Institute for Health and Consumer Protection

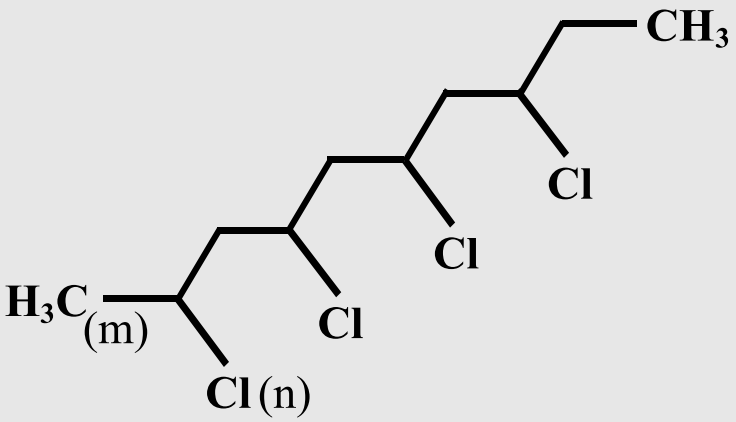
European Chemicals Bureau

Existing Substances

European Union Risk Assessment Report

CAS No.: 85535-84-8 | EINECS No.: 287-476-5

alkanes, C_{10-13}, chloro



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European Union Risk Assessment Report

ALKANES, C_{10-13}, CHLORO-

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RISK ASSESSMENT

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RISK ASSESSMENT

Final report, October 1999

United Kingdom

The rapporteur for the risk evaluation of C10-13 chloroalkanes is the Environment Agency and the Health & Safety Executive acting jointly. The Rapporteur retains responsibility for the risk evaluation and subsequently for the contents of this report.

The scientific work on the environmental part was prepared by the Building Research Establishment (BRE), by order of the Rapporteur.

Contact point:

Environment: Environment Agency
Chemicals Assessment Unit, Ecotoxicology & Hazardous
Substances National Centre
Isis House, Howbery Park
Wallingford
Oxfordshire OX10 8BD
UK

Human health: Health & Safety Executive
New & Existing Substances Section, Chemical
Authorisation & Evaluation Unit
Magdalen House, Stanley Precinct
Bootle
Merseyside L20 3QZ
UK

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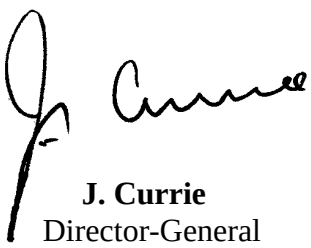
Final report:	**October, 1999**

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 tonnes per year.
There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as "Rapporteur", undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.
The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94[2], which is supported by a technical guidance document[3]. Normally, the "Rapporteur" and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a Meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on 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 risks from exposure to chemicals overall.

H.J. Allgeier
Director-General
Joint Research Centre



J. Currie
Director-General
Environment, Nuclear Safety and Civil Protection

[1] O.J. No L 084 , 05/04/199 p.0001 – 0075
[2] O.J. No L 161, 29/06/1994 p. 0003 –0011
[3] Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]

0 OVERALL RESULTS OF THE RISK ASSESSMENT

CAS-No. 85535-84-8
EINECS-No. 287-476-5
IUPAC name Alkanes, C_{10-13}, chloro

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

This conclusion applies to the sediment and soil compartment for production of short chain length chlorinated paraffins (sediment only), formulation and use of metal working fluids and leather finishing products, use in rubber formulations (sediment only), and also at the regional level. The requirements are:

For soil
- firstly, better information on releases to this compartment to revise the PEC (monitoring data for soil near to sources of release could be useful).
- if the revised PECs do not remove the concern, the PNEC could be revised through toxicity testing on soil-dwelling organisms. The test strategy could be based on the tests recommended in the Technical Guidance Document (currently a plant test involving exposure via soil; a test with an annelid; and a test with microorganisms).

For sediment
- firstly, better information on releases to this compartment to revise the PEC (monitoring data for sediment near to sources of release could be useful).
- if the revised PECs do not remove the concern, the PNEC could be revised through toxicity testing on sediment-dwelling organisms. The test strategy could include firstly a long-term *Chironomid* test; secondly a long-term *Oligochaete* test; and finally a long-term test with *Gammarus* or *Hyalella* (all using spiked sediment).

The risk reduction measures recommended as a result of the assessment of aquatic risks from metal working and leather finishing will also (either directly or indirectly) have some effect on the PECs for sediment and soil. Any further information and/or testing requirements should therefore await the outcome of these risk reduction measures on releases to the environment.[1]

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

This applies to the assessment of
- atmospheric risks;
- risks to waste water treatment plants from production and all uses of short chain length chlorinated paraffins;
- the risk of secondary poisoning arising from production, formulation of metal working fluids and use in rubber formulations, paints and sealing compounds and textile applications;

[1] See Appendix D

- aquatic, sediment and terrestrial risks from use in sealants, backcoating of textiles and paints;
- aquatic and terrestrial risks from use in rubber formulations and from production sites (using site specific data); and
- aquatic risks at the regional level.

This conclusion also applies to the assessment of the risk to human health through occupational exposure, consumer exposure, and exposure via environmental routes.

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

A risk to aquatic organisms exists arising from the local emission of short chain length chlorinated paraffins from metal working and leather finishing applications, and also from the formulation of products for these uses. This conclusion also applies to secondary poisoning arising from formulation and use in leather finishing, and use in metal working applications.

CONTENTS

TABLES

1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

CAS No:	85535-84-8
EINECS No:	287-476-5
IUPAC Name:	Alkanes, C_{10-13}, chloro
Molecular formula:	$C_xH_{(2x-y+2)}Cl_y$, where x=10-13 and y=1-13
Structural formula:	$C_xH_{(2x-y+2)}$)Cly
Molecular weight:	320-500
Synonyms:	alkanes, chlorinated; alkanes (C_{10-13}), chloro-(50-70%); alkanes (C_{10-12}), chloro-(60%); chlorinated alkanes, chlorinated paraffins; chloroalkanes; chlorocarbons; polychlorinated alkanes; paraffins-chlorinated.

There is a range of commercially available C_{10-13} chlorinated paraffins, commonly referred to as short chain length chlorinated paraffins. They are usually mixtures of different carbon chain lengths and different degrees of chlorination, although all have a common structure in that no secondary carbon atom carries more than one chlorine (Willis *et al.*, 1994). Two other groups of chlorinated paraffins are made commercially. These are known as “mid, medium or intermediate chain length” (typically C_{14-17}) and “long chain length” (typically C_{20-30}). This assessment is concerned only with the short chain length (C_{10-13}) chlorinated paraffins but some information on the other types is included when it is considered to be useful and relevant to the assessment.

1.2 PURITY/IMPURITIES, ADDITIVES

1.2.1 Purity

Table 1.1 shows the theoretical % weight chlorine content of several compounds. The amount of chlorine present in the commercial products is usually expressed as a percentage by weight (% wt), but since this refers to a mixture of carbon chain length products it is not possible to identify exactly which compounds are present in the mixture, although **Table 1.1** can be used as a guide. Wherever possible in this report, the actual carbon chain length (or range of carbon chain lengths) and the degree of chlorination will be given.

Commercial products contain 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 chlorine content in any given product (though the work was actually carried out with C_{26} chlorinates). This gives a prediction of approximately 80% of the isomers present lying within ±10% of the stated average chlorine content, or 90% within ±15%. Thus, in a short chain length 50% wt chlorine content 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).

Table 1.1 Theoretical chlorine content of some short chain length chlorinated paraffins

Formula	% Cl by weight	Formula	% Cl by weight	Formula	% Cl by weight
$C_{10}H_{21}Cl$	20.1	$C_{11}H_{19}Cl_5$	54.0		
$C_{10}H_{20}Cl_2$	33.6	$C_{11}H_{16}Cl_8$	65.7	$C_{13}H_{27}Cl$	16.2
$C_{10}H_{18}Cl_4$	50.7	$C_{11}H_{13}Cl_{11}$	72.9	$C_{13}H_{26}Cl_2$	28.1
$C_{10}H_{16}Cl_6$	61.0			$C_{13}H_{24}Cl_4$	44.1
$C_{10}H_{14}Cl_8$	67.9	$C_{12}H_{25}Cl$	17.4	$C_{13}H_{20}Cl_8$	61.7
$C_{10}H_{12}Cl_{10}$	72.9	$C_{12}H_{24}Cl_2$	29.7	$C_{13}H_{18}Cl_{10}$	67.1
		$C_{12}H_{20}Cl_6$	56.5	$C_{13}H_{16}Cl_{12}$	71.2
$C_{11}H_{23}Cl$	18.6	$C_{12}H_{16}Cl_{10}$	68.9	$C_{13}H_{14}Cl_{13}$	73.1
$C_{11}H_{22}Cl_2$	31.6	$C_{12}H_{14}Cl_{12}$	72.9		

Any impurities in commercial chlorinated paraffins are likely to be related to those present in the n-paraffin feedstocks, in which the major non-paraffinic impurity is a small proportion of aromatics, generally in the range 50-100 ppm. However, there is some evidence that the reaction does not favour chlorination of aromatics. No specific methods are available for detection of possible impurities and chlorinated paraffins are generally not amenable to analysis by techniques such as gas chromatography (ICI, 1995).

1.2.2 Additives

Various stabilisers are often added to commercial chlorinated paraffin products in order to improve the thermal stability or light stability. An example of a stabiliser for a short chain length chlorinated paraffin would be epoxidised vegetable oil (typical concentration <0.5%).

1.3 PHYSICO-CHEMICAL PROPERTIES

The physical and chemical properties of the C_{10-13} chlorinated paraffins are determined by the chlorine content (typically 49-70% for commercial substances). There are a wide number of possible chlorinated paraffins (of different 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 interpreting some of the physico-chemical data. Increasing chlorine leads to an increase in viscosity and a decrease in volatility. The C_{10-13} chlorinated paraffins are relatively inert substances, which are resistant to chemical attack and are hydrolytically stable. They possess good thermal stability. However if held at high temperatures (>200^{o}C) for long periods they will darken and release detectable quantities of hydrogen chloride (Hoechst AG, 1990).

The physico-chemical properties are discussed below and summarised in **Table 1.2**.

Table 1.2 Physico-chemical properties of some short chain length chlorinated paraffins

Property	Chlorine content (% wt)	Value	Remarks
Physical state at ntp	49-70	-	clear to yellowish liquid
Pour point	49	-30.5°C	commercial mixtures – no distinct melting point
	70	+20.5°C	
Boiling point (at ntp)		>200°C	decomposition with release of hydrogen chloride
Density (at 25°C)	49-70	1.2-1.6 g/cm^3	
	52-70	1.3-1.6 g/cm^3	
Vapour pressure (at 40°C)	50	0.021 Pa	
Water solubility (at 20°C)	59	0.15-0.47 mg/l	with partial hydrolysis
Log octanol-water partition coefficient	49	4.39-6.93	measured by a high performance thin layer chromatography method except which was measured by a slow stirring method
	60	4.48-7.38 5.85-7.14[a]	
	63	5.47-7.30	
	70	5.68-8.69	
	71	5.37-8.01	
Flash point	50	166°C	closed cup
	56	202°C	
Autoflammability		not stated	decomposes with liberation of hydrogen chloride above 200 °C
Explosivity		not explosive	
Oxidising properties		none	

1.3.1 Physical state (at ntp)

Short chain length chlorinated paraffins are clear or yellowish mobile to highly viscous oily liquids with only a faint odour.

1.3.2 Melting point

Commercial mixtures do not have a distinct melting point. Pour points can be quoted for these materials which are more appropriate. IUCLID presents a pour point range of -30.5°C to +20°C for a chlorine content of approximately 49% to 70% respectively (Hoechst AG, 1990).

1.3.3 Boiling point

The boiling point can be considered to be >200^{o}C at ntp, above which decomposition with release of hydrogen chloride occurs.

1.3.4 Relative density

IUCLID presents densities ranging from 1.18 to 1.55-1.59 g/cm^3 for chlorine contents between 49% and 71% (Hoechst AG, 1990).

1.3.5 Vapour pressure

For a chlorine content of 50%, the vapour pressure has been measured at 0.0213 Pa at 40^{o}C. No data is available for higher chlorine contents.

1.3.6 Solubility

Short chain length chlorinated paraffins are practically insoluble in water. IUCLID presents data for solubility after exposure to water for 6 months, which was estimated to be 0.15-0.47 mg/l (for a chlorine content of 59%). However, these results may have been affected by partial hydrolysis of the chlorinated paraffin (Madeley and Gillings, 1983).

They are highly soluble in chlorinated solvents, aromatic hydrocarbons, esters, ketones and ethers, moderately soluble in aliphatic hydrocarbons and slightly soluble in lower alcohols.

1.3.7 Partition coefficient

Renberg *et al.* (1980) determined the octanol-water partition coefficients for a range of short chain length chlorinated paraffins. The partition coefficients were determined by a high performance thin layer chromatography (HPTLC) method. The range quoted reflects the different HPTLC retention times, and hence octanol-water partition coefficients of the various components of the mixtures. The partition coefficients determined (log values) were 4.39-6.93 (C_{10-13}, 49% wt Cl), 4.48-7.38 ($C_{11.5}$, 60% wt Cl), 5.47-7.30 (C_{10-13}, 63% wt Cl), 5.68-8.69 (C_{10-13}, 70% wt Cl) and 5.37-8.01 (C_{10-13}, 71% Cl).

Sijm and Sinnige (1995) determined the octanol-water partition coefficient of a C_{10-13}, 60% Cl chlorinated paraffin using a "slow-stirring" method at 25^{o}C. The chlorinated paraffin was dissolved in octanol (at concentrations of 25 or 50 µg/l) and was stirred with water for up to 7 days. The log K_{ow} values determined for the individual components of the commercial chlorinated paraffin were determined in the range 5.85 to 7.14, which are in good agreement with the values determined by Renberg *et al.* (1980).

An alternative calculated range for log octanol-water partition coefficient of 6.0->6 for $C_{10}H_{21}Cl$ - $C_{10}Cl_{22}$ was presented by Hoechst AG (1990). The partition coefficients are relatively crude but within the range of the measured values reported by Renberg *et al.*

1.3.8 Flash point

IUCLID presents a flash point of 166°C (closed cup) for a product containing 50% chlorine, with a value of 202°C for a product containing 56% chlorine. Higher chlorine content products all have flash points above 200°C.

1.3.9 Autoflammability

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

1.3.10 Explosivity

Not explosive.

1.3.11 Oxidising properties

No oxidising properties.

1.4 CLASSIFICATION

1.4.1 Current classification

Short chain length chlorinated paraffins are classified as a dangerous substance within the meaning of Directive 67/548/EEC. The classification is:

Carcinogen Category 3: R40, with the symbol Xn; and
Dangerous for the Environment, with the symbol N

They are assigned the risk phrases:

R40 - Possible risk of irreversible effects, and
R50/53 - Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

1.4.2 Proposal of rapporteur

The rapporteur agrees with the current classification.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

Short chain length chlorinated paraffins are currently manufactured by two companies in the EU under a variety of trade names. According to IUCLID, there were five producers in the EU in 1992/3. Based on Euro-Chlor figures, the total EU production volume is now ≤15,000 tonnes/year (Euro-Chlor, 1995).

Chlorinated paraffins are manufactured by adding chlorine gas into the starting paraffin fraction at a temperature of 80-100^{o}C without a solvent. No catalysts are necessary in the reaction although visible light is often used to initiate the reaction. The reaction gives out heat and so the reactor must be cooled. Both batch and continuous processes can be used but batch processes are generally preferred since this allows accurate specification of the different grades to be achieved (Ullmann, 1986).

Short chain length chlorinated paraffins are transported from production sites to formulators' premises in road tankers and in drums.

2.2 USE

The main uses of short chain length chlorinated paraffins are in metal working fluids, sealants, as flame retardants in rubbers and textiles, in leather processing and in paints and coatings.

A breakdown of the uses of short chain length chlorinated paraffins in Western Europe for 1994 is given in **Table 2.1** (Euro-Chlor, 1995).

Table 2.1 Use of short chain length chlorinated paraffins in Western Europe in 1994

Application	Quantity used (tonnes/year)	Percentage of total use
Metal working	9,380	71.02%
Rubber	1,310	9.91%
Paints	1,150	8.71%
Sealants	695	5.26%
Leather	390	2.95%
Textiles	183	1.40%
Others	100	0.75%
Total	13,208	100%

Metal working fluids account for the bulk of short chain chlorinated paraffin use in Europe (approximately 71% of total use), followed by flame retardant use in rubber (approximately 10%) and use in paints (approximately 9%). The other minor uses (approximately 10% in total) include use in leather finishing, sealants and textiles. It has also been reported that chlorinated paraffins (possibly including short chain length) are sometimes used as extreme pressure additives in greases, although the quantities involved are likely to be small.

There is a general decline in the amounts of short chain length chlorinated paraffins used within Europe, particularly in the metal working and leather areas (for instance, in Germany an overall reduction in their use in metal working fluids of around 50% has occurred (ICI, 1995) and their use has practically been discontinued in water-oil emulsions (BUA, 1992).

In Sweden the use of all chlorinated paraffins in metal working fluids has been reduced by 80% overall (a 95% reduction in water-oil emulsions (i.e. 160 tonnes in 1986 and 8.5 tonnes in 1993) and a 75% reduction in straight oil based cutting fluids (i.e. 520 tonnes in 1986 and 130 tonnes in 1993) between 1986 and 1993 and is expected to reduce further. 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 short chain length highly chlorinated paraffins. Uses in some areas, notably the flame retardant/plasticiser uses of short chain length chlorinated paraffins, may increase in future as newer applications are exploited (Stenhammar and Björndal, 1994).

