soya, palm and to some extent rapeseed).

It is clear from the available data reported in **Table E1** that there is a general decrease in the amounts of chlorinated paraffins used in leather fat liquors in the EU. Further, the medium-chain length chlorinated paraffins are much more commonly used that the short-chain length chlorinated paraffins in this application. If all the short-chain were replaced by medium-chain chlorinated paraffins, then the amount supplied for formulation may reach around 2,000 t/year, with around 1,000 t/year of this being subsequently applied to leather in the EU. These figures relate to 1994, and represent the highest usage in recent years. These figures are likely to represent the foreseeable upper limit of the amount of medium-chain chlorinated paraffin used in this application, as it is clear that a decline in use of both medium- and short-chain chlorinated paraffins is occurring.

Effect on predicted environmental concentrations

Environmental releases for regional and continental modelling

Using the extrapolated use figures above, and the release factors detailed in the main report, the following releases to the environment can be estimated:

Metal cutting/working fluids

Assuming a total usage of 12,000 t/year of medium-chain chlorinated paraffins and the same split between oil-based and emulsion fluids as in the main report, gives around 8,060 t/year in oil-based fluids and 3,940 t/year in emulsion fluids, then the following releases can be estimated:

- Formulation of fluids:
- Quantity of medium-chain chlorinated paraffins used = 12,000 t/year
- Release to the environment = 0.25% to waste water
- Total EU release = 30 t/year to waste water
- Regional release = 3 t/year to waste water
- Continental release = 27 t/year to waste water

- Use in Emulsifiable fluids:
- Quantity of medium-chain chlorinated paraffins used = 3,940 t/year
- Release to the environment = 50% to waste water
- Total EU release = 1,970 t/year to waste water
- Regional release = 197 t/year to waste water
- Continental release = 1,773 t/year to waste water

- Use in Oil-based fluids:
- Quantity of medium-chain chlorinated paraffins used = 8,060
- Release to the environment =4% (large/medium facility with swarf reprocessing) to waste water
  =18% (small and medium sized facilities with no swarf reprocessing) to waste water
- Fraction of total use in large/medium facilities = 60%
- Fraction of total use in medium/small facilities = 40%

- Total EU release to environment = $8,060 \cdot ((0.04 \cdot 0.6)+(0.18 \cdot 0.4))$ = 774 t/year to waste water
- Regional release = 77.4 t/year to waste water
- Continental release = 696.6 t/year to waste water

Leather fat liquors

Assuming a total usage of 2,000 t/year of medium-chain chlorinated paraffins in the formulation of leather fat liquors, with around 50% of these liquors (containing 1,000 t/year of medium chain chlorinated paraffins) in the EU, then the following releases can be estimated:

- Formulation of leather fat liquors (default calculation):

- Quantity of medium-chain chlorinated paraffins used   = 2,000 t/year

- Release to the environment   = 0.1% to air
  = 0.3% to waste water

- Total EU release   = 2.0 t/year to air
  = 6.0 t/year to waste water

- Regional release   = 0.2 t/year to air
  = 0.6 t/year to waste water

- Continental release   = 1.8 t/year to air
  = 5.4 t/year to waste water

Use of leather fat liquors:

- Quantity of medium-chain chlorinated paraffins used   = 1,000 t/year

- Release to the environment   = 2% to waste water

- Total EU release   = 20 t/year to waste water

- Regional release   = 2 t/year to waste water

- Continental release   = 18 t/year to waste water

Overall regional and continental releases

Table E.2 shows the total regional and continental releases estimated from the main report for the current usage of medium-chain chlorinated paraffins, and the estimated total taking into account the revised figures for use in metal working/cutting and leather treatment, assuming that medium-chain chlorinated paraffins will totally replace the short-chain chlorinated paraffins in these applications.

Table E.2   Revised releases for the regional and continental environment

Use	Lifestage	Estimated release from original report (current situation)[a]		Estimated release assuming replacement of short-chain by medium-chain chlorinated paraffins in metal working and leather treatment applications	
		Regional	Continental	Regional	Continental
Metal cutting/working fluids	Formulation	1,488 kg/year to water	13,875 kg/year to water	3,000 kg/year to water	27,000 kg/year to water
	Use in oil-based fluids	38,100 kg/year to water	342,900 kg/year to water	77,400 kg/year to water	696,600 kg/year to water
	Use in emulsifiable fluids	99,200 kg/year to water	892,800 kg/year to water	197,000 kg/year to water	1,773,000 kg/year to water
Leather fat liquors	Formulation	315 kg/year to water	2,829 kg/year to water	600 kg/year to water	5,400 kg/year to water
		105 kg/year to air	943 kg/year to air	200 kg/year to air	1,800 kg/year to air
	Use	1,050 kg/year to water	9,430 kg/year to water	2,000 kg/year to water	18,000 kg/year to water
All other uses	All	30,255 kg/year to water	271,748 kg/year to water	30,255 kg/year to water	271,748 kg/year to water
		16,922 kg/year to air	152,250 kg/year to air	16,922 kg/year to air	152,250 kg/year to air
Total		170,408 kg/year to water (split 119,286 kg/year to WWTP and 51,122 kg/year direct to surface water)	1,533,582 kg/year to water (split 1,073,482 kg/year to WWTP and 460,101 kg/year direct to surface water)	310,255 kg/year to water (split 217,179 kg/year to WWTP and 93,077 kg/year direct to surface water)	2,791,748 kg/year to water (split 1,954,198 kg/year to WWTP and 837,550 kg/year direct to surface water)
		17,027 kg/year to air	153,193 kg/year to air	17,122 kg/year to air	154,050 kg/year to air

a)   Figures derived in main report

Local release estimates

In this Section, the local release estimates have been re-calculated using the methods given in the main report, but based on the extrapolated use volumes for medium-chain chlorinated paraffins.

Metal working/cutting fluids

The releases estimated below are based on the same methods as used in the main report. In addition, the possible increase in the medium-chain chlorinated paraffin content from 5% (as assumed in the main assessment) to 10%, as may occur when they are used to replace short-chain chlorinated paraffins for some applications, is also taken into account.

- Formulation of fluids:
- Quantity of medium-chain chlorinated paraffins used = 12,000 t/year
- Quantity of medium-chain chlorinated paraffins used in region = 1,200 t/year
- Fraction used at one site = 1/6 = 200 t/year
- Release to the environment = 0.25% to waste water
- Number of days = 300 days/year
- Local release = 500 kg/year = 1.67 kg/day to waste water

- Use in Emulsifiable fluids:
- Concentration of chlorinated paraffin in oil phase = 10%
- Dilution rate of oil in water = 1:20 oil:water
- Weekly loss rate of fluid = 60 litres/week to waste water
- Loss rate of chlorinated paraffin = 0.30 kg/week
- Number of days = 300 days/year = 6 days/week
- Local release = 0.050 kg/day

In addition, there will be an intermittent loss of 50 kg/event of medium chain chlorinated paraffin when the whole system (10,000 litres) is replaced

- Use in Oil-based fluids:
- Concentration of chlorinated paraffin in fluid = 10%
- Amount of cutting fluid contained at large site = 50,000 litres (containing 5,000 kg of medium-chain chlorinated paraffin)
- Amount of cutting fluid contained at small site = 10,000 litres (containing 1000 kg of medium-chain chlorinated paraffin)
- Release to environment from large site = 4% to waste water
- Release to environment from small site = 18% to waste water
- Number of days = 300 days/year
- Local release (large site) = 200 kg/year = 0.67 kg/day
- Local release (small site) = 180 kg/year = 0.6 kg/day

Leather fat liquors

The local release estimates and PEC calculations will be the same as in the main report as they do not depend on the total amount of medium-chain chlorinated paraffins used in the application.

PEC$_{regional}$ and PEC$_{continental}$

The values for PEC$_{regional}$ and PEC$_{continental}$ estimated using the release data given in **Table E.2** are shown in **Table E.3**. The values for the current situation are taken from the main report.

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Table E.3 $PEC_{regional}$ and $PEC_{continental}$ for medium-chain chlorinated paraffins for the current situation and possible future increased use as a result of risk reduction measures on short-chain chlorinated paraffins

PEC	Current situation (from main report)	Possible future situation
$PEC_{regional(air)}$	$3.35 \cdot 10^{-6}$ mg/m³	$5.45 \cdot 10^{-6}$ mg/m³
$PEC_{regional(surface\ water)}$	0.39 µg/l	0.71 µg/l
$PEC_{regional(agricultural\ soil)}$	50.4 mg/kg wet wt.	91.6 mg/kg wet wt.
$PEC_{regional(sediment)}$	8.80 mg/kg wet wt.	16.0 mg/kg wet wt.
$PEC_{continental(air)}$	$1.03 \cdot 10^{-6}$ mg/m³	$1.7 \cdot 10^{-6}$ mg/m³
$PEC_{continental(surface\ water)}$	0.053 µg/l	0.096 µg/l
$PEC_{continental(agricultural\ soil)}$	5.31 mg/kg wet wt.	9.62 mg/kg wet wt.
$PEC_{continental(sediment)}$	1.21 mg/kg wet wt.	2.18 mg/kg wet wt.

From the PECs reported in **Table E3**, it can be seen that in a worst case, replacement of short-chain chlorinated paraffins by medium-chain chlorinated paraffins in metal working/cutting and leather fat liquoring applications could increase the regional concentrations by around a factor of 2.

It should be born in mind that the available monitoring data indicate that the current regional concentrations in surface water, sediment and soil are less than predicted using the EUSES model. This indicates that the actual regional emissions may be overestimated and/or the actual removal rate in the environment may be underestimated in the model used. This adds uncertainty to the predicted future concentrations.

PEC_{local}

The values obtained for the PEC_{local} for metal working/cutting use, taking into account the possible increased emissions of medium-chain chlorinated paraffins are shown below. For most of the other uses a change in the PEC_{local} may result as a consequence of the increase in the $PEC_{regional}$. The consequences of these changes are considered in later.

Metal cutting/working

The revised PEC_{local} for use in metal working fluids are as follows:

Formulation:
$PEC_{local(water)}$ = 3.81 µg/l
$PEC_{local(sediment)}$ = 48.8 mg/kg wet wt.
$PEC_{local(soil)}$ = 30.0 mg/kg wet wt.
$PEC_{fish(secondary\ poisoning)}$ = 2.15-6.45 mg/kg wet wt.
$PEC_{worm(secondary\ poisoning)}$ = 10.3 mg/kg wet wt.

Use in oil-based fluids: (large site)
$PEC_{local(water)}$ = 1.95 µg/l
$PEC_{local(sediment)}$ = 25.0 mg/kg wet wt.
$PEC_{local(soil)}$ = 13.1 mg/kg wet wt.
$PEC_{fish(secondary\ poisoning)}$ = 1.32-3.96 mg/kg wet wt.
$PEC_{worm(secondary\ poisoning)}$ = 8.9 mg/kg wet wt.

Use in oil-based fluids: (small site)	$PEC_{local(water)}$	= 1.82 µg/l
	$PEC_{local(sediment)}$	= 23.3 mg/kg wet wt.
	$PEC_{local(soil)}$	= 11.9 mg/kg wet wt.
	$PEC_{fish(secondary\ poisoning)}$	= 1.26-3.78 mg/kg wet wt.
	$PEC_{worm(secondary\ poisoning)}$	= 8.8 mg/kg wet wt.
Use in emulsifiable fluids:	$PEC_{local(water)}$	= 0.80 µg/l
	$PEC_{local(sediment)}$	= 10.2 mg/kg wet wt.
	$PEC_{local(soil)}$	= 2.63 mg/kg wet wt.
	$PEC_{fish(secondary\ poisoning)}$	= 0.81-2.43 mg/kg wet wt.
	$PEC_{worm(secondary\ poisoning)}$	= 8.01 mg/kg wet wt.
Use in emulsifiable fluids: (intermittent release)	$PEC_{local(water)}$	= 93.6 µg/l
	$PEC_{local(sediment)}$	= 1,200 mg/kg wet wt.
	$PEC_{local(soil)}$	= 93.5 mg/kg wet wt.
	$PEC_{fish(secondary\ poisoning)}$	= 1.60-4.80 mg/kg wet wt.
	$PEC_{worm(secondary\ poisoning)}$	= 15.7 mg/kg wet wt.