Further information on use of short chain chlorinated paraffins has been obtained from product registers from certain countries. For Sweden in 1995, 104 tonnes were used as fire retardants additives, 116 tonnes in metal cutting fluids, 107 tonnes as a plasticiser in rubber products, with smaller amounts (1-3 tonnes) in paints/varnishes and lubricants, etc. In Norway, the annual consumption of short chain length chlorinated paraffins is thought to be 35 tonnes/year, with the main use being as a flame retardant (18 tonnes/year) and surface active agent (17 tonnes/year). There is no reported use or import of short chain length chlorinated paraffins in the Czech Republic. In Switzerland, short chain length chlorinated paraffins are not used in consumer products.

2.2.1 Metal cutting/working fluids

The major use of short chain length chlorinated paraffins (typically 49-69% wt chlorine content) is as an extreme pressure additive in metal working fluids. These fluids are used in a variety of engineering and metal working operations such as drilling, machining/cutting, drawing and stamping. The chlorinated paraffins are blended with other additives including corrosion inhibitors, emulsifiers, biocides and surface active agents. Approximately 80% of short chain chlorinated paraffins are used in straight oil applications (in solution in a hydrocarbon) and 20% in soluble oil emulsions (dispersed in water). The chlorinated paraffin content of the straight oil metal working fluid usually ranges from 2 to 10% (typically 5%), but can be up to 80% or more for some speciality applications. When used in emulsions, a concentrate containing typically 15% chlorinated paraffin in oil is used, which will be emulsified with water to give an emulsion typically containing 5% oil (hence the chlorinated paraffin content would be 0.75% in the emulsion).

Chlorinated paraffins improve the pressure-accepting capacity of emulsified and non-emulsified metal working fluids. The chlorinated paraffins are thought to work by liberating hydrogen chloride as the metal surface heats up. This leads to the formation of metal chlorides. The metal chlorides have a good lubricating and parting effect and so help prevent the welding together of the metal parts under the high pressures and temperatures involved. In general, the efficiency of the metal working fluid increases as the chlorine content of the chlorinated paraffin increases.

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According to 1995 Euro-Chlor figures (RPA, 1996), the United Kingdom (32.3% of total use), France (29.9% of total use), Italy (14.8% of total use), Germany (12.8% of total use) and Spain (4.8% of total use) are the largest users of short chain length chlorinated paraffins in metal cutting fluids in the EU, although most other EU countries appear to use them in small amounts. The total EU usage in metal working fluids for 1995 was thought to be around 8,500 tonnes/year, similar to the figure for 1994 given in **Table 2.1**.

2.2.2 Rubber industry

Due to their fire retarding properties, the highly chlorinated (typically 63-71% wt Cl) short chain length chlorinated paraffins find use in rubber formulations. In general, they are used in a proportion of 1-10% in conjunction with other flame retarding additives such as antimony trioxide and aluminium hydroxide.

The major use of short chain length chlorinated paraffins in this area appears to be in high density conveyor belts, along with other technical products such as hoses and gaskets. The belts are mainly used in the coal mining industry. The life of the belts is around 10 years and used belts are increasingly being recycled by reduction to powder and subsequent formation of belts, mats, building materials, etc.

2.2.3 Paint industry

Chlorinated paraffins are used as plasticisers in paints and other coating systems. They can also be used to improve the water resistance, chemical resistance and the nonflammability of paints. The paints are mostly solvent based and are used mainly in industrial/specialist applications such as marine primer paints, fire retardant paints and paints for roadmarkings.

Generally, compounds of moderate chlorine content (e.g. 60-65% wt Cl) seem to be used. They are used at proportions of 1-10% in paints based on resins such as chlorinated rubber, vinyl copolymers and acrylics. Actual formulations for paints are not commonly available but the published information indicates that a 10% total chlorinated paraffin content is typical for most paint types. The main types of chlorinated paraffins used in paints are the longer-chain grades, but some short chain length chlorinated paraffins are used, mainly in acrylic base coatings (Bowerman, 1971; Eckhardt and Grimm, 1967; Allsebrook, 1972).

2.2.4 Sealing compounds

Short chain length chlorinated paraffins can be used as additives in sealing compounds (e.g. polysulphide, polyurethane, acrylic and other polymer sealants/adhesives) for use in building, automotive and industrial applications. They act as plasticisers in order to achieve the desired hardness and elasticity. They can also impart flame resistant properties to the sealant. The leachability and volatility of short chain length chlorinated paraffins over the lifetime of the sealant (typically 20 years) is reported to be low.

The short chain length compounds used appear to have chlorine contents in the range 56-65% wt.

2.2.5 Leather industry

Short chain length chlorinated paraffins are reported to be used in the leather industry as fat liquoring agents. They show better adhesion to the animal skin than natural oils, with similar fattening and softening properties. They also impart better washability to the leather than natural oils. They are usually applied to the moist dressed leather in the form of a 10-30% emulsion or are added to sulphated or sulphonated oil or synthetic emulsifying agents. The chlorinated paraffins used generally have a low chlorine content (20-40% wt Cl) (BUA, 1992).

Short chain length chlorinated paraffins are not used in significant quantities in the leather industry in the United Kingdom, Scandinavia/Denmark, Spain or France. When chlorinated paraffins are used in fat liquoring in these countries, they tend to be of longer chain lengths and/or as the sulphochlorinated paraffin. The use of chlorinated paraffins and sulphochlorinated paraffins in this area appears to be decreasing in most countries.

In the United Kingdom, the only use of short chain length chlorinated paraffins identified (1-2 tonne/year) is to produce a surface sheen to certain types of suede slippers.

In a recent survey of the European leather finishing industry (EC, 1996), sulphonated chlorinated paraffins were identified as being used in fat liquoring processes. However, it was also stated that as a result of concerns over the release of adsorbable organic halogens it is possible that chlorinated fat liquoring products will be replaced by other products.

2.2.6 Textile industry

The highly chlorinated short chain length chlorinated paraffins can be used in the production of flame-resistant, water repellent and rot-preventing textile finishes. Applications for such finishes include sail cloths, industrial protective clothing, lorry tarpaulins, etc. The major historical use of chlorinated paraffins was in military tenting, but it is believed that they are no longer used in this application in the EU.

Information provided by the Chlorinated Paraffins Sector Group of Euro-Chlor indicate that current usage of short chain length chlorinated paraffins in textiles in the EU is very low, with the majority being used in back coating of textiles (the short chain length chlorinated paraffin is applied to the textile in a polymer matrix), with smaller amounts being used in other textile treatments. In 1994, 183 tonnes of short chain length chlorinated paraffins were used in the EU in textile applications (see **Table 2.1**). This figure was broken down between 163 tonnes/year used in backcoating operations and 20 tonnes in other textile treatments (e.g. waterproofing). Figures for 1995 indicate that a total of 37 tonnes were used in the EU: 32 tonnes in backcoating and 5 tonnes in other treatments.

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2.3 EXPOSURE CONTROL

The main route of potential worker exposure that exists during manufacture, formulation and use of C_{10-13} chlorinated paraffins is via skin contact. Exposure via skin contact can be controlled by the decontamination of equipment where appropriate and by use of personal protective equipment (PPE). Most users require the use of PPE such as gloves, coveralls, boots and safety goggles to be routinely worn.

Exposure to vapour is generally considered insignificant due to the low vapour pressures involved. However, there is a potential for significant inhalation exposure to C_{10-13} chlorinated paraffins during the formulation of hot melt adhesives and in the use of metal working fluids. Local exhaust ventilation can be used to control inhalation exposure in the hot melt adhesive manufacturing sector. In the metal working sector, inhalation exposure to mists/aerosols of metal working fluids can be controlled by using anti-mist additives in the formulation and by enclosing the workpiece using splash guards.

3 ENVIRONMENT

3.1 EXPOSURE ASSESSMENT

3.1.0 General discussion

In the assessment, releases to the environment are considered in various scenarios. These are explained more fully in the Technical Guidance Document. The local environment is considered to be the environment near to a site of release (e.g. a production or processing site). The regional environment is taken to represent a highly industrialised area (size is 200 km by 200 km with 20 million inhabitants) and it is assumed that 10% of the European production or 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.

3.1.0.1 Releases from production

It is known that in the United Kingdom production of chlorinated paraffins is carried out in a batch process (Willis *et al.*, 1994). This is to enable close control of reaction conditions to be maintained in order to achieve accurate specification of the different grades. Proposals for emission factors from production in batch processes (Main Category Ic) are given in Appendix 1 of the Technical Guidance Document. For short chain length chlorinated paraffins the release fractions are 0 to air, 0.003 (i.e. 0.3%) to waste water and 0.0001 (i.e. 0.01%) to soil.

Mukherjee (1990) reported that the loss of total chlorinated paraffins during production was about 0.1 g/kg (0.01%). The loss is mainly to air, probably as dust for the solid products. However, given the physico-chemical properties of the substance, it is likely that any substance present in air will be adsorbed onto particles which may settle out of the air and eventually enter waste water. It will be assumed that this emission factor is applicable to the production of short chain length chlorinated paraffins throughout the EU and that emissions will be mainly to wastewater (it should be noted that use of the release factor given in the Technical Guidance Document would lead to a larger release to water, and hence a higher PEC).

Information provided on a German production plant indicates that losses to waste water only occur during the manufacture of solid (i.e. long chain length, C_{20-30}, chlorinated paraffins and that the total loss of all chlorinated paraffins to waste water was around 1 kg/year. However, it was also estimated that around 250 kg/year of chlorinated paraffins were released to air (as dust and vapour) in Germany in 1990 (BUA, 1992).

Assuming the maximum likely production at any one site is 10,000 tonnes, the following (local) release estimate can be made using the following emission scenario:

Release factor	= 0.01%
Quantity of chlorinated paraffin produced at 1 site	= 10,000 tonnes/year
Quantity released at 1 site	= 1 tonne/year
	= 3.33 kg/day (assuming 300 days production)

Note that if the Technical Guidance Default release figure of 0.3% is used, the daily release at a production site would be 100 kg/day.

By a similar argument, assuming that a total of 15,000 tonnes/year are made within the EU, the quantity released in the EU would be 1.5 tonnes/year or (45 tonnes/year using the Technical Guidance Default release figure).

Information provided by the two current producers in the EU indicate that the maximum releases of short chain length chlorinated paraffin to waste water are much lower than the figures estimated here and are likely to be less than 9.9-26.7 kg/year.

3.1.0.2 Releases from use

3.1.0.2.1 Use in metal working and extreme pressure lubricating fluids

Formulation

Information on the blending and formulation of metal working fluids in the United Kingdom has been obtained (UCD, 1995). Blending is frequently carried out in a batch process. Usually the additives are added to the base oil either by meter from a bulk storage tank or directly either in neat form or diluted with the base oil. Solid additives which are soluble in the base oil are almost always pre-dissolved in a small quantity of the oil before adding to the blend. 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.

It has been estimated that the highest likely loss of lubricant at a formulation site would typically be in the region of 1%, with a maximum of 2%. 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 fluids containing chlorinated paraffins). Typical losses of the lubricant blend to waste water are thought to be around 0.25%. This figure is derived from information on the discharge consents for oil for blending sites in the United Kingdom (UCD, 1995).

Assuming that 9,380 tonnes/year of short chain length chlorinated paraffins are used in the EU in metal cutting fluids, then the release to waste water at the formulation stage can be estimated as 23.45 tonnes/year. Similarly, the release in the regional model would be around 2.35 tonnes/year (assuming a total usage of 938 tonnes). In the United Kingdom there are thought to be 6 large lubricant blending plants for all types of lubricants. Assuming that each plant produced cutting fluids containing short chain length chlorinated paraffins (there is evidence to suggest that most formulators do or have used short chain length chlorinated paraffins (RPA, 1996), the quantity of chlorinated paraffins used at any one site can be estimated as a sixth of that estimated in a country/regional model (i.e. 156 tonnes/year). Thus the release of short chain length chlorinated paraffins at any one site can be estimated as 391 kg/year, or 1.3 kg/day over 300 days. In addition, there may be some release at sites where drums are recycled/cleaned, however, it is currently not possible to quantify this.

Use

Appendix 3 of the Technical Guidance Document provides some emission scenarios for the release of lubricant additives from water-based fluids but does not give any guidance as to the release from use in oil-based fluids, the major use of short chain length chlorinated paraffins. Appendix 1 (Table A3.7) of the Technical Guidance document gives release figures to waste water for metal working fluid additives of 18.5% from oil-based fluids and 31.6% from water based fluids.

The releases of short chain length chlorinated paraffins from metal working fluids have been discussed in a recent report from Canada (Government of Canada, 1993). It was thought that the majority of the short chain chlorinated paraffins used had chlorine contents in the range 50-60% wt. Release to the environment was thought to occur from disposal of used drums, carry-off from work pieces and disposal of spent fluid. No information was reported on the releases from drum disposal/recycling but it was thought that it would be small.

Using data obtained by the United States Environmental Protection Agency from the Chlorinated Paraffins Industry Association, losses due to carry-off from work pieces were estimated to be 2.5 kg/site/year for a small user (100 l capacity) and 2,500 kg/site/year for a large user (95,000 l capacity) (Government of Canada, 1993). [It is not clear whether these figures refer to short chain length chlorinated paraffin, total chlorinated paraffin or total fluid - as a worst case approach it will be assumed that they refer to the short chain length chlorinated paraffin. This is then consistent with short chain length chlorinated paraffins making up around 5% by weight (see Section 2.2.1) of the metal working fluid (i.e. 95,000 l of cutting fluid would contain around 5,000 kg of short chain length chlorinated paraffin), and a loss rate of 50%]. Release to water from the disposal of spent chlorinated paraffin baths was estimated to vary between 12 to 1,500 kg/site/year, with 90% of the sites being near to the lower end of the range (again, it is not clear if these figures refer to chlorinated paraffin or total fluid).

Information on the use of and release from metal working fluids in the United Kingdom has also been obtained (UCD, 1995). Losses of cutting fluid, and hence any additive 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 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 the UK 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 are thought to be near 50% for a large machine shop, 75% from a medium sized machine shop and 100% from a small machine shop. Not all of this loss, however, is released to water.

A breakdown of the total losses for a large and small machine shop using oil-based cutting fluids are shown **in Table 3.1**.

Table 3.1 Total losses for a large and small machine shop using oil-based cutting fluids

	Large facility with swarf reprocessing		Small facility -no swarf reprocessing	
Misting/evaporation	2%	to air	2%	to air
Overalls	1%	to water	2%	to water
Leaks	1%	to water*	3%	to water*
Dragout/swarf	27%	incinerated	81%	incinerated
	3%	to landfill	9%	to landfill
Dragout/workpiece	1%	to water	1%	to water
	2%	chemical waste	2%	chemical waste
Internal reprocessing	1%	to water*		
External reprocessing	10%	reused/discarded as waste oil		
Total losses	48%		100%	

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

As can be seen from the figures, the losses to waste water from a large and small machine shop can be as low as 4% and 6% respectively. However some of the other losses have the potential for entering waste water. For instance although misting/evaporation losses are initially to air, these have the potential to settle within the facility and reach waste water as a result of cleaning of 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 less well controlled facilities there remains the possibility that this could be discharged to waste water. The major losses of metal cutting fluids are associated with the swarf. It is thought that the vast majority (90%) of the swarf produced (and adhering cutting fluid) is melted for re-use, thus the cutting fluid and any additive will be destroyed by this process. In some situations, the swarf may undergo solvent cleaning prior to melting, and so some short chain length chlorinated could end up in waste solvent at such sites. The remaining 10% of swarf is thought to be disposed of to landfill. The final source of loss is due to dragout of the cutting fluid on the work piece. 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 emission 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 estimated that a worst case loss from a metal finishing facility could be in the region of 18%. The situation with emulsifiable cutting fluids is similar, with estimated emissions to water of between 5 and 13% taking the best and worst case assumptions as above. In addition, it is expected that around 3% of the total amount used will end up in landfill as a result of swarf disposal.

It is thought that a typical large scale metal working plant in the United Kingdom would contain about 50,000 litres of cutting oil. This size will be used as the basis of the local emission scenario. PECs in water will be calculated based on what is thought to be a low emission of 4%/year and a worst case figure of 18%/year (this figure is also consistent with the default figure given in Appendix 3 of the Technical Guidance Document). Assuming that the short chain length chlorinated paraffin makes up around 5% of the cutting fluid, then 50,000 litres of cutting fluid would contain around 2,500 kg of short chain length chlorinated paraffin. Thus the possible emissions from a large metal finishing plant to water can be estimated as 100 kg/year or 450 kg/year of short chain length chlorinated paraffin. Assuming use on 300 days/year these emissions are equivalent to 0.33 kg/day or 1.5 kg/day. These emission estimates are based on an average chlorinated paraffin content of 5% in the cutting

fluid. Much higher contents may be used for some applications (up to 80% chlorinated paraffin content) and so emissions from some facilities may be higher than the figures estimated here.

An EU wide release of short chain length chlorinated paraffins from use in metal working fluids of 1,688 tonnes/year can be estimated by assuming an EU consumption of 9,380 tonnes/year in this application and a release of 18% of use. Similarly, the release in the regional model would be around 169 tonnes/year (assuming total usage of 938 tonnes/year). Again, assuming use on 300 days/year, the releases are equivalent to 563 kg/day in the regional model and 5,627 kg/day in the EU. In addition, it can be estimated that, in the EU, around 281 tonnes/year of short chain length chlorinated paraffins will be disposed of to landfill as a result of swarf disposal.

3.1.0.2.2 Use as a flame retardant in rubber formulations

A recent report from Canada gave Swedish estimates of the release of chlorinated paraffins from use as a flame retardant as <0.001% of that used (Government of Canada, 1993).

If it is assumed that 1,310 tonnes/year are used in the EU or 131 tonnes/year in a region in rubber formulations, the following local and regional emission estimates can be obtained:

Amount used in regional model	= 131 tonnes/year
Percentage released	= 0.001%
No of days of operation	= 300/year
Amount released in regional model	= <1.3 kg/year = <0.004 kg/day
Number of sites of release	= 1
Amount released/site (local model)	= <0.004 kg/day

Similarly, assuming a total EU usage in rubber formulations of 1,310 tonnes gives an EU wide release of <0.04 kg/day.

3.1.0.2.3 Use as a plasticiser in paints and sealing compounds

It is thought that around 1,150 tonnes/year of short chain length chlorinated paraffins are used in paints in the EU. A slightly smaller amount (695 tonnes/year) are thought to be used in sealants in the EU. A recent report from Canada estimated that release of chlorinated paraffins from formulation and use in paints would be minimal (Government of Canada, 1993).

Since the chlorinated paraffins are incorporated into the final finish, they may eventually be released by leaching/volatilisation from the paint. However, the low vapour pressures of chlorinated paraffins mean that volatilisation from the finished painted surface is likely to be low and the low water solubility means that leaching from the paint during use is likely to be minimal. Further, for some applications such as marine paints, the chlorinated paraffin-containing paint is used as a primer (Bowerman, 1971) and is subsequently covered with a top coat of a different type, thus further minimising the possibility of leaching. Release of chlorinated paraffins from disposal of painted articles is also likely to be low as high temperature incineration is likely to destroy the chlorinated paraffins, and leaching from landfill is likely to be low due to the high adsorption of the chemicals onto soil.

Release from use in sealing compounds is likely to be minimal due to the same arguments given above for paints. No default release factors are currently available in the Technical Guidance Document for this use.

3.1.0.2.4 Use in leather applications

The situation over the use of short chain chlorinated paraffins in leather finishing in the EU is very confused. It is not clear if they are sulphonated before use or are used as fat liquoring agents in mixtures with sulphonated compounds. The following scenarios cover the possible uses, although recent information indicates that Scenario B is more realistic of the actual use in the EU (i.e. short chain chlorinated paraffins are not thought to be sulphonated before use in the EU). However, in terms of the risk assessment, the actual releases to the environment estimated for the two Scenarios are similar and would lead to similar conclusions.

Scenario A

There is some confusion over whether short chain length chlorinated paraffins are sulphonated before use in leather applications. The current information available indicates that this is not the case and that Scenario B is more representative of the actual use. However, this scenario covers this possible use and will assume that the chlorinated paraffin is changed during the reaction and that release of the parent chlorinated paraffin during leather processing is likely to be minimal. The main source of release to the environment could be due to the sulphonation process. A worst case scenario can be derived using the default release factors given in the Technical Guidance Document (Industry Category 7: Leather processing industry, Formulation), assuming that all 390 tonnes of short chain length chlorinated paraffins are sulphonated in the EU, with 10% in a region.

Amount of short chain length chlorinated paraffins used/amount of sulphonated compounds produced used in region	= 39 tonnes/year
Release fraction to air	= 0.00001 (Table A1.1, Default –see below)
Release fraction to water	= 0.02 (Table A2.1)
Fraction produced at one site	= 0.9 (Table B2.4)
Number of days of release	= 35 (Table B2.9)
Amount released/site (local model)	= 0.01 kg/day to air and 20 kg/day to waste water
Amount released in region	= 0.39 kg/year to air and 780 kg/year to waste water
Amount released in EU	= 3.9 kg/year to air and 7,800 kg/year to waste water

The default release fraction to air for this substance is given as 0.0025 in Table A2.1 of the Technical Guidance Document. This is derived for substances with vapour pressures <10 Pa at 25^{o}C. The actual vapour pressure for short chain length chlorinated paraffins is much less than this (0.0213 Pa at 40^{o}C) and so the release fraction given in Table A2.1 is likely to be much too high. The default release fraction to air of 0.00001 from Table A1.1(Production) is used instead since this is derived for substances with low vapour pressures.

Scenario B

Industry sources have indicated that short chain length chlorinated paraffins are actually be used as mixtures with sulphonated compounds or other fat liquoring chemicals (natural oils).

The sulphonated compounds are not thought to be derived from short chain length chlorinated paraffins. In this scenario, releases of short chain length chlorinated paraffins could occur during the formulation and processing (use in leather finishing) steps. In the absence of any other information it will be assumed that the actual products used are 50:50 mixtures of short chain length chlorinated paraffins and other compounds. Thus, if 390 tonnes/year of short chain length chlorinated paraffins are used in the EU each year, this would give the total amount of product (50:50 mixture) used of around 780 tonnes/year, with 10% of this i.e. 78 tonnes being used in a region.

The releases from the formulation step can be estimated using the release estimates given in the Technical Guidance Document for (Industry Category 7: Leather processing industry, Formulation):

Amount of 50:50 product produced in region	= 78 tonnes/year
Release fraction to air	= 0.00001 (Table A1.1, Default)
Release fraction to water	= 0.02 (Table A2.1)
Fraction produced at one site	= 0.8 (Table B2.4)
Number of days of release	= 25 (Table B2.9)
Amount of short chain length chlorinated paraffin released/site (local model)	= 0.012 kg/day to air and 25 kg/day to waste water
Amount released in region	= 0.39 kg/year to air and 780 kg/year to waste water
Amount released in EU	= 3.9 kg/year to air and 7,800 kg/year to waste water

Recent data provided by industry indicate that short chain chlorinated paraffins are formulated by blending with natural oils and that the amount of short chain length chlorinated paraffin formulated in the EU has fallen from the 390 tonnes/year reported in 1994 but the amount formulated on a large site is of the same order, but slightly larger than the above estimate.

The release from processing (use) of the 50:50 mixture can be estimated from the Technical Guidance Document as follows:

Amount of 50:50 product used in region	= 78 tonnes/year
Release fraction to air	= 0.001 (Table A3.6)
Release fraction to water	= 0.05 (Table A3.6, MC 2 – inclusion into/onto matrix
Fraction used at one site	= 0.6 (Table B3.4)
Number of days of release	= 47 (Table B2.9)
Amount of short chain length chlorinated paraffin released/site (local model)	= 0.5 kg/day to air and 25 kg/day to waste water
Amount released in region	= 39 kg/year to air and 1,950 kg/year to waste water
Amount released in EU	= 390 kg/year to air and 19, 500 kg/year to waste water

Recent information collected as part of the risk reduction study (RPA, 1997) for this use have indicated that short chain chlorinated paraffins may comprise around 20% of the fat liquoring mix and that around 95-99% of the chlorinated paraffin is taken up by the leather,

leaving 1-5% in the waste washings (the default calculation above assumes a 5% release to waste water). The same report also indicates that the actual use in the EU is currently around 100-150 tonnes/year. If these figures are used in the default calculations as above, the amount of fat liquoring agent used in the EU containing 20% short chain chlorinated paraffin is up to 750 tonnes/year. Thus the amount used in a region is 75 tonnes/year containing 20% chlorinated paraffin. The local releases estimated using this new data would be around 40% of those estimated above based on the 1994 data. This would no alter the overall conclusions for this use.

3.1.0.2.5 Use as a flame retardant in textile applications

No information was provided as to the amount of short chain chlorinated paraffins released from textile applications. It is thought that 183 tonnes/year (163 tonnes/year in backcoating and 20 tonnes/year in other uses) of short chain length chlorinated paraffins were used in textile applications in the EU in 1994, but this had fallen to 37 (32 tonnes/year in backcoating and 5 tonnes/year for other uses) in 1995.

In backcoating, the short chain length chlorinated paraffin is applied to the back of the material in a viscous polymer latex, which is then cured, usually by heating to 130-140^{o}C for a few seconds to drive off water. Once cured, the additive is incorporated in a polymer matrix which should minimise losses due to volatilisation and leaching.

Losses to the environment during the backcoating process are thought to be very low, mainly associated with the cleaning out of the formulation vessels and the application machinery. The losses from these operations are likely to be mainly in the form of a polymer containing the chlorinated paraffin and is likely to be collected for disposal rather than sent to sewer, which should minimise the actual release of chlorinated paraffin to the environment.

Little information is available on the other uses of short chain length chlorinated paraffins, although it is thought that for some applications the chlorinated paraffin is applied in emulsion form and so releases could be to water. However, the quantities involved (around 5 tonnes/year) are small.

3.1.0.3 Summary of release estimates

The release estimates are summarised in **Table 3.2**.

The actual estimates are subject to a very large uncertainty due to the many assumptions that have been made. However, based on the above assumptions, the largest releases on a EU wide basis are associated with metal working applications. Releases from other uses on a regional and continental basis are much less significant.

It should also be noted that the release from production is based on a release rate of 1,000 or 30,000 kg/year to waste water. Information provided by the EU producers indicate that the actual emissions to waste water are much lower than the figures used.

Table 3.2 Summary of release estimates

Source	Amount released/site (local model)	Amount released in region	Amount Released in EU	Main compartment to which release occurs
Production (default)	3.33 or 100 kg/day	1,000 or 30,000 kg/year	1,500 or 45,000 kg/year	Water
Production (site specific information)	<0.089 kg/day	<26.7 kg/year	<36.6 kg/year	Water
Metal working -formulation	1.3 kg/day	2,345 kg/year	23,450 kg/year	Water
Metal working – use	0.33 kg/day or 1.5 kg/day	169 tonnes/year	1,688 tonnes/year	Water
Rubber formulations	<0.004 kg/day	<1.2 kg/year	<12 kg/year	Air/soil/water
Paints and sealing compounds	negligible	negligible	negligible	
Leather formulation (Scenario A)	0.01 kg/day 20 kg/day	0.39 kg/year 780 kg/year	3.9 kg/year 7,800 kg/year	Air Water
Leather formulation (Scenario B)	0.012 kg/day 25 kg/day	0.39 kg/year 780 kg/year	3.9 kg/year 7,800 kg/year	Air Water
Leather use (Scenario B)	0.5 kg/day 25 kg/day	39 kg/year 1,950 kg/year	390 kg/year 19,500 kg/year	Air Water
Textile applications	negligible	negligible	negligible	
Total (for EUSES model)		39.39 kg/year 204.1 tonnes/year	393.9 kg/year 1,784 tonnes/year	Air Water

3.1.0.4 Degradation

3.1.0.4.1 Abiotic degradation

Second order reaction rate constants have been calculated for C_{10-13}, 49-71% wt Cl, chlorinated paraffins as 2.2-8.2 $\cdot 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for reaction with hydroxyl radicals. Assuming an atmospheric concentration of hydroxyl radicals of $5 \cdot 10^5$ molecules/cm^3, allows atmospheric half-lives of 1.9-7.2 days to be estimated (Hoechst AG, 1988 and 1991).

3.1.0.4.2 Biodegradation

The biodegradability of a C_{10-12}, 58% wt Cl, chlorinated paraffin has been tested in the OECD Guideline 301C, Modified MITI I Test. The substance was tested at concentrations of 20 and 100 mg/l using a sludge concentration of 30 mg/l. No oxygen uptake, as measured in a manomeric biological oxygen demand (BOD) apparatus, was observed over a 28 day period. Analysis for residual chlorinated paraffin in the test vessels showed that 98% of the chlorinated paraffin initially added remained, confirming that no biodegradation had taken place (Street *et al.*, 1983). Therefore, the substance is not readily biodegradable. However, it

should be noted that the concentrations tested are well above the apparent solubility of the substance.

A C_{10-12}, 58% wt Cl, chlorinated paraffin has been tested in the OECD Guideline 302B, Inherent biodegradability: Modified Zahn-Wellens Test. Degradation was followed by monitoring CO_2 evolution over 28 days at 22±1°C and comparing this to the theoretical amount of CO_2 that would be evolved, assuming complete biodegradation. The chlorinated paraffin was tested at concentrations of 50 mg C/l (≡137.4 mg/l) and 25 mg C/l (≡68.7 mg/l) and the initial activated sludge concentration was 200 mg/l. The degradation seen during the 28 day period was 7.4% and 16% at the two concentrations respectively. Therefore, the substance is not inherently biodegradable. However, it should be noted that the concentrations tested are well above the apparent solubility of the substance. The high concentration was shown not to have any effect on the biodegradation of aniline, indicating that the chlorinated paraffin was not toxic to the microorganisms present (Mather *et al.*, 1983).

The same C_{10-12}, 58% wt Cl chlorinated paraffin has also been tested in a modified OECD Guideline 303A Coupled Units test. In this case, the commercial chlorinated paraffin was mixed with a ^{14}C-labelled chlorinated n-undecane (59.1% wt Cl) and this was continuously added to the units as an emulsion. The units had a hydraulic retention time of 6 hours and the initial chlorinated paraffin concentration was 10 mg/l. The units were initially seeded with secondary effluent (0.1% vol/vol) and were operated for 51 days (33 days were allowed for establishment of equilibrium conditions). The chlorinated paraffin was found to have no effect on DOC removal within the system, indicating that it was not toxic at the concentration used. The mean concentration (determined by radioactivity measurements) of chlorinated paraffin in the effluent was 0.7 mg/l, indicating an equilibrium removal of 93%. The removal was mainly by adsorption onto the sludge (mean concentration found on sludge was 68,000 mg/kg). It was thought that the chlorinated paraffin found in the effluent was associated with the suspended matter (Street and Madeley, 1983).

Madeley and Birtley (1980) found that under aerobic conditions, microorganisms previously acclimated to specific chlorinated paraffins showed a greater ability to degrade the compounds than non-acclimated microorganisms. In the first series of experiments, microorganisms were obtained from soil near to a chlorinated paraffin production plant. The microorganisms were acclimatised to chlorinated paraffins (concentration 20-50 mg/l as an emulsion) in shake flasks over an 8 week period. The biodegradation of the chlorinated paraffins was then studied over a 25 day period using BOD tests (chlorinated paraffin concentration 2-20 mg/l). The second set of biodegradation experiments were carried out in a similar way using non-acclimated microorganisms from the effluent of a laboratory activated sludge unit treating domestic waste. The results of the experiment, expressed as BOD (g O_2/g chlorinated paraffin) are shown in **Table 3.3** (for comparison, the theoretical oxygen demand (ThOD) for $C_{11}H_{20}Cl_4$ (48% Cl) can be calculated as 1.63 g O_2/g chlorinated paraffin). As can be seen from the results, only the 49% wt Cl short chain length chlorinated paraffin exerted an appreciable BOD.

Table 3.3 Results of BOD experiments using acclimated and non-acclimated microbial populations

Chlorinated paraffin	Type of inoculum	BOD (g O_2/g chlorinated paraffin)				
		5 day	10 day	15 day	20 day	25 day
C_{10-13}, 49% wt Cl	NA	0.02	0.08	0.12	0.20	0.29
	A	0.25	0.46	0.55	0.65	1.02
C_{10-13}, 60% wt Cl	NA	/	/	/	/	/
	A	/	/	/	/	/
C_{10-13}, 70% wt Cl	NA	/	/	/	/	/
	A	/	/	/	/	/

NA = non-acclimated microorganisms
A = acclimated microorganisms

Omori *et al.* (1987) studied the biodegradation of C_{12}, 63% wt Cl chlorinated paraffin using a variety of microbial cultures. Degradation was studied by monitoring the release of chloride ion from the chlorinated paraffin. Firstly the degradation of the chlorinated paraffin was studied using resting cell cultures of *Pseudomonas aeruginosa, Achromobacter delmarvae*, *A. cycloclastes*, *Micrococcus* sp. and *Corynebacterium hydrocarboclastus* grown on glycerol and incubated for 24 hours at 30°C. These bacteria had been shown to dechlorinate 1-chlorohexadecane as well as some other mono- and dichlorinated alkanes. Little or no dechlorination of the C_{12}, 63% wt chlorinated paraffin was seen using these bacteria. Dechlorination of the chlorinated paraffin was shown to occur using bacterial strains isolated from soil (using enrichment cultures with n-hexadecane as sole carbon source). In these experiments, the isolated bacteria were incubated for 48 hours at 30°C with the chlorinated paraffin and n-hexadecane. The highest degree of dechlorination was achieved using a mixed culture of 4 strains of bacteria isolated from soil. Around 21% dechlorination, as measured by chloride ion release, was observed after 36 hours incubation of the chlorinated paraffin and n-hexadecane (Omori *et al.*, 1987). These results show that dechlorination of short chain length chlorinated paraffins may occur in a cometabolic process.

It can be concluded from the biodegradation results that short chain chlorinated paraffins with low chlorine contents (e.g. <50% wt Cl) may biodegrade slowly in the environment, particularly in the presence of adapted microorganisms. Certain bacteria have also been shown to dechlorinate short chain chlorinated paraffins with high chlorine contents in a cometabolic process and so under certain conditions, biodegradation of these compounds might also be expected to occur slowly in the environment.

No information on the anaerobic biodegradation of short chain length chlorinated paraffins is available.

3.1.0.5 Accumulation

Short chain length chlorinated paraffins have been shown to bioconcentrate to a large extent in fish and molluscs.

Madeley and Maddock (1983a) exposed rainbow trout (*Oncorhynchus mykiss*) to measured concentrations of 0.033, 0.1, 1.07 and 3.05 mg/l of a C_{10-12}, 58% wt Cl for 60 days. The concentrations were determined by means of a ^{14}C-labelled chlorinated n-undecane (59.1% wt Cl, radiolabelled in the 6 position) mixed into the commercial product. In addition, parent compound analysis was also undertaken at various times during the test. Whole body bioconcentration factors (BCFs) of 1,173-7,816 were determined based on radioactivity measurements in the fish and BCFs of 574-7,273 were determined based on the parent compound analysis. The BCFs were found to increase with decreasing exposure concentration (this might be explained by the fact that two of the exposure concentrations are above the solubility for chlorinated paraffins) (Madeley and Maddock, 1983a).