Effect on PEC/PNEC ratios

The effects of a total replacement of short-chain chlorinated paraffins by medium-chain chlorinated paraffins in metal working and leather uses on the PEC/PNEC ratios for all uses are considered in **Tables E4 to E7**. The current situation is taken from the main risk assessment report. The future situation includes the effects of the predicted increase in regional concentrations on the PEC/PNEC ratios for all uses.

The results shown in **Tables E.4 to E7** indicate that the biggest potential of the impact of replacement occurs on the PEC/PNECs for the aquatic (surface water, sediment, fish) compartment, with very little change predicted to occur on the PEC/PNEC for the terrestrial compartment.

For surface water and sediment, it can be seen that for many uses, the PEC is dominated by the regional contribution. The use of medium-chain chlorinated paraffins in metal cutting/working fluids is predicted to have the highest contribution to the total releases of the substance to water. In the current situation, the regional contribution to water from this use is around 81% (138,788 kg/year out of a total of 170,408 kg/year), and this is predicted to increase to around 89% (277,400 kg/year out of a total of 310,255 kg/year).

Table E4   Estimated PEC/PNEC ratios for surface water (PNEC = 1 µg/l)

Scenario	Step	Current situation using measured regional concentrations		Future situation	
		PEC (µg/l)	PEC/PNEC	PEC (µg/l)	PEC/PNEC
Production	4 Sites	0.10-0.27	0.10-0.27	0.70-0.87	0.70-0.87
Use in PVC – plastisol coating	Compounding - O	0.15	0.15	0.75	0.75
	Conversion – O	0.44	0.44	1.05	1.05
	Compounding/conversion – O	0.49	0.49	1.10	1.10
Use in PVC – extrusion/other	Compounding - O	0.27	0.27	0.88	0.88
	Compounding – PO	1.03	1.03	1.63	1.63
	Compounding – C	0.18	0.18	0.78	0.78
	Conversion – O	0.62	0.62	1.23	1.23
	Conversion – PO	0.66	0.66	1.26	1.26
	Conversion – C	0.57	0.57	1.18	1.18
	Compounding/conversion – O	0.79	0.79	1.40	1.40
	Compounding/conversion – PO	1.59	1.59	2.19	2.19
	Compounding/conversion – C	0.65	0.65	1.26	1.26
Use in plastics/rubber	Compounding	0.19	0.19	0.79	0.79
	Conversion	0.39	0.39	0.99	0.99
	Compounding/conversion	0.48	0.48	1.08	1.08
Use in sealants	Formulation and use	negligible	<1	negligible	<1
Use in paints	Formulation	0.38	0.38	0.98	0.98
	Industrial application	0.21	0.21	0.82	0.82
	Domestic application	0.10	0.10	0.71	0.71
Use in metal cutting/ working fluids	Formulation	1.64	1.64	3.81	3.81
	Use in oil-based fluids (large)	0.71	0.71	1.32[a] [1.95][b]	1.32[a] [1.95][b]
	Use in oil-based fluids (small)	0.66	0.66	1.26[a] [1.82][b]	1.26[a] [1.82][b]
	Use in emulsifiable fluids	0.15	0.15	0.75[a] [0.80][b]	0.75[a] [0.80][b]
	Use in emulsifiable fluids – intermittent release	46.6	46.6	47.1[a] [93.6][b]	47.1[a] [93.6][b]
Use in leather fat liquors	Formulation	0.29	0.29	0.89	0.89
	Use – complete processing of raw hides	1.77	1.77	2.38	2.38
	Use – processing of wet blue	6.79	6.79	7.39	7.39
Use in carbonless copy paper	Paper recycling	0.43	0.43	1.03	1.03
Regional sources		0.1	0.1	0.71	0.71

a)   Assuming a 5% medium-chain chlorinated paraffin content in the base fluid.
b)   Assuming a 10% medium-chain chlorinated paraffin content in the base fluid.

Table E5 Estimated PEC/PNEC ratios for sediment (PNEC = 5 mg/kg wet wt.)

Scenario	Step	Current situation using measured regional concentrations		Future situation	
		PEC (mg/kg wet wt.)	PEC/PNEC	PEC (mg/kg wet wt.)	PEC/PNEC
Production	4 Sites	1.28-3.46	0.26-0.70	9.0-11.2	1.8-2.2
Use in PVC – plastisol coating	Compounding - O	1.88	0.38	9.6	1.9
	Conversion – O	5.68	1.1	13.4	2.7
	Compounding/conversion - O	6.27	1.3	14.0	2.8
Use in PVC – extrusion/other	Compounding - O	3.46	0.7	11.2	2.2
	Compounding - PO	13.2	2.6	20.9	4.2
	Compounding – C	2.30	0.46	10.0	2.0
	Conversion – O	7.94	1.6	15.7	3.1
	Conversion – PO	8.45	1.7	16.2	3.2
	Conversion – C	7.30	1.5	15.1	3.0
	Compounding/conversion – O	10.1	2.0	17.9	3.6
	Compounding/conversion - PO	20.4	4.1	28.1	5.6
	Compounding/conversion - C	8.32	1.7	16.1	3.2
Use in plastics/rubber	Compounding	2.38	0.48	10.1	2.0
	Conversion	4.99	1.0	12.7	2.5
	Compounding/conversion	6.14	1.2	13.8	2.8
Use in sealants	Formulation and use	negligible	<1	negligible	<1
Use in paints	Formulation	4.86	0.98	12.6	2.5
	Industrial application	2.69	0.54	10.4	2.1
	Domestic application	1.28	0.26	9.04	1.8
Use in metal cutting/working fluids	Formulation	21.0	4.2	48.8	9.8
	Use in oil-based fluids (large)	9.09	1.8	16.9[a] [25.0][b]	3.4[a] [5.0][b]
	Use in oil-based fluids (small)	8.45	1.7	16.2[a] [23.3][b]	3.2[a] [4.7][b]
	Use in emulsifiable fluids	1.92	0.38	9.63[a] [10.2][b]	1.9[a] [2.0][b]
	Use in emulsifiable fluids – intermittent release	597	119	604[a] [1,200][b]	121[a] [240][b]
Use in leather fat liquors	Formulation	3.71	0.74	11.4	2.3
	Use – complete processing of raw hides	22.7	4.5	30.5	6.1
	Use – processing of wet blue	86.9	17.4	94.7	18.9
Use in carbonless copy paper	Paper recycling	5.50	1.1	13.2	2.6
Regional sources		0.7	0.14	16.0	3.2

a)   Assuming a 5% medium-chain chlorinated paraffin content in the base fluid.
b)   Assuming a 10% medium-chain chlorinated paraffin content in the base fluid.

Table E.6   Estimated PEC/PNEC ratios for soil (PNEC = 10.6 mg/kg wet wt.)

Scenario	Step	Current situation using measured regional concentrations		Future situation	
		PEC (mg/kg wet wt)	PEC/PNEC	PEC (mg/kg wet wt.)	PEC/PNEC
Production	4 Sites	negligible	<1	negligible	<1
Use in PVC – plastisol coating	Compounding - O	0.51	0.048	2.21	0.21
	Conversion – O	3.21	0.30	4.92	0.46
	Compounding/conversion – O	3.64	0.34	5.34	0.50
Use in PVC – extrusion/other	Compounding - O	1.64	0.15	3.34	0.32
	Compounding – PO	8.53	0.80	10.2	0.96
	Compounding – C	0.81	0.076	2.51	0.24
	Conversion – O	4.82	0.45	6.52	0.62
	Conversion – PO	5.16	0.49	6.86	0.65
	Conversion – C	4.40	0.42	6.10	0.58
	Compounding/conversion – O	6.37	0.60	8.07	0.76
	Compounding/conversion – PO	13.6	1.28	15.3	1.44
	Compounding/conversion – C	5.12	0.48	6.82	0.64
Use in plastics/rubber	Compounding	0.87	0.082	2.57	0.24
	Conversion	2.71	0.26	4.41	0.42
	Compounding/conversion	3.5	0.33	5.20	0.49
Use in sealants	Formulation and use	negligible	<1	negligible	<1
Use in paints	Formulation	2.62	0.25	4.32	0.41
	Industrial application	1.08	0.10	2.79	0.26
	Domestic application	negligible	<1	negligible	<1
Use in metal cutting/working fluids	Formulation	14.1	1.33	30.0	2.83
	Use in oil-based fluids (large)	5.66	0.53	7.36[a] [13.1][b]	0.69[a] [1.24][b]
	Use in oil-based fluids (small)	5.15	0.49	6.85[a] [11.9][b]	0.64[a] [1.12][b]
	Use in emulsifiable fluids	0.51	0.048	2.21[a] [2.63][b]	0.21[a] [0.25][b]
	Use in emulsifiable fluids – intermittent release	46	4.3	47.6[a] [93.5][b]	4.49[a] [8.82][b]
Use in leather fat liquors	Formulation	1.78	0.17	3.49	0.33
	Use – complete processing of raw hides	15.3	1.44	17.0	1.60
	Use – processing of wet blue	60.8	5.74	62.5	5.90
Use in carbonless copy paper	Paper recycling	3.02	0.28	4.76	0.45
Regional sources		0.088	0.008	91.6	8.64

a)   Assuming a 5% medium-chain chlorinated paraffin content in the base fluid.
b)   Assuming a 10% medium-chain chlorinated paraffin content in the base fluid.

Table E7   Estimated concentrations in fish and earthworms for secondary poisoning (PNEC = 0.17 mg/kg)

Scenario	Step	Current situation using measured regional concentrations				Future situation			
		Fish[c]		Earthworms		Fish[c]		Earthworms	
		PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC
Production	Site A	0.11-0.33	0.64-1.9	negligible	<1	0.77-2.31	4.5-13.6	negligible	<1
	Site B	0.15-0.45	0.88-2.6	negligible	<1	0.81-2.43	4.8-14.3	negligible	<1
	Site C	0.19-0.57	1.1-3.4	negligible	<1	0.84-2.52	4.9-14.8	negligible	<1
	Site D	0.11-0.33	0.64-1.9	negligible	<1	0.77-2.31	4.5-13.6	negligible	<1
Use in PVC – plastisol coating	Compounding - O	0.13-0.39	0.76-2.3	1.7	10.0	0.79-2.37	4.6-13.9	264	1,553
	Conversion – O	0.26-0.78	1.5-4.3	9.3	54.7	0.92-2.76	5.4-16.2	270	1,588
	Compounding/conversion - O	0.28-0.84	1.6-4.9	10.4	61.2	0.94-2.82	5.5-16.6	270	1,588
Use in PVC – extrusion/other	Compounding - O	0.19-0.57	1.1-3.4	4.8	28.2	0.84-2.52	4.9-14.8	267	1,571
	Compounding - PO	0.52-1.56	3.1-9.2	24.1	142	1.18-3.54	6.9-20.8	287	1,688
	Compounding – C	0.14-0.42	0.82-2.5	2.5	14.7	0.80-2.40	4.7-14.1	264	1,553
	Conversion – O	0.34-1.02	2.0-6.0	13.7	80.6	1.00-3.00	5.9-17.6	273	1,606
	Conversion – PO	0.36-1.08	2.1-6.4	14.7	86.4	1.02-3.06	6.0-18.0	277	1,629
	Conversion – C	0.32-0.96	1.9-5.6	12.6	74.1	0.98-2.94	5.8-17.3	273	1,606
	Compounding/conversion – O	0.42-1.26	2.5-7.4	18.1	106	1.08-3.24	6.4-19.1	280	1,647
	Compounding/conversion - PO	0.77-2.31	4.5-13.6	38.3	225	1.43-4.29	8.4-25.2	300	1,764
	Compounding/conversion - C	0.36-1.08	2.1-6.4	14.6	85.9	1.01-3.03	5.9-17.8	277	1,629
Use in plastics/rubber	Compounding	0.15-0.45	0.88-2.6	2.7	15.9	0.81-2.43	4.8-14.3	264	1,553
	Conversion	0.24-0.72	1.4-4.2	7.8	45.9	0.90-2.70	5.3-15.9	270	1,588