Madeley and Maddock (1983b), again using rainbow trout (*Oncorhynchus mykiss*), found high levels of accumulation in the liver and viscera after exposure to measured concentrations of 3.1 and 14.3 µg/l of a short chain length (C_{10-12}), 58% chlorinated paraffin. Exposure was for 168 days at 12°C using a flow-through system. The bioconcentration was measured by means of a ^{14}C-labelled chlorinated n-undecane (59.1% wt Cl, radiolabelled in the 6 position) mixed into the commercial product. Lower bioconcentration factors were observed in the flesh (BCF=1,300-1,600) as compared to liver (2,800-16,000) and viscera (11,700-15,500) and the whole fish BCF was estimated to be 3,600-5,300. These bioconcentration factors were based on the amount of ^{14}C-labelled material present in the various organs. A limited number of parent compound analyses were also carried out at various times during the tests, and these indicated that some of the ^{14}C-label present in the liver and viscera may not have been the parent chlorinated paraffin. Therefore, these measured BCFs are likely to represent maximum values. During depuration (168 days), the following half-lives were determined for the chlorinated paraffin: liver 9.9-11.6 days; viscera 23.1-23.9 days; flesh 16.5-17.3 days; and whole body 18.7-19.8 days. The relatively short half-life observed in the liver is believed to be indicative of rapid metabolism and excretion of the test substance. On days 63-70 of depuration, fish previously exposed to chlorinated paraffins refused to feed and developed behavioural abnormalities. Deaths occurred in both groups previously exposed to chlorinated paraffins and all fish previously exposed to 14.3 µg/l died by day 70 of depuration. In the lower exposure group all abnormal effects ceased after day 70 of depuration. Although no explanation could be found for these events, there were no effects seen at this time or any other time in the control populations and the presence of disease or parasites was eliminated as a possible cause.

Bengtsson *et al.* (1979) studied the uptake and accumulation of several short chain length chlorinated paraffins by bleak (*Alburnus alburnus*). The fish were exposed to 125 µg/l of a chlorinated paraffin (C_{10-13}, 49% wt Cl; C_{10-13}, 59% wt Cl; C_{10-13}, 71% wt Cl) in brackish water ($7^{o}/_{oo}$) for 14 days at 10°C under semi-static conditions (renewed every 2nd or 3rd day). After exposure, the depuration of the chlorinated paraffins was studied for an additional 7 days. The concentration of chlorinated paraffin in the fish was measured by a neutron activation analysis method that determines the total amount of chlorine present (later unpublished work using a mass spectrometry based method specific for chlorinated paraffins showed good agreement with these concentrations (Bengtsson and Baumann-Ofstad, 1982). All three chlorinated paraffins were taken up by the fish but uptake was greatest for the lower chlorinated grades over the 14 day exposure period (whole body BCFs of around 800-1,000

can be estimated from the data for the 49% wt Cl and 59% wt Cl compounds, whereas the BCF was around 200 for the 71% wt Cl compound). High levels of chlorinated paraffin were still detected in the fish after the 7 day depuration period.

The uptake and accumulation of short chain length chlorinated paraffins by bleak (*Alburnus alburnus*) has also been studied via food (Bengtsson and Baumann-Ofstad (1982). The fish were exposed for 91 days to either a C_{10-13}, 49% wt Cl chlorinated paraffin at 590, 2,500 and 5,800 µg/g food or a C_{10-13}, 71% wt Cl chlorinated paraffin at 3,180 µg/g food. Analysis (using the neutron activation analysis method above) of whole fish bodies was carried out during the exposure period and also during a 316 day depuration period. The 49% wt Cl compound was found to be readily accumulated during the first 56 days of exposure and a direct correlation was found between the amount of chlorinated paraffin in food and the amount in fish tissues. During the next two weeks of exposure, fish in the two lower exposure groups showed a steep increase in the chlorinated paraffin tissue concentration, while tissue levels in the high dose group remained constant. This effect was thought to be due to experimental variation. It was estimated that at 91 days, around 45% of the 590 µg/g food dose, 10% of the 2,500 µg/g food dose and 5% of the 5,800 µg/g food dose had been accumulated by the fish, indicating that uptake becomes less efficient and/or metabolism more effective with increasing concentration. After exposure ceased, elimination of this compound from fish tissues was found to be rapid. In the case of the 71% wt Cl compound, uptake by the fish was found to be similar to the 2,500 µg/g food dose of the 49% wt Cl compound, with around 6% of the total dose being accumulated. However, the tissue concentration of the 71% wt Cl compound was found to remain fairly constant throughout the 316 day depuration period, indicating very slow elimination.

A similar experiment has been reported by Lombardo *et al.* (1975) with fingerling rainbow trout (*Oncorhynchus mykiss*). The trout were fed a diet containing 10 mg/kg food of a C_{12}, 60% chlorinated paraffin for 82 days. The amount of food given was maintained at 4% of the fish body weight during the study. The concentration of chlorinated paraffin in the fish was found to increase during the study, reaching a level of 1.1 mg/kg tissue (18 mg/kg fat) when the study was terminated. It was thought that equilibrium had not been reached by the end of the experiment.

Another dietary accumulation study with rainbow trout (*Oncorhynchus mykiss*) has recently been reported (Fisk *et al.*, 1996). In this study, trout (initial weights 2-7 g) were fed ^{14}C-labelled chlorinated paraffin (either C_{12}, 56% Cl or C_{12}, 69% Cl) spiked onto food. The experiment consisted of a 40 day exposure period followed by a 160 day depuration period. The daily feeding rate was 1.5% of the mean body weight and two exposure concentrations for each substance were used (26 and 242 ng/g food for the 56% Cl compound and 21 and 222 ng/g food for the 69% Cl compound). At these feeding rates, neither compound was found to have any negative effect on the growth of juvenile rainbow trout. Accumulation was observed for both compounds but steady state was not reached after the 40 day exposure period. Biomagnification factors of 0.60-0.93 for the 56% Cl compound and 1.76-2.15 for the 69% Cl compound were determined based on the rates of uptake and depuration. The assimilation efficiencies were 20.7-25.3% for the 56% Cl compound and 34.1-37.6% for the 69% compound. The carcass was found to contain the highest amounts of the ^{14}C assimilated and the whole body half-lives were determined as 39-77 days for the 56% Cl compound and 77-87 days for the 69% Cl compound. On day 40 of the uptake period and day 20 of the depuration period HPLC analysis was carried out to try to determine if the species present was chlorinated

paraffin. There was evidence for considerable metabolism of the 56% Cl compound at day 40 of uptake, and the chromatographic profile for both compounds was found to be markedly different from analytical standards at day 20 of depuration, indicating metabolic transformation.

Very high BCFs have been determined for a C_{10-12}, 58% wt Cl chlorinated paraffin in common mussels (*Mytilus edulis*). The chlorinated paraffin was mixed with a ^{14}C-labelled chlorinated n-undecane (59.1% Cl, ^{14}C-labelled in the 6 position) and concentrations were determined by measurement of radioactivity (both water and mussel). Some parent compound analyses were also carried out at various times during the experiment and the concentrations obtained agreed with those obtained from the ^{14}C radioactivity measurements. Mussels were exposed to the chlorinated paraffin at a concentration of 2.35 µg/l for 147 days followed by 98 days depuration or a concentration of 10.1 µg/l for 91 days followed by 84 days depuration using a flow-through system. Accumulation of the chlorinated paraffin was found to be greatest in the digestive gland, with BCFs being measured as 226,400 and 104,000 at the low and high exposure concentrations respectively. Whole mussel BCFs were determined as 40,900 and 24,800 at the low and high exposure concentrations respectively. All tissues expelled the test compound at a similar rate, with half-lives for the whole mussel being calculated as 9.2-9.9 days for the high exposure group and 13.1-19.8 days for the low exposure group. The high exposure concentration (10.1 µg/l) was found to cause a significant number of deaths during the test; 33% of the original 130 exposed mussels died either during the exposure period (23%) or depuration period (10%). Mortalities at the low exposure concentration were not significantly different from controls (Madeley *et al.*, 1983a). Similarly high BCFs (5,785-25,952) have also been measured in mussels after 60 days exposure to a 58% wt Cl short chain length chlorinated paraffin at concentrations of 0.013-0.93 mg/l (Madeley and Thompson, 1983).

3.1.0.6 Environmental distribution

The potential environmental distribution of short chain chlorinated paraffins in the environment has been studied using a generic level III fugacity model. The model used was a four compartment model (FUGMOD version 1, Jan 1992 - developed by Mackay) that has been circulated for use within the OECD HPV program. The model was run using the default settings in the model.

The following chemical specific information was used as input data:

Melting point	-	-30°C
Molecular weight	-	377 g/mole (for $C_{12}H_{20}Cl_6$)
Vapour pressure	-	0.0213 Pa (at 40°C)
Water solubility	-	0.47 g/m^3
Log K_{ow}	-	6.0
Half-life in air	-	173 hours (7.2 days)
Half-life in soil	-	$1 \cdot 10^{11}$ hours (not degraded)
Half-life in water	-	$1 \cdot 10^{11}$ hours (not degraded)
Half-life in sediment	-	$1 \cdot 10^{11}$ hours (not degraded)
Amount of chemical	-	1,000 kg/hour (nominal value)

It should be noted that since short chain length chlorinated paraffins are complex mixtures, individual components of the mixture may have different physico-chemical properties than used here and so may be expected to distribute slightly differently in the environment.

The results of the modelling are shown in **Table 3.5**.

Table 3.5 Environmental distribution short chain length chlorinated paraffins using generic level III fugacity model

Compartment	Release: 100% to air	Release: 100% to water	Release: 100% to soil	Release: 20% to air 80% to water
Air	0.11%	0.05%	<0.001%	0.07%
Water	0.02%	1.16%	0.005%	0.80%
Sediment	0.8%	53.5%	0.23%	36.6%
Soil	99.0%	45.3%	99.8%	62.5%

As can be seen from the results of the modelling exercise, once released into the environment, short chain length chlorinated paraffins are expected to distribute mainly onto the soil and sediment phases. The results also show that if the substance is mainly released to air or water, then transfer to the soil (probably by wet or dry deposition or direct adsorption) and sediment (by direct adsorption from water) is likely to occur. This is also born out in the measured levels and the PECs calculated in the following sections.

It should also be noted that despite the high adsorbability of the substance onto soil and sediment, a small but not insignificant fraction is predicted to distribute into water and air. This means that short chain length chlorinated paraffins may be slightly mobile in the environment and so a small fraction of the release may be transported over a wide area away from sources of release.

3.1.1 Aquatic compartment

3.1.1.1 Calculation of PEC_{local}

Using the emission data given in **Table 3.2** for the estimated amounts released at a site, it is possible to estimate a PEC for surface water for each use by assuming that the amount released/site is released to wastewater and this enters a wastewater treatment plant with an inflow of 2,000 m^3/day of water. It is assumed that no biodegradation or volatilisation occurs during sewage treatment but it will be assumed that removal during sewage treatment is 93% by adsorption onto sludge, based on the result of the Coupled Units Test described in Section 3.1.0.6. This is in line with the estimates given in the Technical Guidance Document for non-degradable chemicals of low volatility with log K_{ow} in the range 5 to 6 (estimated % to sludge 86-91%). The final assumption in calculation of the PEC for water is that the effluent from the sewage treatment plant is diluted by a factor of 10 on entering the surface water.

The PECs estimated are shown below:

Production (default)	-	PEC = 11.6 µg/l or 350 µg/l
Metal working (formulation)	-	PEC = 4.6 µg/l
Metal working (use)	-	PEC = 1.2 µg/l or 5.3 µg/l
Rubber formulations	-	PEC = <0.014 µg/l
Paints and sealing compounds	-	PEC = negligible
Leather (formulation: scenario A)	-	PEC = 70 µg/l
Leather (formulation: scenario B)	-	PEC = 87.5 µg/l
Leather (use: scenario B)	-	PEC = 87.5 µg/l
Textile applications	-	PEC = negligible

The final stage in estimating the PEC_{local} is to model adsorption of the substance to sediment in the receiving water. This is particularly important for highly lipophilic chemicals such as the chlorinated paraffins. Using the equation given in the Technical Guidance Document for risk assessment:

$$PEC_{local}\ (water) = PEC/(1+K_{p(susp)} \cdot C_{susp})$$

where PEC = concentration of chemical from wastewater treatment plant
$K_{p(susp)}$ = suspended matter - water partition coefficient (l/kg)
C_{susp} = concentration of suspended matter in the river ($=1.5 \cdot 10^{-5}$ kg/l)

Since no measured $K_{p(susp)}$ is available for short chain length chlorinated paraffins, it has to be estimated using the octanol-water partition coefficient using the following equation:

$$K_{p(susp)} = K_{oc} \cdot f_{oc} = K_{oc} \cdot 0.1$$

where f_{oc} is the fraction of organic carbon in suspended matter (=10%) and K_{oc} is the soil organic carbon - water partition coefficient.

According to the Technical Guidance Document, the K_{oc} value for halogenated hydrophobic chemicals can be estimated from: $\log K_{oc} = 0.81 \log K_{ow} + 0.10$

Using $\log K_{ow} = 6$ as being typical for short chain length chlorinated paraffins, $K_{p(susp)} = 9{,}120$ l/kg.

The $PEC_{regional}$(water) has been estimated as 0.33 µg/l using EUSES (see Section 3.1.1.2) and has been included in the following estimated values of PEC_{local} (water):

Production (default)	-	PEC_{local}(water) = 10.5 µg/l or 308 µg/l
Metal working (formulation)	-	PEC_{local}(water) = 4.3 µg/l
Metal working (use)	-	PEC_{local}(water) = 1.4 µg/l or 5.0 µg/l
Rubber formulations	-	PEC_{local}(water) = <0.34 µg/l
Paints and sealing compounds	-	PEC_{local}(water) = negligible
Leather (formulation: scenario A)	-	PEC_{local}(water) = 62 µg/l
Leather (formulation: scenario B)	-	PEC_{local}(water) = 77 µg/l
Leather (use: scenario B)	-	PEC_{local}(water) = 77 µg/l
Textile applications	-	PEC_{local}(water) = negligible

The PEC_{local} (sediment) can then be estimated from the sediment-water partition coefficient using the equation:

$$PEC_{local} \text{ (sediment)} = K_{susp\text{-}water/} P_{susp} \cdot PEC_{local}\text{(water)} \cdot 1000$$

where $K_{susp\text{-}water}$ = suspended matter - water partition coefficient = 2,281 m^3/m^3, based on a log K_{ow} of 6
P_{susp} = bulk density of suspended matter = 1,150 kg/m^3

The following PEC_{local} (sediment) can be estimated:

Production (default)	-	PEC_{local}(sediment) = 20.8 or 611 mg/kg wet wt
Metal working (formulation)	-	PEC_{local}(sediment) = 8.5 mg/kg wet wt
Metal working (use)	-	PEC_{local}(sediment) = 2.8 or 9.9 mg/kg wet wt
Rubber formulations	-	PEC_{local}(sediment) = <0.67 mg/kg wet wt
Paints and sealing compounds	-	PEC_{local}(sediment) = negligible
Leather (formulation: scenario A)	-	PEC_{local}(sediment) = 123 mg/kg wet wt
Leather (formulation: scenario B)	-	PEC_{local}(sediment) = 153 mg/kg wet wt
Leather (use: scenario B)	-	PEC_{local}(sediment) = 153 mg/kg wet wt
Textile applications	-	PEC_{local}(sediment) = negligible

Information is available on releases from the two current production sites in the EU. Using this data, the following site specific maximum PEC_{locals} are derived for production:

PEC_{local}(water) = < 0.028 (+ $PEC_{regional}$) = <0.36 µg/l
and < 0.097 µg/l (+ $PEC_{regional}$) = <0.43 µg/l
PEC_{local}(sediment) = <707 and <844 µg/kg wet wt

These values are much lower than the estimated $PEC_{regional}$ for water (0.33 µg/l) and so the concentrations near to production sites can be expected to be dominated by regional sources rather than the small emissions from the production site.

Recently, a measured log K_{oc} value of around 5.3 (K_{oc} = 199,500 l/kg) has been determined for a C_{10}- and C_{13}-paraffin with around 55% wt Cl content (Thompson *et al.*, 1998). Appendix C considers the effect of this value on the calculated PECs and the overall conclusions of the risk assessment.

3.1.1.2 Calculation of $PEC_{regional}$ and $PEC_{continental}$

The calculation of PECs on a regional and continental scale can be done using the EUSES model. The quantities used as inputs into the model were the total amount released in regional model (as described in the Technical Guidance Document) and the total amount released in the EU (continental model). Details of the estimated releases used in the model are given in **Table 3.2** (in the model a 70% connection rate to waste water treatment plants was assumed and the regional releases were subtracted from the total EU release to give the amount released in the continental model as recommended in the Technical Guidance Document). The higher default release from production was used in the model, and it was assumed that there was one large production plant within the region.

In order to run the program, it was assumed that the chemical had the formula $C_{12}H_{20}Cl_6$ (56.5% Cl) and that the predicted behaviour of this chemical would be representative of the group as a whole. Ideally, it would be useful to run the model for a range of short chain length chlorinated paraffins, however, there are insufficient physico-chemical data available for individual chlorinated paraffins to allow this to be undertaken meaningfully. Also, since short chain length chlorinated paraffins are complex mixtures, individual components of the mixture may behave differently in the environment than predicted here. The data used in the modelling and a summary of the results of the modelling are shown in **Table 3.5**. A full printout of the model is given as Appendix B.

In the model, the predicted groundwater (pore water) concentrations are higher than the surface water concentrations, which leads to the drinking water concentrations being higher than the surface water concentrations. The reason for this appears to be the high concentrations estimated in the soil compartments due to the spreading of sewage sludge containing short chain length chlorinated paraffins. High concentrations in the soil lead to relatively high soil pore water concentrations. EUSES then relates these to the groundwater and hence drinking water concentrations. However, it is thought that short chain length chlorinated paraffins are likely to be fairly immobile in soil due to their high octanol-water partition coefficients and so are unlikely to be present at significant concentrations in groundwater. Therefore, the actual groundwater and drinking water concentrations are thought to be negligible.

Table 3.5 Summary of regional and continental modelling in EUSES

	Regional model	Continental model
Amount released to wastewater (kg/day)	392.0	3,028
Amount released to surface water (kg/day)	168.4	1,298
Amount released to air (kg/day)	0.108	0.97
Concentration in air (mg/m^3)	$1.2 \cdot 10^{-5}$	$4.6 \cdot 10^{-6}$
Concentration in surface water (dissolved) (µg/l)	0.33	0.033
Concentration in sediment (mg/kg wet wt)	1.16	0.115
Concentration in pore water (µg/l)	6.7	0.59
Concentration in natural/ industrial soil (mg/kg wet wt)	11.5	4.57
Concentration in agricultural soil (mg/kg wet wt)	10.8	0.95
Concentration in drinking water (µg/l)	6.7	
Concentration in fish (µg/kg wet wt)	2.600	
Concentration in root of plants (mg/kg)	48	
Concentration in leaves of plant/grass (mg/kg)	0.0108	
Concentration in meat (mg/kg wet wt)	0.154	
Concentration in milk (mg/kg wet wt)	0.0486	
Concentration in earthworms (mg/kg wet wt)	268	
Molecular formula	$C_{12}H_{20}Cl_6$ (56.5% Cl)	
Molecular weight	377	
Vapour pressure	0.0213 Pa (at 40°C)	
Log K_{ow}	6	
Fish BCF	7,816 l/kg	
Water solubility	470 µg/l	

3.1.1.3 Levels of short chain length chlorinated paraffins in water and sediment

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 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 are critically discussed in the following paragraphs. The methods have been referred to by the author names that appear in the subsequent sections on environmental levels. Of those available, the methods of Ballschmiter, 1994 and Murray *et al.*, 1987 are similar and are considered to be the best methods currently available for specifically measuring short chain length chlorinated paraffins. 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. Also, the method is relatively insensitive to chemical structure and cannot distinguish between short chain length (C_{10-13}) and intermediate chain length (C_{14-20}) chlorinated paraffins. This method, therefore, is likely to detect all short chain length 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 short chain length chlorinated paraffins are 324-329, 359-364, 367-372 and 393-401 amu. The commercial product, Paroil 1160 (C_{10-12}, 50-60% Cl), was used as reference material. This method is reasonably specific for short chain length chlorinated paraffins, but will only identify the components which give rise to ions in the mass spectrometer in the ranges scanned. Therefore, this method may underestimate the actual concentrations slightly.

Ballschmiter, 1994

This method also uses gas chromatography/mass spectrometry with negative chemical ionisation. In this case the following masses were monitored in the mass spectrum: 361 and 363 ($C_{11}H_{18}Cl_6$, 59% Cl), 375 and 377 ($C_{12}H_{20}Cl_6$, 56% Cl), 395 and 397 ($C_{11}H_{17}Cl_7$, 63%). Hordaflex LC60 (C_{10-13}, 62% Cl) was used as reference. Again, this method may underestimate the actual concentration slightly. This method was used for the results obtained in 1994 and is reasonably specific for short chain length 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, intermediate 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.

Greenpeace, 1995

The method used is similar to the ICI, 1992 method above. On-column reduction to the parent hydrocarbon was used, followed by GC/MS quantification of the parent hydrocarbon. A range of alkanes between C_{10} and C_{24} were used as external standards and an average chlorine content of 50% was assumed for the chlorinated paraffins to allow quantification. The method could apparently distinguish between individual chlorinated paraffins with different carbon chain lengths, thus the concentration of C_{10}, C_{11}, C_{12} and C_{13} chlorinated paraffins could be determined separately. Again, this method ma slightly underestimate the chlorinated paraffin concentration if high chlorine content material is present.

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. Analysis was carried out using GC-ECD and GC-MS with negative chemical ionisation. The following masses were monitored in the analysis: 326 and 327 ($C_{11}H_{19}Cl_5$); 361 and 363 ($C_{11}H_{18}Cl_6$); 375 and 377 ($C_{12}H_{20}Cl_6$); 395 and 397 ($C_{11}H_{17}Cl_7$). The method is similar to that used by Ballschmiter (1994) and Murray *et al.* (1987a and b).

Stern et al., 1997 and Tomy et al., 1997

Analysis was carried out by high resolution gas chromatography electron capture negative ion high resolution mass spectrometry (HRGC-ECNI-HRMS). Selected ion chromatograms were obtained by monitoring ions in the $[M\text{-}Cl]^-$ ion clusters corresponding to the following formula groups: C_{10} (Cl_{5-10}), C_{11} (Cl_{5-10}), C_{12} (Cl_{6-10}) and C_{13} (Cl_{7-9}). The profiles of these formula groups obtained were used for quantitation against a standard by applying correction factors to the most abundant formula group found to account for differences in the distribution of the formula groups found in the samples compared with the samples. Again, the results obtained are dependent on the standard used.

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 short chain chlorinated paraffin, although some methods may not detect all the short chain length chlorinated paraffins present in a sample. Thus they should all be treated as giving approximate concentrations.

3.1.1.3.1 Levels in water

Short chain length chlorinated paraffins are likely to adsorb strongly onto suspended sediments. When interpreting the measured levels of chlorinated paraffins in water it is important to try to distinguish between levels that refer to chlorinated paraffins in the dissolved phase and those that refer to chlorinated paraffin adsorbed onto suspended matter. In most cases, little or no information is given about the sampling method used and so it is assumed that these levels refer to the 'total' concentration (i.e. dissolved + adsorbed) in water.

Analysis of short chain length chlorinated paraffins has been carried out at several locations in the United Kingdom in the summer of 1986 (ICI, 1992). The results are shown in **Table 3.6**, along with the levels on the intermediate chain length chlorinated paraffins. The levels of intermediate chain length chlorinated paraffins found are included here to enable some conclusions to be drawn about the likely concentrations of short chain length chlorinated paraffins in the measurements included later in this section (**Tables 3.8-3.10**).

As can be seen from **Table 3.6**, the short chain length chlorinated paraffins were found in just over half the samples at concentrations ranging between 0.12 and 1.45 μg/l. Intermediate chain length chlorinated paraffins were detected more frequently, with measured concentrations in the range 0.62-3.75 μg/l. The majority of the samples appear to have been collected in urban/industrial areas.

Levels of short chain length chlorinated paraffins have been measured at several sites in Germany and the results are shown in **Table 3.7** (Ballschmiter, 1994). The levels measured in 1987 are similar to those found in the United Kingdom in 1986, however the levels measured in Germany in 1994 are generally lower. It is possible that the lower levels reflect a reduction of the emissions into the environment in Germany as a result of the reduction in use in metal working fluids (it is thought that a 50% reduction may have occurred, with a major decrease in their use in water-based emulsions: see Section 2.2). It should be born in mind that a different method of analysis was used for the two sets of measurements.

Table 3.6 Levels of short and intermediate chain length chlorinated paraffins in the United Kingdom in 1986 (ICI, 1992)

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

Table 3.7 Levels of short chain length chlorinated paraffins in surface water in Germany (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)	0.50	0.075
River Lech at langweid (downstream from a chlorinated paraffin production plant)	0.60	0.10
River Lech at Rain		0.12
River Danube at Marxheim (downstream from the mouth of the River Lech)	1.2	0.06
River Danube at Marxheim (upstream from the mouth of the River Lech)	1.2	0.06

Levels of total short and intermediate chain length chlorinated paraffins have been measured in marine and fresh waters remote from industry and fresh waters in industrialised areas in the United Kingdom (Campbell and McConnell, 1980). These results are shown in **Tables 3.8** to **3.10**. As these levels refer to total chlorinated paraffin in the C_{10-20} range, it is not possible to say anything definite about the likely amounts of C_{10-13} chlorinated paraffins present. However, analysing the results reported in **Table 3.6**, it can be seen that the C_{10-13} chlorinated paraffins make up around 1/4 to 1/3 of the combined total for short and intermediate chain length chlorinated paraffins in those samples. Therefore, if the same approximate distribution applies to the data in **Tables 3.8** to **3.10**, the likely concentrations of the short chain length chlorinated paraffins in these samples can be inferred.

Table 3.8 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in marine waters (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 á Ghlinne	ND
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: N55° 5.7' W1° 9.3'	ND
North Sea: N57° 26.2' W1° 17.0'	ND
North Sea: N57° 56.5' W1° 22.0'	ND

ND = not detected (detection limit = 0.5 µg/l)

Table 3.9 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in fresh and other non-marine waters remote from industry (Campbell and McConnell,1980)

Location	**Concentration of C_{10-20} 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 3.10 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in waters in industrialised areas (Campbell and McConnell,1980)

Location	Concentration of C_{10-20} 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
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)

The concentration of C_{10-20} chlorinated paraffins in marine waters are in the range 0.5-4 µg/l. Around half the samples contained detectable amounts of chlorinated paraffins. By inference, the levels of the short chain length chlorinated paraffins are probably in the range 0.1-1 µg/l.

In the 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 short chain length chlorinated paraffin concentrations of 0.1- 0.3 µg/l.

In the 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 intermediate chain length chlorinated

paraffins are in the range 0.5-6.0 µg/l. This corresponds to probable short chain length chlorinated paraffin concentrations in the range 0.1-2 µg/l. Although it is not clear if any of the samples were taken near to sources of discharge of chlorinated paraffins e.g. metal working operations, textile production, leather production, etc., it is thought that the Wyre Estuary did receive chlorinated paraffin production plant effluent at the time of sampling.

Murray *et al.* (1987a and b) reported the results of monitoring studies carried out near to a chlorinated paraffin manufacturing site in the US. 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 3.11**.

Table 3.11 Levels of short chain length chlorinated paraffins near to a production site

Location	Concentration (µg/l)
Surface lagoon near to its effluent to ditch	Trace (0.1-0.5) (dissolved)[1] 3.3 (particulate)[2]
Surface lagoon near to influent from plant	0.25-0.51 (dissolved)[1] 2.8 (particulate)[2]
Middle of surface lagoon	0.39-0.57 (dissolved)[1] 2.3 (particulate)[2]
Ditch, immediately above point of discharge into Sugar Creek	Trace (0.1-0.5) (dissolved)[1] 2.3 (particulate)[2]
Sugar Creek, upstream of discharge	Not detected (<0.05) (dissolved)[1] Trace (0.05-0.17) (particulate)[2]
Sugar Creek, just upstream of discharge	Not detected (<0.05) (dissolved)[1] 0.27-0.30 (particulate)[2]
Sugar Creek, just downstream of discharge	Not detected (<0.05) (dissolved)[1] 0.20-0.23 (particulate)[2]
Sugar Creek, downstream of discharge	Not detected (<0.05) (dissolved)[1] Trace (0.05-0.17) (particulate)[2]

[1] Dissolved - concentration in dissolved phase
[2] Particulate - concentration in suspended particulate phase (>0.45 µm)

As can be seen from **Table 3.11**, the highest concentrations of short chain length chlorinated paraffins are found in the surface impoundment lagoon. The concentration in the river are generally in the range 0.05-0.3 µg/l, which is consistent with the levels found in other surveys. It should also be noted that in this study, the majority of the chlorinated paraffin in solution was associated with the suspended particulate matter (>0.45 µm).

A similar study was also undertaken by Murray *et al.* (1987a and b) near to a metal working facility that was thought to use lubricating oils containing chlorinated paraffins. Due to analytical interferences, it was not possible to detect chlorinated paraffins in surface water at the site using metal working fluids. However, levels of short chain length (C_{10-12}) chlorinated paraffins of 8.1 µg/l were detected in process wastestreams inside the plant.

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 notdetected (detection limit 10 μg/l) in any of the 51 samples taken in 1979 or any of the 120 samples taken in 1980 (Environment Agency Japan, 1991).

A study of the inputs of short chain length chlorinated paraffins to a sewage treatment plant in Germany has been published (Rieger and Ballschmiter, 1995). The sewage treatment plant processed 100,000 m^3/day of municipal, industrial and mixed waste water. Short chain length chlorinated paraffins were found in all samples taken with levels in two sewage sludge samples of 65 mg/kg dry weight for a 1991 sample and 47 mg/kg dry weight for a 1993 sample. In order to try to identify the source of the short chain length chlorinated paraffins, various samples of sewer films (organic/microbial layers formed on the inside of sewer pipes) were analysed and the levels found indicated that metal working activity was the major source of the short chain length chlorinated paraffins in the plant. Water samples taken from upstream and downstream of the plant had short chain length chlorinated paraffin levels of 80 and 73 ng/l respectively, and a tributary river upstream of the area had a short chain length chlorinated paraffin content of 32 ng/l.

Bearing in mind the possible limitations of the analytical methods used, there is reasonably good agreement between the levels of short chain length chlorinated paraffins found in surface water in the different surveys. It can then be concluded that measured concentrations of short chain chlorinated paraffins are 0.05-0.3 μg/l in waters in areas remote from industry and 0.1-2 μg/l in areas close to industry. These levels are also reasonably consistent with the PECs for surface waters estimated using EUSES in the regional (0.33 μg/l) and continental scenarios (0.033 μg/l). It should also 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 total (i.e. dissolved phase + particulate phase).

The 1994 German levels are generally lower than the other measured levels. This might be explained if there has been a recent reduction in production of short chain length chlorinated paraffins (since the use in certain applications in Germany has reduced). The measured levels are, however, in reasonable agreement with the concentration predicted using the regional and continental scenarios (for instance the highest level measured in 1994 of 0.12 μg/l is similar to the predicted concentration of 0.33 μg/l from the regional model) and so can be assumed to be approaching the background level.

3.1.1.3.2 Levels in sediments

The levels of short chain length chlorinated paraffins have been determined in several sediments in Germany (Ballschmiter, 1994). The results are shown in **Table 3.12**. Short chain length chlorinated paraffins have been detected in a wide range of locations at concentrations up to 80 μg/kg dry weight. The concentrations found near to the chlorinated paraffin production site have reduced from those found in 1987. A similar trend was also seen in the water levels (see **Table 3.9**).

Table 3.12 Levels of short chain length chlorinated paraffins in sediments from Germany

Location	Concentration (µg/kg dry weight)	
	1987	1994
Bodensee (middle)		10 (0-5 cm depth) 6 (5-12 cm depth)
River Rhein (141 km) at Rheinfelden		38
River Rhein (152 km) at Rheinfelden, upper layer		53
River Rhein (152 km) at Rheinfelden, lower layer		26
River Rhein (853.8 km), near German-Dutch border		83
River Rhein (863.8 km), near German-Dutch border		75
River Main (16.2 km)		50
River Main (at Griesheim)		25
River Main (55 km)		26
Outer Alster, Hamburg		36
River Elbe, Hamburg (610 km)		17
River Elbe, Hamburg (629.9 km)		25
River Lech, upstream from chlorinated paraffin production plant	400	<5
River Lech, downstream from chlorinated paraffinp production plant	700	70
Hamburg Harbour (610 km)		17

Another level of C_{10-13} chlorinated paraffins in sediment from Germany has been reported. This was from the River Danube, downstream of the confluence with the River Lech. The level of C_{10-13} chlorinated paraffin found was 300 µg/kg dry weight. The concentration in water at the same site was around 1.2 µg/l (BUA, 1992).

The levels of combined short and intermediate chain length chlorinated paraffins have been measured in several types of sediment, often from the same areas where the levels in water were measured (Campbell and McConnell, 1980). The results of these analyses are shown in **Tables 3.13** to **3.15**.

Table 3.13 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in marine sediments (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
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 3.14 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in fresh and other non-marine sediments remote from industry (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 3.15 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in sediments in industrialised areas (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
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 intermediate chain length chlorinated paraffins have been found in sediments from industrialised areas, but they have also been detected in several samples from remote areas. The sediment levels in industrial areas are generally around 1,000 times the levels found in water in the same area. When considering the levels 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 intermediate chain length (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. 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. For both sets of analyses, the detection limit was 500 µg/kg (Environment Agency Japan, 1991).

Murray *et al.* (1987a and b) 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. Short chain length (C_{10-12}, 50-60% Cl) chlorinated paraffins were detected at levels up to 40,000 µg/kg dry weight in sediment from an impoundment lagoon at the production site. Much lower levels (1.5-7.3 µg/kg) 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.

Recently, Greenpeace (1995) published levels of total chlorinated paraffins 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 and the average chlorine content was thought to be around 50%. Short chain length chlorinated paraffins were found to account for 12-38% of the total chlorinated paraffins present (the estimated concentration of short chain length chlorinated paraffins is between 3 and 47.5 µg/kg).

Levels of short chain chlorinated paraffins in surface sediments in lakes from mid-latitude Canada and the Arctic have recently been reported. Here, the levels found were 176 µg/kg dry weight in Lake Winnipeg (level in surface water in a Red River flowing into the Lake was 16-55 ng/l), 18 µg/kg in Lake Nipigon, 275 µg/kg in Lake Fox and 4.5 µg/kg in Lake Hazon (Arctic) (Tomy *et al.*, 1997).

There are few sediment levels measured for short chain length chlorinated paraffins alone. The sediment levels measured for the combined short and intermediate chain length chlorinated paraffins are reasonably consistent with the sediment levels predicted for C_{10-13} chlorinated paraffins in the regional (1,160 µg/kg wet wt) and continental (115 µg/kg wet wt) scenarios. Higher levels of C_{10-13} chlorinated paraffins were predicted in some of the local scenarios (2.8-611 mg/kg) but it is not clear if any of the measurements from industrial areas were taken in the same regions as which most of the PEC_{local}s refer. However, it is thought that the Wyre Estuary did receive effluent from a chlorinated paraffin production plant at the time of the survey.