Table E7 continued overleaf

Table E7 continued   Estimated concentrations in fish and earthworms for secondary poisoning (PNEC = 0.17 mg/kg)

Scenario	Step	Current situation using measured regional concentrations				Future situation			
		Fish[c]		Earthworms		Fish[c]		Earthworms	
		PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC	PEC (mg/kg)	PEC/PNEC
	Compounding/conversion	0.28-0.84	1.6-4.9	10.0	58.8	0.93-2.79	5.5-16.4	270	1,588
Use in sealants	Formulation and use	negligible	<1	negligible	<1	negligible	<1	negligible	<1
Use in paints	Formulation	0.23-0.69	1.4-4.1	7.6	44.7	0.89-2.67	5.2-15.7	270	1,588
	Industrial application	0.16-0.48	0.94-2.8	3.3	19.4	0.82-2.46	4.8-14.5	264	1,553
	Domestic application	negligible	<1	negligible	<1	negligible	<1	negligible	<1
Use in metal cutting/working fluids	Formulation	0.80-2.40	4.7-14.1	39.7	234	2.15-6.45	12.6-37.9	339	1,994
	Use in oil-based fluids (large)	0.38-1.14	2.2-6.7	16.1	94.7	1.04-3.12[a] [1.32-3.96][b]	6.1-18.4[a] [7.8-23.3][b]	277[a] [293][b]	1,629[a] [1,723][b]
	Use in oil-based fluids (small)	0.36-1.08	2.1-6.4	14.7	86.5	1.02-3.06[a] [1.26-3.78][b]	6.0-18.0[a] [7.4-22.2][b]	277[a] [290][b]	1,629[a] [1,706][b]
	Use in emulsifiable fluids	0.13-0.39	0.76-2.3	1.7	10.0	0.79-2.37[a] [0.81-2.43][b]	4.6-13.9[a] [4.8-14.3][b]	264[a] [264][b]	1,552[a] [1,552][b]
	Use in emulsifiable fluids – intermittent release	0.52-1.56	3.1-9.2	129	759	1.18-3.54[a] [1.6-4.8][b]	6.9-20.8[a] [9.4-28.2][b]	389[a] [517][b]	2,288[a] [3,041][b]
Use in leather fat liquors	Formulation	0.19-0.57	1.1-3.4	5.2	30.6	0.85-2.55	5.0-15.0	267	1,571
	Use – complete processing of raw hides	0.86-2.58	5.1-15.2	43.0	253	1.51-4.53	8.9-26.6	303	1,782
	Use – processing of wet blue	3.10-9.30	18.2-54.7	171	1,006	3.75-11.3	22.1-66.2	432	2,541
Use in carbonless copy paper	Paper recycling	0.23-0.69	1.4-4.1	8.8	51.8	0.89-2.67	5.2-15.7	270	1,588

a)   Assuming a 5% medium-chain chlorinated paraffin content in the base fluid.
b)   Assuming a 10% medium-chain chlorinated paraffin content in the base fluid.
c)   The concentration in fish is estimated using the methods outlined in the Technical Guidance Document, taking into account accumulation through the food chain. The range reflects the range for the BMF (1-3).

References

RPA (1996). Risk-benefit analysis on the use of short chain length chlorinated paraffins in cutting fluids in the metal working industry. Produced for the Department of the Environment. Risk and Policy Analysts Limited.

RPA (1997). Risk-benefit analysis on the use of short-chain chlorinated paraffins in leather processing. Stage 1 Report for the Department of the Environment, Transport and the Regions. Risk and Policy Analysts Limited.

Appendix F Estimation of waste remaining in the environment and further consideration of diffusive emissions from articles

Introduction

This Appendix considers an alternative approach to that given in the main risk assessment report to estimating the possible diffusive emissions of medium-chain chlorinated paraffins from products over their lifetimes. The basis of the approach taken here is that outlined in the November 1999 and May 2000 draft Risk Assessment Reports for di-(2-diethylhexyl) phthalate (DEHP), for which Sweden is the rapporteur country. The approach considers both losses of the substance itself over the products lifetime and also the production of any waste containing the substance that may be released to the environment over the products' lifecycle.

DEHP is the major plasticiser used in PVC, and accounts for around 51% of the total phthalate plasticiser use. In some calculations in this Appendix it is assumed that the use pattern of PVC (and other polymers) containing medium-chain chlorinated paraffins is similar to that of PVC containing DEHP. This assumption is reasonable as medium-chain chlorinated paraffins in PVC are mainly used as secondary plasticisers alongside the primary plasticisers (phthalates such as DEHP).

In order to use the data given in the DEHP report, the relative market share of PVC containing medium-chain chlorinated paraffins is needed. This can be estimated roughly as follows (the information on DEHP is taken from the May 2000 draft of the risk assessment for that substance):

> Quantity of DEHP used in PVC (and other polymers) in the EU = 462,000 t/year
> Typical DEHP content of PVC = 30%
> Estimated quantity of PVC containing DEHP produced in EU = $1.54 \cdot 10^6$ t/year

As DEHP accounts for around 51% of the phthalate plasticiser usage in PVC, the total amount of phthalate plasticised PVC produced in the EU can be estimated at approximately $3 \cdot 10^6$ t/year.

> Quantity of medium-chain chlorinated paraffins used in PVC (and other polymers) in EU = 53,973 t/year
> Typical medium-chain chlorinated paraffin of PVC = 10-15%
> Estimated quantity of PVC containing medium-chain chlorinated paraffins produced in EU = $0.36\text{-}0.54 \cdot 10^6$ t/year

Therefore, based on the above calculations, medium-chain chlorinated paraffins could be present in around 12-18% of the total PVC (or other polymers) containing plasticisers (phthalates) produced in the EU. A figure of 18% of the total plasticiser use will be used in the following Sections as a worst case.

In the draft DEHP risk assessment, the uses of flexible PVC were split between indoor and outdoor uses, with 78% of the flexible PVC used in indoor applications and 22% used in outdoor applications. This split will also be assumed to be applicable for PVC containing medium-chain chlorinated paraffins here.

It should be noted that the actual amounts of medium-chain chlorinated paraffins used in the various PVC applications considered are less well defined than is the case for DEHP. This therefore introduces further uncertainty into the emissions estimated. Information has been provided on the amounts of medium chain chlorinated paraffins used in certain applications, but the data set is incomplete (the actual final use of a large fraction of the total tonnage could not be

determined in the survey, and the applicability to the EU as a whole is uncertain) and so can only act as a guide. This information is discussed in the relevant Sections below and shows that in general the approach taken appears to be reasonable.

Estimated emissions from volatilisation from PVC

In Section 3.1.1.2.9 of the main risk assessment report, an emission figure to air for medium chain chlorinated paraffins of $5 \cdot 10^{-4}$ $\mu g/m^2/s$ was determined for volatilisation from PVC over 21 days. Assuming this emission rate remains constant with time this emission figure is equivalent to 15.8 $mg/m^2/year$. This is used here to estimate releases to the environment taking into account the surface area of products in a similar way as carried out for DEHP.

Indoor applications

PVC flooring

In the draft DEHP risk assessment the total annual production of PVC-flooring in the EU was taken as $2.3 \cdot 10^8$ $m^2/year$, with a lifetime of 20 years. If it is assumed that medium-chain chlorinated paraffins are present in 18% of the flooring, the amount of flooring containing medium-chain chlorinated paraffins produced in the EU is $4.14 \cdot 10^7$ $m^2/year$, and the total amount present in the EU is $8.28 \cdot 10^8$ m^2 assuming a 20 year life-span.

Using the emission factor of 15.8 $mg/m^2/year$ for on the total area of flooring estimated to contain medium-chain chlorinated paraffins present in the EU gives an estimated air emission of 13.1 t/year from this source.

A supplier of medium-chain chlorinated paraffins has indicated that around 20% of the total supplied for PVC applications is used in flooring. Assuming this percentage is applicable to all suppliers, the total amount of medium-chain chlorinated paraffin used PVC flooring can be estimated at around 10,700 t/year. Assuming that PVC flooring has a density of 1,300 kg/m^3 and a thickness of 2 mm (0.002 m) (taken from the draft DEHP report), and a medium-chain chlorinated paraffin content of 10-15%, the total annual surface area of PVC-flooring containing medium-chain chlorinated paraffins can be estimated as $2.7\text{-}4.1 \cdot 10^7$ $m^2/year$, or a total surface area present in the EU of $5.4\text{-}8.2 \cdot 10^8$ m^2 over a 20 year lifetime. This is in good agreement with the figure estimated above and leads to an estimated air emission of 8.5-13.0 t/year using the same emission factor as above.

Further information has also been provided to indicate that around 50-60% of cushion vinyl flooring is coated with polyurethane in order to improve the wear resistance and stain resistance of the product. This coating will obviously affect the potential for volatilisation of medium-chain chlorinated paraffins from the product but no information is available on this. If it is assumed that 50% of the PVC flooring has this type of coating, and the coating reduces the emission rate by a factor of 10, then the estimated air emission for medium-chain chlorinated paraffins would be of the order of 5.1-7.8 t/year.

Vinyl wall covering

In the draft DEHP risk assessment the total annual production of vinyl wall covering in the EU was taken as $4 \cdot 10^8$ $m^2/year$, with a lifetime of 7 years. If it is assumed that medium-chain chlorinated paraffins are present in 18% of the wall covering, the total amount of wall covering containing medium-chain chlorinated paraffins present in the EU = $4 \cdot 10^8 \cdot 7 \cdot 0.18 = 5.0 \cdot 10^8$ m^2.

Using the emission factor of 15.8 mg/m^2/year for medium-chain chlorinated paraffins, gives an estimated air emission of 7.9 t/year from this source.

A supplier of medium-chain chlorinated paraffins has indicated that around 11% of the total supplied for PVC applications is used in wall coverings. Assuming this percentage is applicable to all suppliers, the total amount of medium-chain chlorinated paraffin used in PVC wall coverings can be estimated at around 5,900 t/year. Assuming that PVC wall covering has density of 1,300 kg/m^3 (taken from the draft DEHP report), a thickness of 0.5 mm (0.005 m; estimate) and a medium-chain chlorinated paraffin content of 10-15%, the total annual surface area of PVC-wall covering containing medium-chain chlorinated paraffins can be estimated as 6.0-9.0 · 10^7 m^2/year or a total of 4.2-6.4 · 10^8 m^2 over a 7 year lifetime. This is in good agreement with the figure estimated above, and leads to an estimated air emission of 6.6-10.0 t/year from this source using the same emission factor as above.

Coated products, film and sheet

In the draft DEHP risk assessment the relevant statistics for the production of coated products, film and sheet (e.g. upholstery, packaging, stationary products, luggage, clothing etc.) containing phthalate plasticisers could not be obtained. Instead the worst case assumption of 40 t/year for total phthalate emissions from these products as determined by the European Council for Plasticisers and Intermediates (ECPI, 1996) was used as the basis of the release estimate. This estimate was based on a product lifetime of 7 years.

If it is assumed that medium-chain chlorinated paraffins are present in 18% of these products and that the emission rate is similar to that of the phthalates present, then an air emission of 7.2 t/year for medium-chain chlorinated paraffins can be estimated from this source.

Information provided from a supplier of medium-chain chlorinated paraffins indicates that around 6.6% of the total supplied for PVC applications is used in textiles and coated products. Assuming that this percentage is applicable to all suppliers, the total amount of medium-chain chlorinated paraffins used in this type of product can be estimated at around 3,600 t/year. It is not possible to relate this figure the information reported above for DEHP. As a rough approximation, assuming a density of PVC of 1,300 kg/m^3, an average thickness for this type of product of 1 mm (0.001m) and a 10-15% medium-chain chlorinated paraffin content, the annual surface area for this type of product containing medium-chain chlorinated paraffins produced each year can be estimated at 1.8-2.7 · 10^7 m^2/year. This should be considered a very crude estimate as the actual thickness of products in this group could be very variable. Assuming the products have a 7 year lifetime, the total surface area present in the EU is 1.3-1.9 · 10^8 m^2. Using the emission factor of 15.8 mg/m^2/year for on the total area estimated to contain medium-chain chlorinated paraffins present in the EU gives an estimated air emission of t/year from this source of 2-3 t/year. This figure also assumes that emissions only occur from one side of the products. If emissions occur from both sides, then the surface area figures, hence release figures, would be doubled i.e. 4-6 t/year. This is of a similar order to the value obtained above based on the DEHP data. No distinction is made here in the amounts of these products used from indoor and outdoor applications, although it is likely that most are used in indoor applications.

Cable

In the draft DEHP risk assessment report the relevant statistics for the production of cable containing phthalate plasticisers could not be obtained. Instead the worst case assumption of 50 t/year for total phthalate emissions from these products as determined by the European

Council for Plasticisers and Intermediates (ECPI, 1996) was used as the basis of the release estimate.

If it is assumed that medium-chain chlorinated paraffins are present in 18% of these products and that the emission rate is similar to that of the phthalates present, then an air emission of 9 t/year for medium-chain chlorinated paraffins can be estimated from this source.

Information provided from a supplier of medium-chain chlorinated paraffins indicates that around 17% of the total supplied for PVC applications is used in cable products. Assuming that this percentage is applicable to all suppliers, the total amount of medium-chain chlorinated paraffins used in this type of product can be estimated at around 9,200 t/year. It is not possible to relate this figure the information reported above for DEHP. Assuming a density of PVC of 1,300 kg/m^3, and average thickness for this type of product of 1.5 mm (0.0015m; taken from draft DEHP assessment) and a 10-15% medium-chain chlorinated paraffin content, the annual surface area for this type of product containing medium-chain chlorinated paraffins produced each year can be estimated at $3.1\text{-}4.7 \cdot 10^7 \, \text{m}^2$/year. Assuming the products have a 30 year lifetime (from DEHP report), the total surface area present in the EU is $9.3\text{-}14.1 \cdot 10^8 \, \text{m}^2$. Cabling can be used in both indoor and outdoor applications. In the draft DEHP risk assessment, the overall split of PVC applications between indoor and outdoor was 78%:22%. The actual split for cabling is unknown and so this split will be assumed to apply here. This gives the total surface area of cabling present in indoor applications in the EU as $7.3\text{-}10.9 \cdot 10^8 \, \text{m}^2$.

Using the emission factor of 15.8 mg/m^2/year for on the total area estimated to contain medium-chain chlorinated paraffins present in the EU gives an estimated air emission from this source of 11.5-16.7 t/year. This is of a similar order to the value obtained above based on the DEHP data. Emissions from outdoor cabling applications are considered later.

Hose and profile

In the draft DEHP risk assessment report the relevant statistics for the production of hose and profile containing phthalate plasticisers could not be obtained. Instead it was assumed that, as the surface to volume ratio and lifetime were similar to PVC-flooring, the overall releases of DEHP would be similar to flooring. The relative amounts of DEHP used in flooring:profile/hose (74,708 t/year:55,911 t/year or 1.34:1) was used to scale the estimated emissions from PVC flooring to give an estimate from this use.

If it is assumed that medium-chain chlorinated paraffins are present in PVC-flooring and hoses/profile in a similar ratio to found for DEHP (i.e. 1.34:1) the releases to air from this application can be estimated using the above scaling factor from those estimated for medium-chain chlorinated paraffin in PVC-flooring. Thus the estimated release to air of medium-chain chlorinated paraffins is 13.1/1.34 = 9.8 t/year.

No information is available on the actual amounts of medium-chain chlorinated paraffins used in these applications.

Outdoor applications

The draft risk assessment report on DEHP provided estimated figures for the emitting surface areas for various outdoor PVC products produced each year containing DEHP. These are shown below, along with the estimated lifetimes of the product. These figures were estimated from the known DEHP yearly consumption in these applications and applying a 'surface correction factor' to convert the consumption figures to an annual surface area produced figure. Since

DEHP accounts of around 51% of the total phthalate plasticiser use in PVC, the surface area of all flexible (phthalate plasticised) PVC produced each year in these applications will be around twice the values given.

Annual emitting surface area Lifetime
(based on DEHP annual production)

car undercoating	3,703,700 m^2/year	12 year
roofing material	529,100 m^2/year	20 year
coil coating	26,455,000 m^2/year	10 year
fabric coating	22,222,200 m^2/year	10 year
cable and wires (above ground)	2,116,400 m^2/year	30 year
cable and wires (buried)	8,465,600 m^2/year	30 year
hoses and profiles	1,587,300 m^2/year	10 year
shoe soles	3,174,600 m^2/year	5 year

Assuming medium-chain chlorinated paraffins occur in around 18% of all plasticised PVC used in the above applications and using an emission rate of 15.8 mg/m^2/year, the following emission estimates can be obtained to air for medium-chain chlorinated paraffins over the lifetime of the PVC products (emission = $2 \cdot$ annual surface area produced based on DEHP$\cdot$lifetime$\cdot 0.18 \cdot 15.8$ mg/year):

Estimated medium-chain chlorinated paraffin emission

car undercoating	{0.25 t/year}[a]
roofing material	0.060 t/year
coil coating	1.50 t/year
fabric coating	1.26 t/year
cable and wires (above ground)	0.36 t/year
cable and wires (buried)	(1.44 t/year – emissions will be to soil compartment)
hoses and profiles	0.09 t/year
shoe soles	0.09

Note: a) Medium-chain chlorinated paraffins are not thought to be used in car undercoating – calculation given only as an example.

Information on the actual amounts of medium-chain chlorinated paraffins used in various PVC applications have been provided in a survey carried out by an EU supplier. The figures are uncertain as a) they are incomplete (the actual end-use of a large proportion of the total amount was not known and b) there is some uncertainty over the applicability of the figures to the EU as a whole.

The information provided confirmed that medium-chain chlorinated paraffins were not used in car undercoating and no use in the production of roofing materials could be identified.

For the other applications, the use of medium-chain chlorinated paraffins in shoe soles was estimated to be 0.6% of the total use in PVC. Assuming this percentage applies to the total amount supplied in the EU for PVC applications, the amount of medium-chain chlorinated paraffins used in production of shoe soles each year would be around 320 t/year. Assuming that the density of PVC is 1,300 kg/m^3, the average thickness of shoe soles is 10 mm (0.01 m; taken from draft DEHP assessment) and the medium-chain chlorinated paraffin content is 10-15%, then the annual surface area of shoe soles containing medium-chain chlorinated paraffins

produced each year can be estimated as 164,000-246,000 m^2/year. Assuming a life time of 5 years, and an emission factor of 15.8 mg/m^2/year, the total air emission of medium-chain chlorinated paraffins from shoe soles can be estimated as 0.013-0.019. This is slightly lower than, but of a similar order of magnitude to, the estimate made above.

For coating applications, some figures for the actual amounts used have been provided been provided in the survey, but these have been considered in the indoor emissions earlier, as it was not possible to distinguish between indoor and outdoor applications. This lead to a similar order of magnitude estimate for the overall emissions as reported above.

No information was provided in the survey on the amounts of medium-chain chlorinated paraffins used in hoses and profiles or coil coating in outdoor applications.

For cable, information provided in the survey allowed an estimate of for the total area of PVC containing medium-chain chlorinated paraffin to be made as $9.3\text{-}14.1 \cdot 10^8$ m^2 to be made, with the area present in outdoor applications being around $2.0\text{-}3.1 \cdot 10^8$ m^2 (based on a 30 year lifetime and 22% of the total being used outdoors; see Section 2.1). Using the emission factor for medium-chain chlorinated paraffins of 15.8 mg/m^2/year, and assuming that 80% of the cable is deep-buried and 20% is above ground, the total emission to air of medium-chain chlorinated paraffins can be estimated as 0.63-0.98 direct to air and 2.5-3.9 t/year to soil. These values are similar to those estimated above based on the DEHP data.

Estimated emissions from leaching from PVC

Indoor applications

In these estimates it is assumed that medium-chain chlorinated paraffins have a similar potential for leaching from PVC as DEHP (see main Section 3.1.1.2.9 of main risk assessment report).

Washing clothing with PVC printing

It is not known if medium-chain chlorinated paraffins are used in this application. In the draft risk assessment report for DEHP a total EU release of DEHP from this application was estimated at 99 t/year (range 18-180 t/year), based on measurements of phthalate loss carried out in Denmark. If it is assumed that medium-chain chlorinated paraffins are used in this application, then a release of 34.7 t/year can be estimated based on the relative amounts of PVC containing DEHP and medium-chain chlorinated paraffins estimated earlier (i.e. medium-chain chlorinated paraffins may be present in 18% of the total plasticised PVC or 35% of the PVC containing DEHP). There is a large uncertainty in this figure due to uncertainties in the release rate and the relative amounts of medium-chain chlorinated paraffins used in this application (if they are used at all).

Washing PVC flooring

An emission figure for DEHP of 5 μg/dm^2 (=500 μg/m^2) per cleaning event (10 day interval) was reported in the draft DEHP risk assessment, based on experimental data from Sweden. The study was designed only to determine the leaching loss and did not include any loss due to abraded particulates.

In the draft DEHP risk assessment report the total annual production of PVC-flooring in the EU was taken as $2.3 \cdot 10^8$ m^2/year, with a lifetime of 20 years. If it is assumed that medium-chain chlorinated paraffins are present in 18% of the flooring, the total amount of flooring containing medium-chain chlorinated paraffins present in the EU = $2.3 \cdot 10^8 \cdot 20 \cdot 0.18 = 8.28 \cdot 10^8$ m^2. A

similar estimate of $5.4\text{-}8.2\cdot10^8$ m^2 is obtained using information provided by a supplier on the likely amounts of medium-chain chlorinated paraffins used in this application (see Section 1). Using the above emission figure and cleaning of the flooring once per week, the estimated emission of medium-chain chlorinated paraffin is 14.0-21.5 t/year.

Further information has also been provided to indicate that around 50-60% of cushion vinyl flooring is coated with polyurethane in order to improve the wear resistance and stain resistance of the product. This coating will obviously affect the potential for leaching of medium-chain chlorinated paraffins from the product but no information is available on this. If it is assumed that 50% of the PVC flooring has this type of coating, and the coating reduces the emission rate by a factor of 10, then the estimated leaching emission for medium-chain chlorinated paraffins would be of the order of 8.4-12.9 t/year.

The draft DEHP risk assessment report also considered abrasion loss from PVC flooring. The assessment used data from standard tests from abrasion loss that indicated about 0.1-0.15 mm (average 0.125 mm) of the surface will be worn away over the lifetime of the flooring. Assuming the flooring is typically 2 mm thick, this abrasion loss corresponds to a loss rate of around 6.25% over the lifetime of the PVC flooring or 0.31%/year. This loss was assumed to occur on all PVC flooring were walking occurred frequently and was estimated to be around 50% of the total PVC area.