The results of the survey of short chain length chlorinated paraffins from Germany indicate that the current sediment levels in that country (typically 10-80 µg/kg dry weight) may be lower than levels found in the past. However, the measured levels are in good agreement with those predicted using the continental scenario (115 µg/kg) and so can be assumed to be approaching the background concentration.

3.1.2 Terrestrial compartment

Predicted concentrations of short chain length chlorinated paraffins in soil have been calculated using EUSES (see Section 3.1.1.2). The concentrations obtained in the regional model were 11.5 µg/kg wet wt in natural/industrial soil and 10.8 mg/kg wet wt in agricultural soil. Similarly the levels calculated using the continental model were 4.6 µg/kg wet wt in natural/industrial soil and 0.95 mg/kg wet wt in agricultural soil respectively. The high level predicted in agricultural soil is mainly due to the assumption that high levels of chlorinated paraffins will be present in sewage sludge applied to the soil.

Short chain length chlorinated paraffins have been measured at levels of 47-65 mg/kg dry weight in sewage sludge from a waste water treatment plant in Germany that received both

industrial and domestic wastewater (see Section 3.1.1.3) and so may represent a "regional" environment. Using the values outlined in the Technical Guidance Document (i.e. dry sludge application rates of 0.5 kg/m^2 for agricultural land, a mixing depth of 0.2 m and a soil bulk density of 1,700 kg/m^3), the maximum likely concentration resulting in soil from a single application of sewage sludge containing 65 mg/kg dry weight of chlorinated paraffin is 0.10 mg/kg wet weight.

High levels of short chain chlorinated paraffins will also be expected in agricultural soil in the local scenario due to application of sewage sludge from a local sewage treatment plant. Using EUSES (see Section 3.1.1.2), the following concentrations in agricultural soil were estimated, averaged over 30 days (the same values are obtained if the average over 180 days is taken; the levels estimated for grass land are around 3-5 times lower than these values (see Appendix B).

Production (default)	-	PEC_{local} (soil)	= 51.5 or 1,550 mg/kg wet wt
Metal working (formulation)	-	PEC_{local} (soil)	= 20.1 mg/kg wet wt
Metal working (use)	-	PEC_{local} (soil)	= 5.1 or 23.2 mg/kg wet wt
Rubber formulations	-	PEC_{local} (soil)	= <0.073 mg/kg wet wt
Paints and sealing compounds	-	PEC_{local} (soil)	= negligible
Leather (formulation: scenario A)	-	PEC_{local} (soil)	= 310 mg/kg wet wt
Leather (formulation: scenario B)	-	PEC_{local} (soil)	= 385 mg/kg wet wt
Leather (use: scenario B)	-	PEC_{local} (soil)	= 385 mg/kg wet wt
Textile applications	-	PEC_{local} (soil)	= negligible

The PEC_{local}(soil) for production was estimated using the default release factors (giving a release of 1,000 or 30,000 kg/year to waste water). Information provided on the two production sites in the EU indicate that the maximum actual release from the sites is of the order of <26.7 kg/year and that no sewage sludge is spread onto land from the sites. Therefore, the resulting PEC_{local}(soil) based on site specific information is practically zero.
No measured data appear to exist on levels of short chain length chlorinated paraffins in soil.

The above PECs are calculated using a K_{oc} value of 91,200 l/kg estimated from a log K_{ow} of 6 using the methods outlined in the Technical Guidance Document. Recently, a measured K_{oc} value of 199,500 l/kg has been determined for a C_{10}- and C_{13}-paraffin with around 55% wt Cl content (Thompson *et al.*, 1998). Appendix C considers the effect of this value on the calculated PECs and the overall conclusions of the risk assessment.

3.1.3 Atmosphere

Predicted concentrations of short chain length chlorinated paraffins in air have been calculated using EUSES for the local, regional and continental scenarios (see Section 3.1.1.2). The estimated regional air concentration is 11.6 ng/m^3. It is thought that direct emissions of chlorinated paraffin vapour to the atmosphere from local sources are likely to be very low (most emissions will be to water), therefore the PEC_{local} (air) is likely to be very low. The predicted concentrations in air from EUSES are <2.79 ng/m^3 for most local scenarios, which are lower than the regional background concentration of 11.6 ng/m^3. The one exception to this is the leather use (scenario B), where a direct releases to air give an estimated concentration during an emission event of 138 ng/m^3 and an annual average PEC_{local} (air) of 17.8 ng/m^3. In the regional and continental model, very little direct input into the atmosphere was assumed and so the levels reflect the small, but measurable volatility of the substance (see also Section 3.1.0.7).
No measured data appear to exist on the air levels of short chain length chlorinated paraffins.

3.1.4 Non compartment specific exposure relevant to the food chain

3.1.4.1 Predicted concentrations

Predicted concentrations of short chain length chlorinated paraffins have been calculated in the local, regional and United Kingdom scenarios for various parts of the food chain using EUSES (see Section 3.1.1.2) and these are reproduced in **Table 3.16.**

There is considerable uncertainty inherent in the approach EUSES takes for estimating the concentrations of substances with high log K_{ow} values in various parts of the food chain. For instance, the concentrations estimated in drinking water are very high, frequently close to or above the water solubility of the substance, and are much higher than the levels predicted/found in surface waters. This is because in EUSES the drinking water concentrations are taken as the soil pore water concentrations. For highly lipophilic substances such as short chain length chlorinated paraffins, very high concentrations in soil are predicted due to application of sewage sludge containing the substance. This leads to high estimated soil pore water concentrations, which in turn also leads to very high concentrations in plant roots (the estimated plant root - pore water partition coefficient for short chain chlorinated paraffins is around 7,200 kg/l) and hence other parts of the food chain related to plant concentrations, e.g. leaves, meat and milk.

Table 3.16 Estimated concentrations of short chain length chlorinated paraffins in food

Scenario	Estimated concentration					
	Drinking water	Fish	Plant roots	Plant leaves	Meat	Milk
Production (default)[a]	0.032 or 0.96 mg/l[a]	68.5 or 1,980 mg/kg[a]	229 or 6,870 mg/kg[a]	0.013 or 0.085 mg/kg[a]	0.30 or 8.51 mg/kg[a]	0.095 or 2.69 mg/kg[a]
Metal working (formulation)	0.013 mg/l	28.3 mg/kg	89.3 mg/kg	0.011 mg/kg	0.128 mg/kg	0.041 mg/kg
Metal working (use)	0.003 or 0.014 mg/l	9.12 or 32.5 mg/kg	22.7 or 103.3 mg/kg	0.011 or 0.011 mg/kg	0.046 or 0.209 mg/kg	0.014 or 0.064 mg/kg
Rubber formulations	<0.09 µg/l	<2.68 mg/kg	<0.33 mg/kg	<0.010 mg/kg	<0.018 mg/kg	<0.006 mg/kg
Paints and sealing compounds	negligible	negligible	negligible	negligible	negligible	negligible
Leather (formulation: scenario A)	0.19 mg/l	48.9 mg/kg	1,380 mg/kg	0.026 mg/kg	1.72 mg/kg	0.55 mg/kg
Leather (formulation: scenario B)	0.24 mg/l	79.7 mg/kg	1,710 mg/kg	0.045 mg/kg	2.16 mg/kg	0.68 mg/kg
Leather (use: scenario B)	0.24 mg/l	79.7 mg/kg	1,710 mg/kg	0.045 mg/kg	2.16 mg/kg	0.68 mg/kg
Textile applications	negligible	negligible	negligible	negligible	negligible	negligible
Regional	6.7 µg/l	2.6 mg/kg	48 mg/kg	0.011 mg/kg	0.154 mg/kg	0.049 mg/kg

[a]Site specific information from production sites indicates that no significant route to soil exists (i.e. no sewage sludge is spread on land) and so the concentrations in drinking water (i.e. groundwater), plants, meat and milk will not be significant. The site specific concentration in fish is around 3 mg/kg

For the secondary poisoning scenario, the concentrations in fish and earthworms are used. These have been estimated for various local sources using EUSES. The concentrations derived assume 50% of the exposure is from local sources and 50% is from regional sources.

The estimated concentrations for predators are shown below:

Production (default)	-	PEC(fish)	= 35.6 or 991 mg/kg wet wt
		PEC(earthworm)	= 773 or 19,300 mg/kg wet wt
Metal working (formulation)	-	PEC(fish)	= 15.5 mg/kg wet wt
		PEC(earthworm)	= 383 mg/kg wet wt
Metal working (use)	-	PEC(fish)	= 5.9 or 17.6 mg/kg wet wt
		PEC(earthworm)	= 197 or 422 mg/kg wet wt
Rubber formulations	-	PEC(fish)	= <2.64 mg/kg wet wt
		PEC(earthworm)	= <135 mg/kg wet wt
Paints and sealing compounds	-	PEC	= negligible
Leather (formulation: scenario A)	-	PEC(fish)	= 25.7 mg/kg wet wt
		PEC(earthworm)	= 3,980 mg/kg wet wt
Leather (formulation: scenario B)	-	PEC(fish)	= 41.2 mg/kg wet wt
		PEC(earthworm)	= 4,910 mg/kg wet wt
Leather (use: scenario B)	-	PEC(fish)	= 41.2 mg/kg wet wt
		PEC(earthworm)	= 4,910 mg/kg wet wt
Textile applications	-	PEC	= negligible

Very high concentrations are estimated in earthworms. It is possible that the equations used in the Technical Guidance Document/EUSES to estimate the earthworm bioconcentration factor (BCF = 24.8 kg/kg) are not applicable to this substance, which has a high log K_{ow} value. The concentrations obtained by such an approach may be unrealistic, for instance an earthworm concentration of 19,300 mg/kg is equivalent to the earthworm consisting of 1.9% by weight of chlorinated paraffin. For this reason, the earthworm food chain will not be considered further in the assessment.

As seen in Section 3.1.1.1., the site specific emission data for production does not lead to concentrations in the receiving water significantly above the $PEC_{regional}$, thus the PEC(fish) will be the same as the regional value.

3.1.4.2 Measured levels

3.1.4.2.1 Levels in aquatic organisms

Levels of combined short and intermediate chain length chlorinated paraffins (i.e. C_{10-20}) 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 3.17.**

Table 3.17 Concentration of combined short and intermediate chain length 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)

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

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. The results are shown in **Table 3.18**.

Table 3.18 Concentrations of chlorinated paraffins 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

*Refers to chlorinated paraffins with 6-16 chlorine atoms and so may contain chlorinated paraffins otthan C_{10-13}

Levels of short chain length chlorinated paraffins in marine mammals from various regions of the Arctic have recently been reported (Stern, 1997). The levels found were: beluga (western Greenland) 199 µg/kg wet wt; beluga (Mackenzie Delta) 206 µg/kg wet wt; seal (Ellesmere Island) 526 µg/kg wet wt; walrus (western Greenland) 426 µg/kg wet wt.

Beluga from the St Lawrence River estuary had levels of 785 µg/kg wet wt. In the same study, short chain length chlorinated paraffins, at levels of 10.6-16.5 ng/g lipid (mean 12.8 ng/g lipid) were detected in 3 samples of human milk taken from women living in settlements along the Hudson Strait.

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 short chain length (C_{10-12}) chlorinated paraffin detected was 280 µg/kg compared with 7-22 µg/kg upstream of the discharge.

Little information appears to be available on the levels of short chain length chlorinated paraffins alone in aquatic organisms. The levels of C_{10-20} chlorinated paraffins measured in fish range between <50-200 µg/kg. Mussels from the Wyre Estuary, which was thought to receive chlorinated paraffin plant effluent at the time of the survey, contain around 1,000 µg/kg of C_{10-20} chlorinated paraffin in general and 6,000-12,000 µg/kg close to the effluent discharge. The levels measured in the organisms are generally close to those in sediments below the water in which they live. However, the levels in sediments are approximately 100-1,000 times those in water, indicating that bioconcentration in biota appears to be taking place. Although it is not possible to say what fraction the C_{10-13} chlorinated paraffins make to the total C_{10-20} levels measured in this study, it is known that the C_{10-13} chlorinated paraffins are more bioaccumulative than the longer chain chlorinated paraffins (Willis *et al.*, 1994) and so may make up the major fraction of these measured levels.

Levels of total (C_{10}-C_{24}) chlorinated paraffins in food, fish and marine animals have recently been reported (Greenpeace, 1995). The 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. The average chlorine content of the chlorinated paraffins detected was thought to be around 33%. Short chain length chlorinated paraffins were thought to make up a very small percentage of the total in mackerel, fish oil, porpoise and fin whale, around 7% in human milk, 11.5% in margarine, 21% in cows milk and 30% in pork.

The predicted concentrations in fish using the regional model is 2,600 µg/kg wet weight, which is higher than levels generally found in the environment. The predicted concentrations in fish in most of the local scenarios are much higher than the measured levels but it is not clear if the measured levels are representative of the local scenarios considered. In the case of the measured levels in mussels, it is clear that the levels are much higher near to the potential source of discharge.

3.1.4.2.2 Levels in other biota

Levels of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) have been measured in several parts of the food chain in the United Kingdom (Campbell and McConnell, 1980). The results of the analyses are shown in **Tables 3.19** to **3.22**. As can be seen from **Tables 3.19** to **3.22**, short and intermediate chain length chlorinated paraffins have been detected in birds, eggs and human foodstuffs in the United Kingdom. They have also been detected in sheep near to a chlorinated paraffin production site. Although it is not possible to say what fraction the C_{10-13} chlorinated paraffins make to the total C_{10-20} levels

reported, it is known that the C_{10-13} chlorinated paraffins are more bioaccumulative than the longer chain chlorinated paraffins (Willis *et al.*, 1994) and so may make up the major fraction of these measured levels.

Jansson *et al.* (1993) reported levels of chlorinated paraffins (of unspecified chain carbon length, with 6-16 chlorine atoms/molecule) 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 in and around Sweden. The results are shown in **Table 3.23**.

Table 3.19 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in seabirds' eggs (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

Table 3.20 Concentration of combined short and intermediate chain length 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 3.21 Concentration of combined short and intermediate chain length chlorinated paraffins (C_{10-20}) in human foodstuff (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 3.22 Concentration of combined short and intermediate chain length 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
	mesenteric fat	50
	kidney	50
	perinephritic fat	ND

ND = not detected (detection limit = 50 µg/kg)

Table 3.23 Concentrations of chlorinated paraffins in pooled samples from in and around Sweden (Jansson *et al.*, 1993)

Sample	Number of samples	Location/date	Lipid content	Concentration * (µg/kg lipid)
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_{10-13}

Although it is not possible to compare directly the levels predicted by EUSES (see Section 3.1.4.1) with the measured levels, it can be seen that the levels predicted by EUSES in milk and meat in the regional scenario are reasonably consistent with the measured levels found in the environment.

3.1.5 Summary of exposure estimates for short chain length chlorinated paraffins

Tables 3.24 and **3.25** summarise the predicted concentrations in various media that will be used in the risk assessment.

Table 3.24 Summary of predicted environmental concentrations from the local scenario for use in the risk assessment

Media	Release source	PEC_{local}	Comments
Surface water	Production (default) Production (site specific)	10.5 or 308 µg/l <0.36 and <0.43 µg/l	Used for assessment of effects on aquatic organisms
	Metal working (formulation)	4.3 µg/l	
	Metal working (use)	1.4 or 5.0 µg/l	
	Rubber formulations	<0.34 µg/l	
	Paints and sealing compounds	negligible	
	Leather (formulation: scenario A)	62 µg/l	
	Leather (formulation: scenario B)	77 µg/l	
	Leather (use: scenario B)	77 µg/l	
	Textile applications	negligible	
Sediment	Production (default) Production (site specific)	20.8 or 611 mg/kg <0.71 and <0.84 mg/kg	Used for assessment of effects on sediment dwelling organisms
	Metal working (formulation)	8.5 mg/kg	
	Metal working (use)	2.8 or 9.9 mg/kg	
	Rubber formulations	<0.67 mg/kg	
	Paints and sealing compounds	negligible	
	Leather (formulation: scenario A)	123 mg/kg	
	Leather (formulation: scenario B)	153 mg/kg	
	Leather (use: scenario B)	153 mg/kg	
	Textile applications	negligible	
Agricultural soil	Production (default) Production (site specific)	51.5 or 1,550 mg/kg negligible	Used for assessment of effects on terrestrial organisms
	Metal working (formulation)	20.1 mg/kg	
	Metal working (use)	5.1 or 23.2 mg/kg	
	Rubber formulations	<0.073 mg/kg	
	Paints and sealing compounds	negligible	
	Leather (formulation: scenario A)	310 mg/kg	
	Leather (formulation: scenario B)	385 mg/kg	
	Leather (use: scenario B)	385 mg/kg	
	Textile applications	negligible	

Table 3.25 Summary of the predicted environmental concentration/doses from the regional and continental scenarios for risk assessment

Media	Predicted concentration/dose in regional scenario $PEC_{regional}$	Predicted concentration/dose in continental scenario $PEC_{continental}$	Comments
Surface water	0.33 µg/l	0.033 µg/l	Assessment of effects on aquatic organisms
Air	12 ng/m^3	4.6 ng/m^3	Assessment of effects on mammals by inhalation
Sediment	1.16 mg/kg	0.12 mg/kg	Assessment of effects on sediment dwelling organisms
Fish	2,600 µg/kg	-	Assessment of effects on fish-eating birds/mammals through diet
Agricultural soil Natural/industrial soil	10.8 mg/kg 11.5 µg/kg	0.95 mg/kg 4.6 µg/kg	Assessment of effects on terrestrial organisms

From the preceding sections, it can be seen that the majority of the predicted environmental concentrations obtained in the regional and continental scenarios are consistent with the measured data. There are some problems in interpreting the measured levels, due mainly to the difficulties in analysing for short chain length chlorinated paraffins. As a result, the predicted concentrations from the models will be used for risk assessment, as they are consistent with, and representative of, most of the measured data.