Earlier, it was estimated that around $8.28\cdot10^8$ m^2 of PVC-flooring could contain medium-chain chlorinated paraffins at around 10% by weight of the PVC could be present in the EU. Assuming an initial thickness of 0.002 m (2 mm) and a representative density of around 1,200-1,300 kg/m^3 for plasticised PVC (from Draft risk assessment of DEHP), the amount of PVC containing medium-chain chlorinated paraffins in flooring can be roughly estimated as $2.15\cdot10^6$ t at any one time (assuming a 20 year lifetime). If the abrasion rate is 0.31%/year, and 50% of the available flooring is subject to abrasion, then the amount of PVC abraded as particulates is 3,333 t/year. The medium chain chlorinated paraffin could be present at up to 10% in these particulates, i.e. 333 t/year of chlorinated paraffin.

Information has been provided by a supplier of medium-chain chlorinated paraffins to indicate that around 20% of the amount used in PVC applications is in flooring. This equates to around 10,700 t/year of medium-chain chlorinated paraffins in flooring, assuming that this percentage is applicable to the total amount supplied to the EU. Using the same assumptions as above (a 20 year lifetime, abrasion rate of 0.31%/year and 50% of the available flooring is subject to abrasion), then the amount of medium-chain chlorinated paraffins lost in particulates is around 332 t/year. This is in very good agreement with the above figure. Again, it also needs to be taken into account that around 50-60% of cushion vinyl flooring is coated with polyurethane which will reduce the wear rate of the product, and hence emission of medium-chain chlorinated paraffin. No information is available on this but if it is assumed that 50% of the PVC flooring has this type of coating, and the coating reduces the wear rate/emission factor by a factor of 10, then the estimated air emission for medium-chain chlorinated paraffins would be of the order of 200 t/year.

These particulates are likely to end up in waste water (by washing) or landfill (by cleaning methods not involving water). In the May 2000 draft of the DEHP risk assessment, it was assumed that 50% of these emissions would end up in waste water (around 100-166 t/year of medium chain chlorinated paraffins).

Outdoor applications

The annual release of plasticiser from roofing materials has been estimated from studies carried out by Pastruska et al., 1988 and Pastruska and Just, 1990). These gave overall loss figures (includes volatilisation, leaching and degradation) of phthalates from the roofing material of 0.15%/year for open air exposures and 0.35%/year for a surface covered with gravel. In the draft risk assessment report for DEHP these figures were converted into surface area emission figures for DEHP of 1.98 g/m^2/year for uncovered surfaces and 4.62 g/m^2/year for gravel-covered surfaces. These figures were assumed to represent the leaching loss from the PVC, and were expected to be distributed 50% to surface water and 50% to soil.

Using a similar methodology as used for DEHP, the following surface area emission figures can be estimated for medium-chain chlorinated paraffins using the above data:

> 1 m^2 of roofing material (1.5 mm thickness) = $1.5 \cdot 10^6$ mm^3 volume
> Density of PVC (unplasticised) = 1.406 mg/mm^3
> Density of DEHP = 0.985 mg/mm^3
> Density of MCCP = 1.3 mg/mm^3
> Overall density of plasticised PVC (10% MCCP and 35% DEHP) = 1.248 mg/mm^3
> 1 m^2 of roofing material (1.5 mm thickness) = 1872 g
> Amount of MCCP present in 1 m^2 roofing material = 10% = 187.2 g/m^2
> Annual emission rate = 0.15%/year or 0.35% year
> Surface area emission factor for MCCP = 0.28 g/m^2/year or 0.65 g/m^2/year

These calculations assume that the medium-chain chlorinated paraffins are as equally susceptible to removal (leaching) as DEHP. Processes other than leaching (e.g. biodegradation) could have occurred in these experiments with phthalates, which may not be applicable to medium-chain chlorinated paraffins, resulting in an overestimate of the leaching loss.

Assuming medium-chain chlorinated paraffins occur in around 18% of all plasticised PVC used in the outdoor applications outlined in Section 2.2 and using an emission rate of 0.65 g/m^2/year for gravel covered surface and 0.28 g/m^2/year for open surfaces, the following estimated leaching losses can be obtained for medium-chain chlorinated paraffins over the lifetime of the PVC products (emission = $2 \cdot$ annual surface area produced based on DEHP $\cdot$ lifetime $\cdot$ 0.18 $\cdot$ emission factor g/year):

	Emission factor	Estimated leaching loss
car undercoating	{0.28 g/m^2/year	4.5 t/year}[a]
roofing material	0.65 g/m^2/year	2.5 t/year
coil coating	0.28 g/m^2/year	26.7 t/year
fabric coating	0.28 g/m^2/year	22.4 t/year
cable and wires (above ground)	0.28 g/m^2/year	6.4 t/year
cable and wires (buried)	0.65 g/m^2/year	(59.4 t/year – emissions will be to soil compartment)
hoses and profiles	0.28 g/m^2/year	1.6 t/year
shoe soles	0.65 g/m^2/year	3.7 t/year

Note: a) Medium-chain chlorinated paraffins are not thought to be used in car undercoating – calculation given only as an example.

In addition, a figure of 47 t/year of DEHP was estimated to be released to waste water during the washing of car underbodies in the draft risk assessment for DEHP. The 'scaled' emission for

medium-chain chlorinated paraffins (taking into account the relative amounts used in PVC applications) would be around 16 t/year. However, it is thought that medium-chain chlorinated paraffins do not have a significant use in car undercoating.

Information on the actual amounts of medium-chain chlorinated paraffins used in various PVC applications have been provided in a survey carried out by an EU supplier. The information provided confirmed that medium-chain chlorinated paraffins were not used in car undercoating and no use in the production of roofing materials could be identified.

For the other applications, the use of medium-chain chlorinated paraffins in shoe soles was estimated to be 0.6% of the total use in PVC. Assuming this percentage applies to the total amount supplied in the EU for PVC applications, the amount of medium-chain chlorinated paraffins used in production of shoe soles each year would be around 320 t/year. Assuming that the density of PVC is 1,300 kg/m^3, the average thickness of shoe soles is 10 mm (0.01 m) and the medium-chain chlorinated paraffin content is 10-15%, then the annual surface area of shoe soles containing medium-chain chlorinated paraffins produced each year can be estimated as 164,000-246,000 m^2/year. Assuming a life time of 5 years, and an emission factor of 0.65 g/m^2/year, the total emission via leaching of medium-chain chlorinated paraffins from shoe soles can be estimated as 0.53–0.80 t/year. This is slightly lower than the estimate made above.

For fabric coating applications, some figures for the actual amounts used have been provided by Industry, but these have been considered in the indoor emissions earlier, as it was not possible to distinguish between indoor and outdoor applications.

No information was provided in the Industry survey on the amounts of medium-chain chlorinated paraffins used in hoses and profiles or cable coating in outdoor applications.

For cable, information provided by Industry allowed an estimate of the total area of PVC containing medium-chain chlorinated paraffin to be made as 9.3-14.1·10^8 m^2 to be made, with the area present in outdoor applications being around 2.0-3.1·10^8 m^2 (based on a 30 year lifetime and 22% of the total being used outdoors; see Section 2.1). Using the emission factor for medium-chain chlorinated paraffins of 0.28 g/m^2/year for above ground cables and 0.65 g/m^2/year for buried cables, and assuming that 80% of the cable is deep-buried and 20% is above ground (taken from the draft DEHP assessment), the total emission via leaching of medium-chain chlorinated paraffins can be estimated as 11.2-17.4 t/year from above ground cables and 104-161 t/year from below ground cables. These values are slightly higher than those estimated above based on the DEHP data.

Emissions during waste disposal

<u>Car shredding</u>

As well as PVC-coated underbodies (which are unlikely to contain medium-chain chlorinated paraffins); cars may contain other PVC articles (e.g. cable or wiring) that may contain medium-chain chlorinated paraffins. The draft risk assessment report on DEHP includes an emission scenario for this endpoint and this information has been used here to estimate the worst case emissions of medium-chain chlorinated paraffins during the process as follows:

- Amount of PVC per car = 16 kg
- Percentage of PVC that is plasticised = 35%
- Amount of plasticised PVC/car = 5.4 kg
- Amount of medium-chain chlorinated paraffin/car = 0.54 (assuming 10% content in PVC)
- Total number of cars processed in EU = 10,600,000 per year

- Total amount of medium-chain chlorinated paraffins present = 5,724 t/year
- Number of shredder sites in EU = 252
- Average amount of medium-chain chlorinated paraffins processed/site = 22.7 t/year
- Number of days of operation = 300
- Emission factor to air = 0.05%
- Local release of medium-chain chlorinated paraffins to air = 11.4 kg/year = 0.038 kg/day
- Total EU release of medium-chain chlorinated paraffins to air = 2.86 t/year

Incineration of municipal waste

No information is available on levels of medium-chain chlorinated paraffins in the exhaust gases from municipal waste incinerators and so it is not possible to estimate a release from this source. The conditions present during municipal waste incineration would be expected to effectively destroy any medium-chain chlorinated paraffins present.

Municipal landfill

No information is available on the amounts of medium-chain chlorinated paraffins subject to leaching from municipal landfills. In the draft Risk Assessment of DEHP it was estimated that around 15 t/year of DEHP could be leached from landfills to waste water in the EU. If it is assumed that medium-chain chlorinated paraffins have a similar potential to leach as DEHP then the amount of medium-chain chlorinated paraffins leached could be estimated to be roughly around 2 t/year, based on scaling the DEHP figure to the relative total volumes of DEHP (476,000 t/year) and medium-chain chlorinated paraffins (65,256 t/year) used in all applications in the EU.

Waste remaining in the environment

Waste remaining in the environment can be considered to be particles of polymer product (e.g. PVC, paint, sealant etc.) which contain the medium-chain chlorinated paraffin. These particles are primarily released to the urban/industrial soil compartment, but which may also end up in sediment or air. End-products with outdoor uses are most likely to be sources of this waste. The release can occur both over the lifetime of the product (due to weathering, wear etc.) and at disposal (particularly where articles are dismantled or subjected to other mechanical processes).

In the draft DEHP risk assessment, waste remaining in the environment was identified to be produced from the following outdoor applications of PVC:

- car undercoating
- roofing material
- coil coating
- fabric coating
- cables and wires
- hoses and profiles
- shoe soles

Further it was stated that 22% of the DEHP in PVC was used in these outdoor applications. The actual breakdown of the use of medium-chain chlorinated paraffins between these different sources is not known and so it will be assumed that around 22% of the medium-chain chlorinated paraffin is also used in PVC for outdoor applications. This assumption is probably reasonable since one of the major uses of medium-chain chlorinated paraffins in PVC appears to be for flooring (an indoor use).

In addition, medium-chain chlorinated paraffins are also used in outdoor paints and building sealants which also need to be considered as possible sources of waste remaining in the environment. The use in leather fat liquors, carbonless copy paper and metal working/cutting fluids are not considered to contribute significantly to these types of release. **Table F1** outlines the relevant tonnages for the applications considered.

These emission factors used for these types of losses in the draft DEHP risk assessment were around 2-10% over the lifetime of the product, with the higher factor being applied to articles subject to high wear rates (such as car underbodies and shoe soles), and 2% during disposal operations. The assumptions behind the derivation of these factors were not given in the report. These releases were thought to occur mainly to urban/industrial soil. A similar approach is taken here as a worst case, using similar factors as used for DEHP. Only outdoor applications are considered to contribute significantly to the waste over the lifetime of the articles.

This approach assumes the following:

- the quantity of articles/products containing medium-chain chlorinated paraffins disposed of each year is equal to the quantity of new articles/products containing medium-chain chlorinated paraffins produced each year.

- the emissions factors estimate the total release over the entire service life of the product/article (i.e. for high wear articles, 10% of the product is worn away as particles/dust over the lifetime of the product)

In the calculations, the amount of medium-chain chlorinated paraffin lost by volatilisation and or leaching and during processing and formulation (as estimated earlier or in the main risk assessment report) is also taken into account to avoid double counting.