There are not enough data available referring to the local emission scenarios to make any judgement on the validity of the estimated PEC_{local}s. In the absence of any further information, the predicted PEC_{local}s will be used for the risk assessment. It should be noted that the releases to the regional and continental scenarios, which fit the measured data quite well, were estimated using very similar methods to the emissions used in the local scenario.

It should also be noted that in countries where the use of short chain length chlorinated paraffins has reduced in recent years (e.g. Germany, particularly in water-based metal working fluids: see Section 2.2) the measured levels in water and sediment appear to be lower than in previous years. In these cases, the measurements are reasonably consistent with the predicted concentrations in the regional and continental model (i.e. background concentrations).

Further, the emission of short chain length chlorinated paraffin to waste water from actual production plants are much lower than the default estimates given above. PEC_{local}s derived from site specific data will be taken into account in the assessment. For use in leather, it is thought that Scenario B is most representative of the actual use of short chain length chlorinated paraffins and will be used in the assessment. Similar conclusions would be obtained from Scenario A.

3.2 EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT) ASSESSMENT

3.2.1 Aquatic compartment (incl. sediment)

A large number of aquatic toxicity studies have been carried out using short chain length chlorinated paraffins. The toxicity information in the assessment is generally of good quality and it is certainly all of sufficient quality for risk assessment, given that the substance is of fairly low solubility and so is difficult to test. Many of these studies, particularly the long term studies, have been carried out according to GLP. Further details on the test methods used and an assessment of the reliability of the data is given in Appendix A.

3.2.1.1 Fish

The toxicity of short chain length chlorinated paraffins to fish is summarised in **Table 3.25**. Short chain length chlorinated paraffins appear to be of low acute toxicity to fish with 48 and 96 hour LC_{50}s in excess of 100 mg/l. However, it should be noted that such values are well in excess of the solubility of this group of compounds. Chronic toxicity values include a 60 day LC_{50} at 0.34 mg/l and no observed effect concentrations of <0.040 and 0.28 mg/l for rainbow trout and sheepshead minnow respectively.

During fourteen day exposures to 125 µg/l of short chain length paraffins ($C_{10\text{-}13}$, 49% Cl; $C_{10\text{-}13}$, 59% Cl; $C_{10\text{-}13}$, 71% Cl) behavioural effects including sluggish movements, lack of shoaling and abnormal posture were noted in the bleak *Alburnus alburnus*. These effects were reversible after two days in clean brackish water (Bengtsson *et al.*, 1979).

Madeley and Maddock (1983a) assessed the toxicity of chlorinated paraffin compounds to the rainbow trout *Oncorhynchus mykiss*. A 58% chlorinated short chain length ($C_{10\text{-}12}$) paraffin was used at mean measured concentrations of 0.033, 0.1, 0.35, 1.07 and 3.05 mg/l. Significant mortality was observed in the highest three concentrations. LT_{50}s (median lethal times) were calculated for these three concentrations as 44.7, 31.0 and 30.4 days respectively. Madeley and Maddock (1983b) exposed rainbow trout to the same chlorinated paraffin as part of a bioconcentration study for 168 days at concentrations of 3.1 and 14.3 µg/l followed by a 105 day depuration period. By day 70 of the depuration period all trout previously exposed to 14.3 µg/l and 50% of those exposed to 3.1 µg/l had died. No explanation (e.g. presence of disease or parasite) could be found for these events seen in the bioconcentration test.

Hill and Maddock (1983a) found that hatchability and survival of larvae of the sheepshead minnow *Cyprinodon variegatus* was unaffected by 28 day exposure to measured concentrations of 54.8, 22.1, 6.4, 4.1 and 2.4 µg/l of a 58% chlorinated short chain length n-paraffin. The results of this study reveal that all concentrations tested elicited a significant increase in larval growth compared to the acetone control. In a second study, sheepshead minnow larvae were exposed to 620.5, 279.7, 161.8, 71.0 and 36.2 µg/l of the same chlorinated paraffin for 32 days. In this study, larvae from the highest exposure group were significantly smaller than those from the acetone control; however, at lower exposure concentrations (71.0 and 36.2 µg/l) larvae were significantly larger than controls. The highest no observed effect concentration (NOEC) in this study was 279.7 µg/l. No effect on survival or hatchability was observed (Hill and Maddock, 1983b).

Table 3.26 Toxicity of short chain length chlorinated paraffins to fish

Species	Chlorinated paraffin	Test type	Comments	Temp. (°C)	Duration	Toxicity endpoint (mg/l)	Reference
Bleak *Alburnus alburnus*	C_{10-13}, 49% wt Cl	Static	Acetone as cosolvent	10	96 hour	LC_{50} >5,000	Linden *et al.* (1979)
(estuarine)	C_{10-13}, 56% wt Cl	Static	Acetone as cosolvent	10	96 hour	LC_{50} >10,000	Linden *et al.* (1979)
	C_{10-13}, 63% wt Cl	Static	Acetone as cosolvent	10	96 hour	LC_{50} >5,000	Linden *et al.* (1979)
	$C_{11.5}$, 70% wt Cl	Static	Acetone as cosolvent	10	96 hour	LC_{50} >10,000	Linden *et al.* (1979)
	C_{10-13}, 71% wt Cl	Static	Acetone as cosolvent	10	96 hour	LC_{50} >5,000	Linden *et al.* (1979)
Channel catfish *Ictalurus punctatus*	C_{10-12}, 58% wt Cl	Static		20	96 hour	LC_{50} >300	Howard *et al.* (1975)[2]
Bluegill *Lepomis macrochirus*	C_{10-12}, 58% wt Cl	Static		20	96 hour	LC_{50} >300	Howard *et al.* (1975)[2]
Golden orfe *Leuciscus idus*	C_{10-13}, 52% wt Cl	Static			48 hour	LC_{50} >500	Hoechst (1977)
	C_{10-13}, 56% wt Cl	Static			48 hour	LC_{50} >500	Hoechst (1977)
	C_{10-13}, 58% wt Cl	Static			48 hour	LC_{50} >500	Hoechst (1977)
	C_{10-13}, 62% wt Cl	Static			48 hour	LC_{50} >500	Hoechst (1977)
	C_{10-13}, 70% wt Cl	Static			48 hour	LC_{50} >500	Hoechst (1976)
Fathead minnow *Pimephales promelas*	C_{10-12}, 58% wt Cl	Static		20	96 hour	LC_{50} >100	Howard *et al.* (1975)[2]
Rainbow trout *Oncorhynchus mykiss*	C_{10-12}, 58% wt Cl	Static		10	96 hour	LC_{50} >300	Howard *et al.* (1975)[2]
	C_{10-12}, 58% wt Cl	Flow		10	15-20 day	NOEC <0.040[1]	Howard *et al.* (1975)[2]
	C_{10-12}, 58% wt Cl	Flow	Acetone as cosolvent		60 day	LC_{50} = 0.34	Madeley and Maddock (1983a)
Sheepshead minnow *Cyprinodon variegatus*	C_{10-12}, 58% wt Cl	Flow	Acetone as cosolvent; salinity = 25‰	25	32 day	NOEC = 0.28	Hill and Maddock (1983b)

[1]Sublethal effects observed at 0.040 mg/l (progressive loss of motor function leading to immobilisation
[2]Information also available in Johnson an Finley (1980)

3.2.1.2 Aquatic invertebrates

The toxicity of short chain length chlorinated paraffins to *Daphnia magna* and other aquatic invertebrates is summarised in **Tables 3.27** and **3.28**. Twenty four hour EC_{50}s for daphnids range from 0.3 to 11.1 mg/l with acute no observed effect concentrations ranging from 0.06 to 2 mg/l. There appears to be no clear pattern with regard to the effects of the carrier substance or the degree of chlorination on the acute toxicity of short chain length paraffins to *D. magna*. In 21 day tests EC_{50}s ranged from 0.101 to 0.228 mg/l; NOECs ranged from 0.005 to 0.05 mg/l. The NOEC of 0.005 mg/l for the 58% chlorinated short chain length paraffin means that this species is the most sensitive aquatic species tested.

The second instar of the midge *Chironomus tentans* was exposed to a C_{10-12}, 58% chlorinated paraffin at levels ranging from 18 to 162 µg/l for 48 hours. This caused no adverse effects on the test organism. The use of this paraffin over the whole 49 day life cycle at concentrations of 61 to 394 µg/l also gave no significant response except in halting adult emergence at 121 and 394 µg/l. This led to a maximum acceptable toxicant concentration (MATC) for this paraffin of between 78 and 121 µg/l, with a geometric estimated value for the MATC of 97 µg/l. The NOEC for this study is 61 µg/l (E & G Bionomics, 1983).

Thompson and Madeley (1983d) studied the toxicity of a 58% chlorinated short chain length paraffin to the mysid shrimp *Mysidopsis bahia* and found the 96 hour LC_{50} to be between 14.1 and 15.5 µg/l, with the lowest concentration causing a significant mortality at 13.7 µg/l. The chronic toxicity of this compound was studied in 28 day exposures to concentrations of 0.6, 1.2, 2.4, 3.8 and 7.3 µg/l. Significant mortalities were observed in some of the groups during the test but these were not treatment related. There was no treatment-related effect on reproductive rate (offspring per female) or growth over the 28 day test period. A no effect level was determined as 7.3 µg/l.

Madeley and Thompson (1983) studied the toxicity of the 58% chlorinated short chain length paraffin (C_{10-14}) to the mussel *Mytilus edulis* over a period of 60 days. Tests were carried out at measured concentrations of 0.013, 0.044, 0.071, 0.13 and 0.93 mg/l (nominal concentrations were 0.018, 0.056, 0.1, 0.32 and 3.2 mg/l). There was significant mortality at 0.071, 0.13 and 0.93 mg/l with LT50s of 59.3, 39.7 and 26.7 days for the three exposure concentrations respectively. There was no significant mortality observed at concentrations of 0.013 and 0.044 mg/l; reductions in filtration rate were reported but these were not measured quantitatively. The 60-day LC_{50} was estimated to be 0.074 mg/l based on measured concentrations.

A further study on mussels *Mytilus edulis* using a 58% chlorinated short chain length chlorinated paraffin has been carried out by Thompson and Shillabeer (1993). The study was carried out as a follow up to a bioaccumulation study and only two exposure concentrations were used. Groups of 30 mussels were exposed to measured concentrations of 2.3 µg/l or 9.3 µg/l in seawater for 12 weeks in a flow-through system. No mortalities were seen in any of the exposure groups or controls, but growth (as assessed by increase in shell length and tissue weight) was significantly reduced in the group exposed to 9.3 µg/l. No significant effects were seen in the group exposed to 2.3 µg/l.

Table 3.27 Toxicity of short chain length chlorinated paraffins to *Daphnia magna*

Chlorinated paraffin	Test Conditions	Temp. (°C)	Duration	Toxicity endpoint (mg/l)	Reference
C_{10-13}, 20% wt Cl	With emulsifier (stabilised)		21 day	NOEC = 0.05 EC_{50} = 0.228	Huels AG (1986)
C_{10-13}, 56% wt Cl	Acetone as cosolvent (stabilised)	21	24 hour	NOEC = 0.1 EC_{50} = 0.44	Huels AG (1984)
	With emulsifier (stabilised)	21	24 hour	NOEC = 0.13 EC_{50} = 0.45	Huels AG (1984)
	With emulsifier (unstabilised)	21	24 hour	NOEC <0.1 EC_{50} = 0.55	Huels AG (1984)
	Acetone as cosolvent (unstabilised)	21	24 hour	NOEC = 0.1 EC_{50} = 0.7	Huels AG (1984)
	With emulsifier (unstabilised)	21	24 hour	NOEC = 0.13 EC_{50} = 0.82	Huels AG (1984)
	Acetone as cosolvent (stabilised)	21	24 hour	NOEC = 2 EC_{50} = 11	Huels AG (1984)
	Acetone as cosolvent (unstabilised)	21	24 hour	NOEC <0.3 EC_{50} = 11.1	Huels AG (1984)
	With emulsifier (unstablised)		21 day	NOEC = 0.05 EC_{50} = 0.137	Huels AG (1984)
C_{10-12}, 58% wt Cl	With emulsifier	21	24 hour	NOEC = 0.5 EC_{50} = 1.9	Huels AG (1984)
	Acetone as cosolvent	21	24 hour	NOEC = 0.5 EC_{50} = 1.9	Huels AG (1984)
		20	48 hour	EC_{50} = 0.53	Thompson and Madeley (1983a)
	Flow-through test	20	72 hour	EC_{50} = 0.024	Thompson and Madeley (1983a)
	Flow-through test	20	96 hour	EC_{50} = 0.018	Thompson and Madeley (1983a)
	Flow-through test	20	5 day	EC_{50} = 0.014	Thompson and Madeley (1983a)
	With emulsifier		21 day	EC_0 = 0.03 EC_{50} = 0.124	Huels AG (1986)
	Flow-through test	20	21 day	NOEC = 0.005 EC_0 = 0.0089	Thompson and Madeley (1983a)

Table 3.27 continued overleaf

Table 3.27 continued Toxicity of short chain length chlorinated paraffins to *Daphnia magna*

Chlorinated paraffin	Test Conditions	Temp. (°C)	Duration	Toxicity endpoint (mg/l)	Reference
C_{10-13}, 60% wt Cl	With emulsifier (stabilised)	21	24 hour	NOEC = 0.06 EC_{50} = 0.51	Huels AG (1984)
	Acetone as cosolvent (stabilised)	21	24 hour	NOEC = 0.1 EC_{50} = 0.7	Huels AG (1984)
	With emulsifier (unstabilised)	21	24 hour	NOEC = 1.0 EC_{50} = 4.0	Huels AG (1984)
	Acetone as cosolvent (unstabilised)	21	24 hour	NOEC = 0.5 EC_{50} = 0.95	Huels AG (1984)
	With emulsifier (unstabilised)		21 day	NOEC <0.05 EC_{50} = 0.101	Huels AG (1986)
C_{10-13}, 61% wt Cl	With emulsifier (stabilised)	21	24 hour	NOEC <0.1 EC_{50} = 0.51	Huels AG (1984)
	Acetone as cosolvent (stabilised)	21	24 hour	NOEC = 0.1 EC_{50} = 3	Huels AG (1984)
	With emulsifier (unstabilised)	21	24 hour	NOEC = 0.1 EC_{50} = 1.02	Huels AG (1984)
	Acetone as cosolvent (unstabilised)	21	24 hour	NOEC <0.3 EC_{50} = 0.3	Huels AG (1984)
	With emulsifier (unstabilised)		21 day	NOEC = 0.02 EC_{50} = 0.104	Huels AG (1986)

EC_{50}s are based on immobilisation; static tests unless stated otherwise

Table 3.28 Toxicity of short chain length chlorinated paraffins to other aquatic invertebrates

Species	Chlorinated paraffin	Comments	Temp. (°C)	Duration	Toxicity endpoint (mg/l)	Reference
midge *Chironomus tentans*	C_{10-12}, 58% wt Cl	Acetone (unstabilised)	21-23	48 hour	NOEC > 0.162	E & G Bionomics (1983)
	C_{10-12}, 58% wt Cl	acetone (unstabilised)	21-23	49 day	NOEC = 0.061	E & G Bionomics (1983)
mysid shrimp *Mysidopsis bahia*	C_{10-12}, 58% wt Cl	acetone (unstabilised); salinity = 20‰	25	96 hour	LC_{50} = 0.014	Thompson and Madeley (1983d)
	C_{10-12}, 58% wt Cl	acetone (unstabilised); salinity = 20‰	25	28 day	NOEC = 0.007	Thompson and Madeley (1983d)
mussel *Mytilus edulis*	C_{10-12}, 58% wt Cl	acetone (unstabilised); salinity ~35‰	15	60 day	LC_{50} = 0.074	Madeley and Thompson (1983)
	C_{10-12}, 58% wt Cl	acetone (unstabilised); salinity ~34 ‰	15	12 weeks	Effects on growth seen at 0.0093	Thompson and Shillabeer (1983)

The mysid shrimp test was a flow-through test (salinity = 20‰);
MATC = Maximum Acceptable Toxicant Concentration

3.2.1.3 Algae

The toxicity of short chain length chlorinated paraffins to algae is summarised in **Table 3.29**. Ninety-six hour EC_{50}s range from 0.043 to 3.7 mg/l with the marine alga *Skeletonema costatum* appearing to be more sensitive to short chain length paraffins than the freshwater alga *Selenastrum capricornutum*. A NOEC of 12.1 µg/l was reported in the study on *S. costatum*. It should be noted that the EC_{50} values given for *Selenastrum* exceeded the highest mean measured concentrations of the test substance; they are, therefore, extrapolated values. Further, the toxic effects seen with the marine alga were transient, with no effects being seen at any concentration after 7 days exposure.