For use in rubber/polymers (other than PVC), sealants/adhesives and paints, a particulate emission factor of 2% over the technical lifetime of the product and 2% at disposal is used (in the May 2000 draft of the DEHP assessment a figure of 5% over the technical lifetime (and 5% at disposal) was used for paints and sealants, and so these values are also considered). However, for PVC applications there may be some high wear products produced (e.g. shoe soles) and so a higher particulate emission factor may be appropriate to some of these applications. Since the actual breakdown of the use of medium-chain chlorinated paraffins between these various PVC end-uses is currently unknown, an emission factor of 6% over the lifetime of the technical product was used (average of the low and high wear factors), with 2% emission at disposal.

The emissions are likely to be mainly to soil. In the draft DEHP assessment it was assumed that 75% of the emission would be to industrial/urban soil and 0.1% to air, with the remainder occurring to surface water (sediment). The same split of the emissions will be used here in the absence of any further information.

There are many uncertainties inherent in these emission estimates. Further, since this 'waste' is essentially polymeric particles (e.g. rubber, sealant, paint) containing the medium-chain chlorinated paraffin, it is not known if this is 'available' in the environment and so would lead to actual exposure of organisms to medium-chain chlorinated paraffin.

In addition to these particulate releases, an estimated 166 t/year of medium-chain chlorinated paraffins may be emitted to waste water (and 166 t/year to landfill/disposal) as particulates for PVC flooring as a result of wear and subsequent washing (see earlier).

Table **F1**   Estimation of waste remaining in the environment

		Uses considered for waste remaining in environment			
		PVC	Rubber/polymers (other than PVC)	Sealants/ adhesives	Paints
Total quantity of MCCP used in applications		51,827 t/year	2,146 t/year	2,360 t/year	1,180 t/year
Quantity of MCCP emitted from other formulation and processing (accounted for elsewhere in assessment)		216[b] t/year	2.58[b] t/year	negligible[b]	5.9[b] t/year
Percentage used in outdoor applications (worst case assumptions)		22%	100%	100%	100%
Quantity of MCCP present in outdoor applications		11,354 t/year	2,143 t/year	2,360 t/year	1,174 t/year
Volatilisation and leaching loss during product lifetime for outdoor applications (accounted for elsewhere in assessment)		143[a] t/year	1.07[b] t/year	107.2[b] t/year	45.4[b] t/year
Quantity of MCCP remaining in outdoor applications after volatilisation and leaching losses		11,211 t/year	2,142 t/year	2,253 t/year	1,129 t/year
Percentage particulate emission over technical lifetime of product		6%	2%	2-5%	2-5%
Amount of MCCP emitted as waste remaining in the environment over technical lifetime of product		673 t/year	42.8 t/year	45.1-112.7 t/year	22.6-56.4 t/year
Amount of MCCP remaining in product at disposal		10,538 t/year	2,099 t/year	2,140-2,208 t/year	1,073-1,106 t/year
Percentage particulate emission at disposal		2%	2%	2-5%	2-5%
Amount of MCCP emitted as waste remaining in the environment at disposal		211 t/year	42.0 t/year	44.2-107.0 t/year	22.1-53.6 t/year
Total amount of MCCP as waste remaining in the environment		884 t/year	84.8 t/year	89.3-219.7 t/year	44.7-110 t/year
Distribution of emission	urban soil	75%	75%	75%	75%
	surface water	24.9%	24.9%	24.9%	24.9%
	air	0.1%	0.1%	0.1%	0.1%

Table F1 continued overleaf

Table F1 continued Estimation of waste remaining in the environment

	Uses considered for waste remaining in environment			
	PVC	Rubber/polymers (other than PVC)	Sealants/ adhesives	Paints
Total amount of MCCP as waste remaining in the environment to urban soil	663 t/year	63.6 t/year	67.0-164.7 t/year	33.5-82.5 t/year
Total amount of MCCP as waste remaining in the environment to surface water	220 t/year	21.1 t/year	22.2-54.7 t/year	11.1-27.4 t/year
Total amount of MCCP as waste remaining in the environment to air	0.9 t/year	0.085 t/year	0.089-0.22 t/year	0.045-0.11 t/year

a)   Figures taken from this Appendix.
b)   Figures taken from main assessment report.

Summary of emissions estimated

Table F2 summarises the emissions estimated here for diffusive losses of medium-chain chlorinated paraffins during the lifetime of PVC (and other polymers) products and during disposal of articles. **Table F3** summarises the emissions of medium-chain chlorinated paraffins as particulates (waste remaining in the environment) over the lifecycle of products.

In order to generate these figures, a large number of 'worst case' assumptions have had to be made. This leads to a large uncertainty in the figures obtained, and the approach taken may grossly overestimate the actual releases. In particular, the information on leaching losses from products outdoors is based on a study where the overall loss (including leaching, degradation and particulate loss due to wear/weathering) of phthalate plasticiser from roofing material was determined. In the study, it was not possible to distinguish between these types of loss and so it has been assumed that all the loss was due to leaching. The applicability of this approach to estimating the leaching loss of medium-chain chlorinated paraffins from products outdoors is unknown.

Table F 2   Summary of diffusive losses of medium-chain chlorinated paraffins from PVC (and other polymers) during product lifetimes and disposal

Lifestage		Emission of medium chain chlorinated paraffin (t/year)	
		Volatility losses to air	Leaching loss to water and soil
Product lifetime	flooring – indoor	5.1-13.1	8.4-21.5[b]
	wall covering – indoor	6.6-10.0	
	coated products, film and sheet – indoor	4.0-7.2	34.7[a,b]
	cable – indoor	9-16.7	
	hose and profile – indoor	9.8	
	roofing material – outdoor	{0.060}[d]	{2.5}[c,d]
	coil coating – outdoor	1.50	26.7[c]
	fabric coating – outdoor	1.26	22.4[c]
	cable – outdoor	0.36-0.98 (+1.44-3.9 to deep soil)	6.44[c]-17.4[c] (+59.4-161 to deep soil)

Table F2 continued overleaf

Table F2 continued Summary of diffusive losses of medium-chain chlorinated paraffins from PVC (and other polymers) during product lifetimes and disposal

Lifestage		Emission of medium chain chlorinated paraffin (t/year)	
		Volatility losses to air	Leaching loss to water and soil
	hoses and profile - outdoor	0.09	1.6[c]
	shoe soles	0.013-0.09	0.53[c]-3.7[c]
Total from PVC over product lifetime		37.8-60.8 (to air) (+1.44-3.9 to deep soil)	73.2-93.4 (to waste water) 30.1-37.2 (to urban/industrial soil) (+59.4-161 to deep soil)
Waste disposal	car shredding	2.86	
	incineration		
	municipal landfill		2[b]
Total from PVC at disposal		2.86 (to air)	2 (to waste water)

a)   Estimated for washing clothing with PVC printing – it is not known if medium-chain chlorinated paraffins are used in this application.
b)   Losses primarily to wastewater.
c)   Losses to soil and water (assumed to be split 50:50 between surface water and industrial/urban soil).
d)   This was not identified as a use of medium-chain chlorinated paraffins in an Industry survey.

Table F3   Summary of waste remaining in the environment during product lifetimes and disposal

Lifestage		Emission of medium chain chlorinated paraffin as particulates (t/year)			
		Air	Surface water	Waste water	Soil
Product lifetime	PVC	0.7	168	100-166[a]	504
	Rubber/polymers (other than PVC)	0.04	10.7		32.1
	Sealants/adhesives	0.05-0.11	11.2-28.1		33.8-84.5
	Paints	0.02-0.06	5.6-14.0		17.0-42.3
Waste disposal	PVC	0.2	52.5		158
	Rubber/polymers (other than PVC)	0.04	10.5		31.5
	Sealants/adhesives	0.04-0.11	11.0-26.6		33.2-80.3
	Paints	0.02-0.05	5.5-13.3		16.6-14.2
Total		1.1-1.3	275-324	100-166	826-973

a)   Emission to waste water from washing PVC-flooring. A further 100-166 t/year estimated to end up in landfill.

References

ECPI (1996). European Council for Plasticisers and Intermediates. Assessment of the release, occurrence and possible effects of plasticisers in the environment. Phthalate esters used in plasticised PVC. CEFIC, September 1996. (as quoted in the November 1999 draft of the ESR risk assessment report for DEHP).

Pastruska G, Kerner-Gang W and Just U (1988). Langzeitverhalten von PVC-P-Dachbahnen. Kautschuk Gummi Kunststoffe **41**, 451-454. (as quoted in the November 1999 draft of the ESR risk assessment report for DEHP).

Pastruska G and Just U (1990). Weichmacherverlust aus langjährig freibewitternten PVC-P-Dachbahnen. Kautschuk Gummi Kunststoffe **43**, 1093-1094. (as quoted in the November 1999 draft of the ESR risk assessment report for DEHP).

Appendix G Volatility losses from PVC

This Appendix considers further the available information on the volatility of medium chain chlorinated paraffins from PVC that is discussed in Section 3.1.1.2.1 of the main risk assessment report. Information on the volatility relative to DEHP is shown in **Table G1 and G2**.

The data shows that the 45% wt. Cl product is around 3 times as volatile as DEHP from PVC and this figure is used in the main risk assessment report as a worst case for estimation of local releases.

The data for the 52% wt. Cl product shows that this is around 1.4 times as volatile as DEHP from PVC. The effect of this lower volatility on the estimated releases and subsequent PECs is shown in **Tables G3 to G5**.

Table G1   Ageing loss from PVC (BS 2782 methods 465A and B)

For DEHP alone			
Parts DEHP	Parts MCCP	% loss	% DEHP loss/parts DEHP
56	0	0.55	0.0098

For C_{14-17}, 45% wt. Cl with DEHP						
Parts DEHP	Parts MCCP	% loss	Calculated contribution from DEHP	Residual from MCCP	% MCCP loss/parts MCCP	Relative loss MCCP/DEHP
50	10	0.85	0.490	0.360	0.036	3.673
43	20	1.00	0.421	0.579	0.029	2.952
36	30	1.15	0.353	0.797	0.027	2.712
Average for C_{14-17}, 45% wt. Cl						3.112

For C_{14-17}, 52% wt. Cl with DEHP						
Parts DEHP	Parts MCCP	% loss	Calculated contribution from DEHP	Residual from MCCP	% MCCP loss/parts MCCP	Relative loss MCCP/DEHP
51	10	0.60	0.500	0.100	0.010	1.022
43	20	0.70	0.421	0.279	0.014	1.421
37	30	0.85	0.363	0.487	0.016	1.658
Average for C_{14-17}, 52% wt. Cl						1.367

Table G2   Weight loss on heating of plasticiser

Plasticiser	Weight loss after 4 hours heating at 150ºC (%)	Weight loss after 4 hours heating at 180ºC	Relative weight loss (MCCP/DEHP) at 150ºC	Relative weight loss (MCCP/DEHP) at 180ºC
DEHP	0.3	1.9		
C14-17, 45% wt. Cl	0.7	2.8	2.3	1.5
C14-17, 52% wt. Cl	0.5	1.4	1.7	0.7
C14-17, 58% wt. Cl	0.3	0.8	1.0	0.4

Table G3   Exposure estimates for C$_{14-17}$, 52% wt. Cl substance

Use	Tonnages (t/year)			Release factors for waste water (%)		Release factors for air (%)		Current release estimates for waste water			Revised release estimates for 52% Cl for waste water			Current release estimates for air			Revised release estimates for 52% Cl for air			Number of days
	Total	Local	Regional	Current	52% Cl	Current	52% Cl	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	
Production									65	45		65	45							
PVC - compounding site - plastisol process		74.4		0.010	0.010	0.000	0.000	0.025			0.025			0.000			0.000			300
PVC - Processing site - plastisol process		74.4		0.075	0.035	0.075	0.035	0.186			0.087			0.186			0.087			300
PVC - Combined compounding/ processing site - plastisol process		74.4		0.085	0.045	0.075	0.035	0.211			0.112			0.186			0.087			300
PVC - Compounding site - secondary plasticiser - open system		112		0.025	0.017	0.015	0.007	0.093			0.063			0.056			0.026			300
PVC - Compounding site - secondary plasticiser - partially open system		599		0.025	0.017	0.015	0.007	0.499			0.339			0.300			0.140			300
PVC - Compounding site - secondary plasticiser - closed system		51		0.025	0.017	0.015	0.007	0.043			0.029			0.026			0.012			300

Table G3 continued overleaf

Table G3 continued Exposure estimates for C14-17, 52% wt. Cl substance

Use	Tonnages (t/year)			Release factors for waste water (%)		Release factors for air (%)		Current release estimates for waste water			Revised release estimates for 52% Cl for waste water			Current release estimates for air			Revised release estimates for 52% Cl for air			Number of days
	Total	Local	Regional	Current	52% Cl	Current	52% Cl	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	
PVC - Processing site - secondary plasticiser - open system		112		0.075	0.035	0.075	0.035	0.280			0.131			0.280			0.131			300
PVC - Processing site - secondary plasticiser - partially open system		599		0.015	0.007	0.015	0.007	0.300			0.140			0.300			0.140			300
PVC - Processing site - secondary plasticiser - closed system		51		0.150	0.070	0.150	0.070	0.255			0.119			0.255			0.119			300
PVC - Combined compounding/ processing site - secondary plasticiser - open system		112		0.100	0.052	0.090	0.042	0.373			0.194			0.336			0.157			300
PVC - Combined compounding/ processing site - secondary plasticiser - partially open system		599		0.040	0.024	0.030	0.014	0.799			0.479			0.599			0.280			300

Table G3 continued overleaf

Table G3 continued Exposure estimates for C14-17, 52% wt. Cl substance

Use	Tonnages (t/year)			Release factors for waste water (%)		Release factors for air (%)		Current release estimates for waste water			Revised release estimates for 52% Cl for waste water			Current release estimates for air			Revised release estimates for 52% Cl for air			Number of days
	Total	Local	Regional	Current	52% CI	Current	52% CI	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	
PVC - Combined compounding/ processing site - secondary plasticiser - closed system		51		0.175	0.087	0.165	0.077	0.298			0.148			0.281			0.131			300
PVC (general) - raw materials handling	51,800		5,180	0.010	0.010	0.000	0.000		518	4,662		518	4,662							300
PVC (general) - compounding	36,260		3,626	0.015	0.007	0.015	0.007		351	3,155		351	3,155		351	3,155		351	3,155	300
PVC (general) - processing - open systems	13,468		1,346.8	0.750	0.350	0.750	0.350		6,510	58,586		6,510	58,586		65,10	58,586		6,510	58,586	300
PVC (general) - processing - partially open and closed systems	38,332		3,833.2	0.150	0.070	0.150	0.070		3,705	33,349		3,705	33,349		3,705	33,349		3,705	33,349	300
Total PVC									11,083	99,751		11,083	99,751		10,565	95,089		10,565	95,089	300
Rubber/other plastics - compounding site								0.047	32.250	290.300	0.047	32.250	290.300	0.016	10.750	96.750	0.016	10.750	96.750	300
Rubber/other plastics - processing site								0.155	107.500	966.000	0.155	107.500	966.000	0.155	107.500	966.000	0.155	107.500	966.000	300
Rubber/other plastics - combined compounding/ processing site								0.202			0.202			0.171			0.171			300

Table G3 continued overleaf

Table G3 continued Exposure estimates for C14-17, 52% wt. Cl substance

Use	Tonnages (t/year)			Release factors for waste water (%)		Release factors for air (%)		Current release estimates for waste water			Revised release estimates for 52% Cl for waste water			Current release estimates for air			Revised release estimates for 52% Cl for air			Number of days
	Total	Local	Regional	Current	52% Cl	Current	52% Cl	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	
Paints - formulation site								0.15	354	3,186	0.15	354	3,186	0.05	118	1,062	0.05	118	1,062	300
Paints - industrial application								0.059	118	1,062	0.059	118	1,062							300
Paints - application by general public								3.00×10^{-7}			3.00×10^{-7}									300
Metal cutting/working fluids - formulation								0.83	1488	13,875	0.83	1488	13,875							300
Metal cutting/working fluids - oil based – large site								0.33	38,100	342,900	0.33	38,100	342,900							300
Metal cutting/working fluids - oil based – small site								0.3			0.3									300
Metal cutting/working fluids - emulsion								0.025	99,200	892,800	0.025	99,200	892,800							300
Metal cutting/working fluids - emulsion - intermittent discharge								25			25									6
Leather fat liquors - formulation								1.1	315	2,829	1.1	315	2,829	0.35	105	943	0.35	105	943	300

Table G3 continued overleaf

Table G3 continued Exposure estimates for C14-17, 52% wt. Cl substance

Use	Tonnages (t/year)			Release factors for waste water (%)		Release factors for air (%)		Current release estimates for waste water			Revised release estimates for 52% Cl for waste water			Current release estimates for air			Revised release estimates for 52% Cl for air			Number of days
	Total	Local	Regional	Current	52% Cl	Current	52% Cl	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	Local (kg/day)	Regional (kg/year)	Continental (kg/year)	
Leather fat liquors - processing of raw hides								0.9	1,050	9,430	0.9	1,050	9,430							
Leather fat liquors - processing of wet blue								3.6			3.6									300
Carbonless copy paper - recycling								14.8	3,705	33,345	14.8	3,705	33,345							250
Polymers - service life									14,790	133,110		14,790	133,110	6,120	55,035		6,120	55,035		300
All other uses									159,260	1,433,793		159,260	1,433,793	6,461	58,103		6,461	58,103		
Total from all sources									170,408	1,533,590		170,408	1,533,590	17,027	153,192		17,027	153,192		
								via WWTP	119,286	1,073,513	via WWTP	119,286	1,073,513							
								direct	51,122	460,077	direct	51,122	460,077							

Table G4   Local PEC calculations for a C14-17, 52% Cl substance

Use	Size of WWTP (m³/day)	% to WWTP	Dilution factor	C_{local}(water) (ug/l)		PEC_{local}(water) (ug/l)		PEC_{local}(sediment) (mg/kg wet wt.)	
				current (45% Cl)	52% Cl	current (45% Cl)	52% Cl	current (45% Cl)	52% Cl
Production	2,000	7	10	0.170	0.170	0.558	0.558	7.143	7.143
PVC - compounding site - plastisol process	2,000	7	10	0.046	0.046	0.434	0.434	5.56	5.56
PVC - Processing site - plastisol process	2,000	7	10	0.346	0.161	0.734	0.549	9.39	7.03
PVC - Combined compounding/ processing site - plastisol process	2,000	7	10	0.392	0.207	0.780	0.595	9.98	7.62
PVC - Compounding site - secondary plasticiser - open system	2,000	7	10	0.173	0.118	0.561	0.506	7.19	6.48
PVC - Compounding site - secondary plasticiser - partially open system	2,000	7	10	0.928	0.631	1.316	1.019	16.84	13.04
PVC - Compounding site - secondary plasticiser - closed system	2,000	7	10	0.079	0.054	0.467	0.442	5.98	5.65
PVC - Processing site - secondary plasticiser - open system	2,000	7	10	0.520	0.243	0.908	0.631	11.63	8.08
PVC - Processing site - secondary plasticiser - partially open system	2,000	7	10	0.557	0.260	0.945	0.648	12.09	8.29
PVC - Processing site - secondary plasticiser - closed system	2,000	7	10	0.474	0.221	0.862	0.609	11.03	7.80
PVC - Combined compounding/ processing site - secondary plasticiser - open system	2,000	7	10	0.694	0.361	1.082	0.749	13.85	9.59
PVC - Combined compounding/ processing site - secondary plasticiser - partially open system	2,000	7	10	1.484	0.891	1.872	1.279	23.97	16.37
PVC - Combined compounding/ processing site - secondary plasticiser - closed system	2,000	7	10	0.553	0.275	0.941	0.663	12.04	8.49

Table G4 continued overleaf

Table G4 continued Local PEC calculations for a C14-17, 52% Cl substance

Use	Size of WWTP (m³/day)	% to WWTP	Dilution factor	C local(water) (µg/l)		PEC local(water) (µg/l)		PEC local(sediment) (mg/kg wet wt.)	
				current (45% Cl)	52% Cl	current (45% Cl)	52% Cl	current (45% Cl)	52% Cl
Rubber/other plastics - compounding site	2,000	7	10	0.086	0.086	0.474	0.474	6.07	6.07
Rubber/other plastics - processing site	2,000	7	10	0.288	0.288	0.676	0.676	8.65	8.65
Rubber/other plastics - combined compounding/ processing site	2,000	7	10	0.375	0.375	0.763	0.763	9.77	9.77
Paints - formulation site	2,000	7	10	0.279	0.279	0.667	0.667	8.54	8.54
Paints - industrial application	2,000	7	10	0.110	0.110	0.498	0.498	6.37	6.37
Paints - application by general public	2,000	7	10	0.000	0.000	0.388	0.388	4.97	4.97
Metal cutting/working fluids - formulation	2,000	7	10	1.543	1.543	1.931	1.931	24.71	24.71
Metal cutting/working fluids - oil based - large site	2,000	7	10	0.613	0.613	1.001	1.001	12.82	12.82
Metal cutting/working fluids - oil based - small site	2,000	7	10	0.558	0.558	0.946	0.946	12.10	12.10
Metal cutting/working fluids - emulsion	2,000	7	10	0.046	0.046	0.434	0.434	5.56	5.56
Metal cutting/working fluids - emulsion - intermittent discharge	2,000	7	10	46.462	46.462	46.850	46.850	599.72	599.72
Leather fat liquors - formulation	2,000	7	10	2.044	2.044	2.432	2.432	31.14	31.14
Leather fat liquors - processing of raw hides	2,000	7	10	1.673	1.673	2.061	2.061	26.38	26.38
Leather fat liquors - processing of wet blue	2,000	7	10	6.691	6.691	7.079	7.079	90.61	90.61
Carbonless copy paper - recycling	2,000	7	10	27.505	27.505	27.893	27.893	357.06	357.06

Table G5 Predicted regional concentrations for a C14-17, 52% wt. Cl substance

Substance	Water (ug/l)	Sediment (mg/kg)	Agricultural soil (mg/kg)	Natural soil (mg/kg)	Air (mg/m³)
Current (45% wt. Cl)	0.388	8.79	50.4	1.1	$3.35 \cdot 10^{-6}$
52% wt. Cl	0.388	8.79	50.4	1.1	$3.35 \cdot 10^{-6}$

Appendix H Effects of variability in physico-chemical properties and degradation rate on the environmental modelling of medium-chain chlorinated paraffins

Physico-chemical properties

Medium-chain chlorinated paraffins are complex mixtures. This presents some problems over the values of physico-chemical properties to be chosen for the environmental modelling of these substances. In order to simplify the environmental modelling the main risk assessment report a set of physical chemical properties were chosen as being representative of the medium chain chlorinated paraffins as a group. However, for the majority of the physico-chemical properties relevant for the environmental modelling, a range of values has been determined. This Appendix considers the effect of varying some of the key physico-chemical properties within the range measured on the predicted environmental concentration. In order to do this simply, the EUSES model was run several times using the release estimates for one local scenario (Use in rubber/plastics – conversion site; this is chosen as an example as it has releases to both air and waste water) and the total regional and continental releases as determined in the main report. This then allows the resulting concentrations to be compared directly with those obtained in the main report.

The physico-chemical properties for medium-chain chlorinated paraffins are discussed in Chapter 1 of the main risk assessment report. The values used as input data used in the various example calculations are shown in **Table H1**. The values chosen reflect the range of values measured for medium-chain chlorinated paraffins. In all calculations, 93% removal in the waste water treatment plant due to adsorption onto sewage sludge was assumed. **Table H2** gives the resulting PECs from this approach.

Table H3 outlines the PEC/PNEC ratios obtained for surface water, sediment, soil and secondary poisoning, using the various physico-chemical properties (the PNECs for sediment and soil are based on the equilibrium partitioning approach). For the soil and sediment endpoints, both the PEC and PNEC depend on the value for the organic carbon-water partition coefficient used.

Table H1   Input data for EUSES model for the various scenarios considered

Model input	Value used in EUSES calculation										
	Main assessment	A	B	C	D	E	F	G	H	I	J
Molecular weight (g/mole)	488	488	405c	419d	468e	481	488	488	488	488	488
Water solubility (µg/l)	27	5	27	27	27	27	27	27	27	27	27
Vapour pressure (Pa)	$2.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$5 \cdot 10^{-5}$ c	$2 \cdot 10^{-5}$ d	$2 \cdot 10^{-6}$ e	$9 \cdot 10^{-7}$ f	$2.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$
Henrys Law constant[a] $(Pa.m^3.mole^{-1})$	4.88	26.4	0.75	0.31	0.035	0.016	4.88	4.88	4.88	4.88	4.88
Log Kow	7	7	7	7	7	7	5.5	6	6.5	7.5	8
Koc[b] (l/kg)	$5.89 \cdot 10^5$	$5.89 \cdot 10^5$	$5.89 \cdot 10^5$	$5.89 \cdot 10^5$	$5.89 \cdot 10^5$	$5.89 \cdot 10^5$	$3.59 \cdot 10^4$	$9.13 \cdot 10^4$	$2.32 \cdot 10^5$	$1.5 \cdot 10^6$	$3.8 \cdot 10^6$
PNEC$_{water}$ (µg/l)	1	1	1	1	1	1	1	1	1	1	1
PNEC$_{sediment}$ (mg/kg wet wt.)[g]	12.8	12.8	12.8	12.8	12.8	12.8	0.78	2.0	5.0	32.6	82.6
PNEC$_{soil}$ (mg/kg wet wt.)[g]	10.4	10.4	10.4	10.4	10.4	10.4	0.63	1.6	4.1	26.5	67.1
PNEC$_{secondary poisoning}$ (mg/kg food)	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17
Continental release	153,193 kg/year to air, 1,073,482 kg/year to waste water and 460,101 kg/year to surface water										
Regional release	17,027 kg/year to air, 119,286 kg/year to waste water and 51,122 kg/year to surface water										
Local release (Use in rubber/plastics – conversion site)	0.155 kg/day to air and 0.155 kg/day to waste water over 300 days										

a)   Henrys law constant estimated from water solubility and vapour pressure (also depends on the molecular weight).
b)   Koc estimated by EUSES from log Kow.
c)   Vapour pressure and molecular weight appropriate for C_{14}, 51-53% wt. Cl congeners.
d)   Vapour pressure and molecular weight appropriate for C_{15}, 51-53% wt. Cl congeners.
e)   Vapour pressure and molecular weight appropriate for C_{16}, 51-53% wt. Cl congeners.
f)   Vapour pressure and molecular weight appropriate for C_{17}, 51-53% wt. Cl congeners.
g)   PNECs for sediment and soil calculated by the equilibrium partitioning method – dependent on Koc value.

Table H2   Resulting concentrations for the various scenarios considered

Endpoint	Value estimated in EUSES calculation										
	Main assessment	A	B	C	D	E	F	G	H	I	J
Local concentrations (use in rubber/plastics – conversion site)											
Surface water (µg/l)	0.68	0.48	0.87	0.91	0.93	0.93	1.23	1.14	0.96	0.39	0.18
Sediment (mg/kg wet wt.)	8.7	6.1	11.2	11.6	11.9	12.0	0.96	2.27	4.84	12.5	15.1
Agricultural soil (30 days average) (mg/kg wet wt.)	3.72	3.58	3.88	3.79	3.67	3.66	2.41	2.96	3.45	3.64	3.43
Pore water (agricultural soil) (µg/l)	0.36	0.34	0.37	0.36	0.35	0.35	3.8	1.83	0.84	0.14	0.051
Air (during emission episode) (mg/m^3)	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$
Fish (for secondary poisoning) (mg/kg wet wt.)[a]	0.55-1.65	0.33-0.99	0.76-2.28	0.80-2.40	0.83-2.49	0.83-2.49	1.01-3.03	0.94-2.82	0.79-2.37	0.31-0.93	0.15-0.45
Earthworms (for secondary poisoning) (mg/kg wet wt.)	152	92.2	175	178	178	178	30.0	59.3	102	188	204
Total daily human intake (mg/kg bw/day)	0.137	0.127	0.138	0.132	0.126	0.125	0.053	0.076	0.109	0.157	0.172
Predicted regional concentrations											
Surface water (µg/l)	0.39	0.19	0.58	0.62	0.64	0.65	0.72	0.67	0.56	0.22	0.10
Sediment (mg/kg wet wt.)	8.80	4.27	13.2	14.0	14.6	14.6	0.97	2.32	4.95	12.5	15.0
Agricultural soil (mg/kg wet wt.)	50.4	29.4	58.6	59.6	60.2	60.2	8.23	17.9	33.3	63.0	69.9
Pore water (agricultural soil) (µg/l)	4.9	2.8	5.6	5.7	5.8	5.8	13	11.1	8.2	2.4	1.04
Air (mg/m^3)	$3.4 \cdot 10^{-6}$	$6.2 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$	$8.9 \cdot 10^{-7}$	$6.6 \cdot 10^{-7}$	$6.5 \cdot 10^{-7}$	$6.4 \cdot 10^{-6}$	$5.8 \cdot 10^{-6}$	$4.7 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$
Total daily human intake (mg/kg bw.day)	1.71	1.0	1.99	2.02	2.04	2.04	0.173	0.44	0.97	2.51	3.27

a)   The concentration in fish is estimated using the methods outlined in the Technical Guidance Document, taking into account accumulation through the food chain. The range reflects the range for the BMF (1-3).

Table H3   Resulting PEC/PNEC ratios for the various scenarios considered

Endpoint	PEC/PNEC ratio										
	Main assessment	A	B	C	D	E	F	G	H	I	J
Local concentrations (use in rubber/plastics – conversion site)											
Surface water	0.68	0.48	0.87	0.91	0.93	0.93	1.23	1.14	0.96	0.39	0.18
Sediment	0.68	0.48	0.87	0.91	0.93	0.93	1.23	1.14	0.96	0.39	0.18
Agricultural soil (30 days average)	0.35	0.34	0.37	0.36	0.35	0.35	3.83	1.85	0.84	0.14	0.05
Fish (for secondary poisoning)	3.3-9.9	2.0-6.0	4.5-13.5	4.8-14.4	5.1-15.3	5.1-15.3	6.0-18.0	5.7-17.1	4.8-14.4	1.8-5.4	0.9-2.7
Earthworms (for secondary poisoning)	894	542	1,029	1,047	1,047	1,047	176	348	600	1,106	1,200
Predicted regional concentrations											
Surface water	0.39	0.19	0.58	0.62	0.64	0.65	0.72	0.67	0.56	0.22	0.10
Sediment	0.69	0.33	1.03	1.09	1.14	1.14	1.24	1.16	0.99	0.38	0.18
Agricultural soil	4.8	2.8	5.6	5.7	5.8	5.8	13.0	11.2	8.1	2.4	1.0

As can be seen from **Table H3**, there is some variation in the results obtained. Lowering the water solubility (or increasing the Henrys law constant to values of around 25 $Pa.m^3.mole^{-1}$) and increasing the log Kow value above 7-7.5 appeared to have the largest effects on the resulting PEC/PNEC ratio, leading to generally lower ratios for surface water, sediment and soil.

The extremes of the PEC/PNEC ratios obtained vary by a factor of around 7 for surface water and sediment and by a factor of up to 60 for agricultural soil. However, for most scenarios (e.g. B, C, D, E, F, G, H) the variation in PEC/PNEC ratio seen is much less than this, and indicates that only the extremes of the values of the range of physico-chemical properties would result in a significant change to the PEC/PNEC ratios obtained. The values for physico-chemical properties used in the main assessment results in PEC/PNEC ratios that are generally in the middle to upper end of the range determined, and indicate that the results are reasonably representative for the majority of the components of the commercial mixtures.

Degradation rate

Since medium-chain chlorinated paraffins are not readily biodegradable, the appropriate default rate constants for degradation in surface water ($6.93 \cdot 10^{-7}$ day^{-1}), soil ($6.93 \cdot 10^{-7}$ day^{-1}) and sediment ($6.93 \cdot 10^{-8}$ day^{-1}) were used in the EUSES modelling in the main report. These correspond to degradation half-lives of the order of 2,740 years in soil and surface water, and 27,400 years in bulk sediment. The regional concentrations estimated using these values were generally higher than the available monitoring data indicated. One explanation for this would be if medium-chain chlorinated paraffins are less persistent in the environment than is indicated by these default degradation halflives. Therefore the sensitivity of the calculations to these degradation rates was investigated. In this analysis the physico-chemical properties and regional and continental releases were as in the main report and the EUSES model was run several times with different values for the degradation rate constants. The results are shown in **Table H4**.

Table H4   Effects of varying the biodegradation half-life on predicted regional concentrations

Biodegradation		Half-life		$PEC_{regional}$		
Surface water, soil	Bulk sediment	Surface water, soil	Bulk sediment	Surface water	Sediment	Agricultural soil
$6.93 \cdot 10^{-7}$	$6.93 \cdot 10^{-8}$	2,740 years	27,400 years	0.39 µg/l	8.8 mg/kg wet wt.	50.4 mg/kg wet wt.
$6.93 \cdot 10^{-6}$	$6.93 \cdot 10^{-7}$	274 years	2,740 years	0.27 µg/l	6.04 mg/kg wet wt.	10.6 mg/kg wet wt.
$6.93 \cdot 10^{-5}$	$6.93 \cdot 10^{-6}$	27.4 years	274 years	0.24 µg/l	5.32 mg/kg wet wt.	1.19 mg/kg wet wt.
$6.93 \cdot 10^{-4}$	$6.93 \cdot 10^{-5}$	2.74 years	27.4 years	0.21 µg/l	4.71 mg/kg wet wt.	0.12 mg/kg wet wt.
$1.90 \cdot 10^{-3}$	$1.90 \cdot 10^{-4}$	1 year	10 years	0.19 µg/l	3.92 mg/kg wet wt.	0.044 mg/kg wet wt.
$6.93 \cdot 10^{-3}$	$6.93 \cdot 10^{-3}$	100 days	2.74 years	0.13 µg/l	2.3 mg/kg wet wt.	0.012 mg/kg wet wt.
0.0139	$1.93 \cdot 10^{-3}$	50 days	1.37 years	0.10 µg/l	1.45 mg/kg wet wt.	0.006 mg/kg wet wt.
0.0231	$2.31 \cdot 10^{-3}$	30 days	300 days	0.08 µg/l	0.97 mg/kg wet wt.	0.004 mg/kg wet wt.
Measured data				0.1 µg/l	0.7 mg/kg wet wt.	0.088 mg/kg wet wt.

As can be seen from the data presented in **Table H4**, the regional soil concentration is particularly sensitive to the value of the degradation rate chosen. A degradation half-life in soil of around 2 years leads to predicted levels that are consistent with the measured data.

The report provides the comprehensive risk assessment of the substance alkanes, C$_{14-17}$, chloro (MCCP). It 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 humans and the environment, laid down in Commission Regulation (EC) No. 1488/94.

Part I - Environment

This part of the evaluation considers the emissions and the resulting exposure to the environment in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined.

The environmental risk assessment concludes that there is concern for the aquatic and terrestrial compartments. This conclusion also applies to secondary poisoning via the earthworm and fish food chains. There is at present no concern for the atmospheric compartment and the waste water treatment plants.

Part II – Human Health

This part of the report is not yet completed, and will be published later.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commission's committee on risk reduction strategies set up in support of Council Regulation (EEC) N. 793/93.

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