Table 3.29 Toxicity of short chain length chlorinated paraffins to algae

Species	Chlorinated paraffin	Comments	Temp. (°C)	Duration	Toxicity endpoint (mg/l)	Reference
Selenastrum capricornutum	C_{10-12}, 58% wt Cl	Cell density by particle count	24	96 hour	EC_{50} = 3.7*	Thompson and Madeley (1983b)
	C_{10-12}, 58% wt Cl	Cell density by particle count	24	7 day	EC_{50} = 1.6*	Thompson and Madeley (1983b)
	C_{10-12}, 58% wt Cl	Cell density by particle count	24	10 day	NOEC = 0.39	Thompson and Madeley (1983b)
	C_{10-12}, 58% wt Cl	Cell density by particle count	24	10 day	EC_{50} = 1.3*	Thompson and Madeley (1983b)
Skeletonema costatum	C_{10-12}, 58% wt Cl	Cell density by absorbance; salinity = 30.5‰	20	96 hour	EC_{50} = 0.056	Thompson and Madeley (1983c)
	C_{10-12}, 58% wt Cl	Cell density by particle count; salinity = 30.5‰	20	96 hour	EC_{50} = 0.043	Thompson and Madeley (1983c)
	C_{10-12}, 58% wt Cl	salinity = 30.5‰	20	96 hour	NOEC = 0.012	Thompson and Madeley (1983c)
	C_{10-12}, 58% wt Cl	Growth rate; salinity = 30.5‰	20	48 hour	EC_{50} = 0.032	Thompson and Madeley (1983c)

*These EC_{50} values exceeded the highest mean measured concentrations of the test substance employed in the study (1.2 mg/l). This was considered the maximum that could be tested due to the low solubility of the test substance

3.2.1.4 Microorganisms

The toxicity of short chain length chlorinated paraffins to microorganisms is shown in **Table 3.30**. Short chain length chlorinated paraffins appear to be of low toxicity to the microorganisms tested. In anaerobic microorganisms, Madeley *et al.* (1983b) used measurements of gas production and its inhibition to assess the toxicity of a short chain length C_{10-12}, 58% chlorinated paraffin to the anaerobic sludge digestion process. This study showed that significant (>10%) inhibition of gas production occurred when chlorinated paraffin concentrations of 3.2, 5.6 and 10% on digester volatile suspended solids were employed. These effects were observed on the first 3 to 4 days of the experiment, after which, gas production recovered to normal levels until day 10 when the study was terminated. It was concluded that the compound tested caused transient partial inhibition of gas production with rapid recovery and no longer-term effects.

Table 3.30 Toxicity of short chain length chlorinated paraffins to microorganisms

Source of microorganisms	Chlorinated paraffin	Effect	Reference
Anaerobic activated sludge	C_{10-12}, 58% wt Cl	Toxic* at concentrations of ≥32,000 mg/l over 24 hours	Madeley *et al.* (1983b)
Anaerobic bacteria from a domestic wastewater treatment plant	C_{10-13}, 52% wt Cl	Toxic at 5,000 mg/l over 24 hours	Hoechst AG (1977)
Anaerobic bacteria from a domestic wastewater treatment plant	C_{10-13}, 56% wt Cl	Toxic at 1,700 mg/l over 24 hours	Hoechst AG (1977)
Anaerobic bacteria from a domestic wastewater treatment plant	C_{10-13}, 58% wt Cl	Toxic at 2,500 mg/l over 24 hours	Hoechst AG (1977)
Anaerobic bacteria from a domestic wastewater treatment plant	C_{10-13}, 62% wt Cl	Toxic at 2,000 mg/l over 24 hours	Hoechst AG (1977)
Anaerobic bacteria from a domestic wastewater treatment plant	C_{10-13}, 70% wt Cl	Toxic at 600 mg/l over 24 hours	Hoechst AG (1976)

*Inhibition of gas production

3.2.1.5 Predicted no effect concentration (PNEC) for the aquatic compartment

There is a complete 'base set' of acute toxicity data for short chain length chlorinated paraffins, i.e. there are short term $L(E)C_{50}$ studies from each of three trophic levels (fish, *Daphnia* and algae). There are reported no observed effect concentrations (NOEC) for fish, *Daphnia* and algae. Therefore, the PNEC is derived from the most sensitive NOEC from the daphnid studies with an assessment factor of 10.

The most sensitive NOEC was from a 21 day multi-generation study on *Daphnia magna* using the 58% chlorinated short chain paraffin (C_{10-12}). The study was scrutinised carefully and although there was a problem with one of the three control groups it was decided that the study was still valid. The 21 day NOEC was 0.005 mg/l and applying an assessment factor of 10 to this value gives a PNEC of 0.5 µg/l for the aquatic compartment.

In addition to the freshwater toxicity data, several marine/estuarine data are also available. There were NOECs available for fish (sheepshead minnow), invertebrate (mysid shrimp) and algae. The shrimp NOEC was the most sensitive at 0.007 mg/l. Thus the marine data is similar to the freshwater data in that invertebrates appear to be the most sensitive species. If similar assessment factors to those used for freshwater organisms are applied (assessment factor of 10), this would lead to a tentative PNEC for the marine/estuarine subcompartment of 0.7 µg/l.

There are toxicity data available for anaerobic bacteria from a domestic wastewater treatment plant. Applying an assessment factor of 100 to the lowest toxic concentration of 600 mg/l, gives a $PNEC_{microorganisms}$ of 6 mg/l.

3.2.1.6 Predicted no effect concentration (PNEC) for sediment-dwelling organisms

There are no studies available on sediment-dwelling organisms exposed via sediment (information is available on midge *Chironomus tentans*, but exposure was via water only).

In the absence of any ecotoxicological data for sediment-dwelling organisms, the PNEC may provisionally be calculated using the equilibrium partitioning method from the PNEC for aquatic organisms and the sediment/water partition coefficient.

$$PNEC_{sed} = K_{sed\text{-}water} / P_{susp} \cdot PNEC_{aquatic\ organisms} \cdot 1000$$

where $K_{susp\text{-}water}$ = sediment - water partition coefficient = 2,281 m^3/m^3 (log K_{ow} = 6).
P_{sed} = bulk density of wet sediment = 1,300 kg/m^3

This gives a tentative PNEC of 0.88 mg/kg wet weight for the sediment compartment. However, the ingestion of the sediment-bound substance by sediment-dwelling organisms may not be sufficiently explained by this relationship for substances with a log K_{ow} greater than 5. The Technical Guidance Document suggests that in such cases the PEC/PNEC ratio is increased by a factor of 10.

3.2.2 Terrestrial compartment

There are no studies available on plants, earthworms or other soil-dwelling organisms. In the absence of any ecotoxicological data for soil-dwelling organisms, the PNEC may provisionally be calculated using the equilibrium partitioning method with the PNEC for aquatic organisms and the soil/water partition coefficient.

$$PNEC_{soil} = K_{soil\text{-}water} / P_{soil} \cdot PNEC_{aquatic\ organisms} \cdot 1000$$

where $K_{soil\text{-}water}$ = soil - water partition coefficient = 2,736 m^3/m^3 for a log K_{ow} of 6.
P_{soil} = density of soil = 1,700 kg/m^3

However, the ingestion of the soil-bound substance by soil-dwelling organisms may not be sufficiently explained by this relationship for substances with a log K_{ow} greater than 5. The Technical Guidance Document suggests that the PEC/PNEC ratio is increased by a factor of 10 to take account of ingestion.

The reported log K_{ow} for short chain length chlorinated paraffins range from 4.39-8.69 and so the equilibrium partitioning method is not really applicable to these substances. However, in the absence of any other data a tentative PNEC for soil can be calculated assuming a $K_{soil\text{-}water}$ of 2,736 m^3/m^3. This gives a PNEC for soil of 0.80 mg/kg wet weight.

It must be borne in mind that data obtained for aquatic organisms cannot replace data for terrestrial organisms because the effects on aquatic species can only be considered as effects on soil-dwelling organisms which are exposed exclusively to the interstitial water of the soil.

3.2.3 Atmosphere

Direct emissions of chlorinated paraffins to the atmosphere are likely to be very low. Predicted levels reflect the small but measurable volatility of this group of substances. Therefore, neither biotic nor abiotic effects are likely because of the limited release and low volatility of chlorinated short chain paraffins.

Short chain length chlorinated paraffins have been raised as a concern with regard to long range atmospheric transport. This is currently being discussed within the appropriate international fora.

3.2.4 Non compartment specific effects relevant to the food chain (secondary poisoning)

3.2.4.1 Bioaccumulation

Reported log K_{ow} ranging from 4.39 to 8.69 indicate a high potential for bioaccumulation. High bioconcentration factors (ranging from 1,000 to 50,000 for whole body, with high values for individual tissues) have been reported with a variety of freshwater and marine organisms. Chlorinated paraffins were taken up rapidly; uptake may be slower at the higher end of the chlorination range.

Most studies report moderate loss of bioaccumulated chlorinated paraffins on return to 'clean' water. Depuration half-lives have been reported at between 9 and 20 days. A single study suggests that 71% chlorinated compounds may be retained longer. It has been suggested that more rapid depuration from the liver, as compared to whole body, is indicative of metabolism and excretion.

3.2.4.2 Avian toxicity

A good quality avian reproduction study using Mallard ducks has been carried out with a C_{10-12}, 58% Cl chlorinated paraffin. The study was carried out to GLP and was based on the Mallard Reproduction Test (August 1982) of the EPA Environmental Effects Test Guidelines (EPA 560/6-82-002). This method appears to correspond with the OECD 206 Avian Reproduction Test (April 1984 version), with a few minor variations.

The study was a 22 week feeding study, including a 9 week pre-egg-laying period without photostimulation, a 3 week pre-egg-laying period with photostimulation and a 10 week egg-laying period with photostimulation. The principle of the test is that adult birds are fed a diet containing the test substance over a period not less than 20 weeks. Birds are induced (by photoperiod manipulation) to lay eggs. Eggs are collected over a 10 week period and the young are observed for 14 days (note the young are not fed with the test substance). Mortality of adults, egg production, cracked eggs, egg shell thickness, viability, hatchability and effects on young birds are all compared to controls.

The test concentrations used were nominally 28, 166 and 1000 ppm (mg/kg) in diet. The mean measured concentrations were found to be 29, 168 and 954 ppm. Twenty pairs of adults were used at each concentration and as control.

A large number of endpoints are looked at in the study and can be summarised under various headings:

Appearance and mortality

Only one bird in the 166 ppm group died during the test. This was attributed to egg yolk peritonitis and was not thought to be related to the test substance. All other adults (controls and exposed) appeared normal in appearance and behaviour.

All surviving hatchlings were normal in appearance and behaviour during the 14-day post hatch period.

A small number of hatchlings did not survive the 14-day observation period. The incidence of mortalities were 3/567 (0.5%), 6/493 (1.2 %), 6/529 (1.1%) and 12/427 (2.8%) in the control, 28, 166 and 1,000 ppm groups respectively. These are normal for this type of test (the OECD Guideline gives the expected survival rate to be between 94-99%).

Adult body weight and food consumption

No significant difference in adult body weight was seen between exposed groups and control.

A statistical analysis of food consumption generally revealed no significant difference between control and exposed groups. A statistically significant increase in food consumption was seen during week 17 in the 28 ppm group. This was not considered to be of biological importance as a similar increase was not seen at other time periods or in other groups.

Egg, hatching and hatchling parameters

A slight, but statistically significant, decrease (by 0.020 mm) in the mean egg shell thickness was noted in the 1,000 ppm group. The biological significance of this is questionable since the mean egg shell thickness in the 1,000 ppm group (0.355 mm) was still in the range of normal values given in the OECD guidelines (0.35-0.39 mm), and no increase in cracked eggs was seen at this dose.

No significant difference in the number of eggs laid, number of cracked eggs or mean egg weight was seen in any treatment group when compared with controls.

A decrease of approximately 10% in 14-day embryo viability over the 10 week egg-laying period was seen in the 1,000 ppm group when compared to controls. Although this decrease was not statistically significantly over the 10 week period, decreases at two weekly intervals (weeks 3 and weeks 6) during the 10 weeks were statistically significant when compared to controls. The decrease resulted from substantially lower viability of embryos in just 3 out of the twenty pairs, rather than a generally lower viability throughout the 20 pens. The conclusions of the authors of the report was that this reduced viability was treatment related and may represent an effect on reproductive performance.

No statistically significant differences in the number of live 21-day embryos, hatchlings or 14-day old survivors were seen in any treatment group. Body weights of hatchlings at day 0 and day 14 were not statistically different from controls in any treatment group.

Gross pathology

No changes that were treatment related were noted. Most changes were of a type that are thought to occur normally in Mallard ducks at the end of a controlled reproduction study.
From the above, it can be seen that slight effects on reproduction may have been seen at 1,000 ppm in diet. Therefore the NOAEL is 166 ppm in diet (166 mg/kg food).

3.2.4.3 Mammalian toxicity

The following is a brief summary of the relevant mammalian toxicity from the Human Health Assessment (Section 4 - consult that section for full details and discussion):

Single exposure studies: No oral LD_{50} available. Some signs of systemic toxicity at doses up to 13 g/kg in rats and 27 g/kg in mice.

Repeated dose studies: Reduction in body weight and increases in kidney weight in rats at doses of >100 mg/kg body weight/day over 14-90 days. In mice, general signs of toxicity over 90 days at doses >1000 mg/kg body weight/day. Main target organs (not relevant for human health) in rats and mice are liver and thyroid. Effects on liver weight appear to occur at concentrations of around 100 mg/kg body weight and above. In a rat 14-day feeding study, similar effects on liver weight were seen at 900 ppm diet and above (this dose is approximately equivalent to 100 mg/kg body weight/day).

Mutagenicity: Not mutagenic.

Carcinogenicity: In rodent studies, toxicologically significant incidence of adenomas and carcinomas in liver and thyroid of mice. Similar effects were seen in a poor quality study in rats. Male rats also showed an increased incidence of kidney tubular cell adenomas, thought to be formed by a male rat specific mechanism (this effect was not seen in female rats or in mice of either sex).

Toxicity for reproduction: No changes seen in reproductive organs of rats and mice treated for 13 weeks with up to 5,000 and 2,000 mg/kg body weight/day respectively. Developmental effects seen in rats at doses that caused severe maternal toxicity but no effects seen at doses of 500 mg/kg body weight/day or less.

From the above summary, it can be seen that effects on laboratory rodents have been seen at concentrations of 100 mg/kg body weight and above. Chlorinated paraffins have also been shown to be carcinogenic in rodents. No clear no effect levels were determined in the carcinogenicity studies, but they were all carried out at relatively high concentrations (e.g. 312 mg/kg body weight/day and above for rats and 125 mg/kg body weight/day and above for mice) and thus fit in with the overall picture from other studies of short chain length chlorinated paraffins causing adverse effects in mammals at concentrations of or above 100 mg/kg body weight.

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 short chain length chlorinated paraffins is the Mallard reproduction study, from which a NOAEL of 166 mg/kg in diet was obtained. The lowest level seen to cause slight effects in this study was 1,000 mg/kg food.

The laboratory rodent data is consistent with the data obtained in birds since a dose of 100 mg/kg body weight/day in rats is approximately equal to 1,000 mg/kg food, using the conversion factor of 10 from Appendix VIII of the Technical Guidance Document.

Since the NOAEL is from a reproductive study, the Technical Guidance Document suggests that an indicative assessment factor of 10 can be used. Thus, the $PNEC_{oral}$ is 16.6 mg/kg food.

3.3 RISK CHARACTERISATION

3.3.1 Aquatic compartment (incl. sediment)

3.3.1.1 Water

A PNEC of 0.5 µg/l has been derived for the freshwater aquatic compartment.

The PEC_{local} for fresh surface water depends on the release source. The worst case ratios are summarised in **Table 3.31**.

Table 3.31 PEC/PNEC ratios for the aquatic compartment

Scenario	PEC/PNEC ratio
PEC_{local} Production (2 sites)	<0.72- site specific <0.86 - site specific
PEC_{local} Metal working (formulation)	8.6
PEC_{local} Metal working (use)	2.8 or 10
PEC_{local} Rubber formulations	<0.68
PEC_{local} Paints and sealing compounds	negligible
[PEC_{local} Leather (formulation: scenario A)]	[124]
PEC_{local} Leather (formulation: scenario B)[1]	154
PEC_{local} Leather (use: scenario B)[1]	154
PEC_{local} Textile applications	negligible
$PEC_{regional}$	0.66
$PEC_{continental}$	0.066

[1]Scenario B is more representative of the current usage in this area

The PEC/PNEC ratios indicate a significant risk to freshwater aquatic organisms from some local sources. For use in metal working applications, the PEC has been derived assuming a 5% chlorinated paraffin content in the cutting fluid. Higher concentrations, e.g. 10% up to 80%, can be used in some applications, and so in some instances the PEC/PNEC ratio may be higher than estimated here. Further information is unlikely to reduce the PEC/PNEC ratio significantly and so risk reduction methods should be considered. A risk to the aquatic

environment is also indicated from metal working fluid formulation and leather processing fluid formulation and use. For leather processing, very little information on how short chain length chlorinated paraffins are used has been obtained. Several possible scenarios have been developed based on the available data (Scenario B appears to be most realistic for use in leather), each of which indicates a risk to the aquatic environment. Further information on releases of short chain length chlorinated paraffins from these sources would be useful to confirm these ratios, but based on the information available, a risk to the aquatic environment cannot be ruled out. Site specific information for production sites indicates low concern.

The strong adsorption of short chain length chlorinated paraffins to sediment would tend to ameliorate effects since the compounds would have reduced bioavailability to benthic organisms. Similar considerations might suggest that the flow-through tests done on organisms do not reflect the real situation. The demonstrated bioaccumulation of the compounds would allow uptake and retention from low water concentrations away from point sources. Overall it must be concluded that there is a potential risk to organisms local to release sources, though exposure in the general environment poses a much reduced risk.

A PNEC of 6 mg/l has been derived for wastewater treatment microorganisms. According to the Technical Guidance Document, this PNEC should be compared to the predicted concentration in the aeration tank of a wastewater treatment plant, which should be similar to the effluent concentration. Since a standard factor of 10 has been used for dilution of effluent in the receiving water, then the predicted concentrations in effluent will be 10 · the predicted concentration in surface water. For all scenarios the PEC/PNEC ratios are <1. Thus it can be concluded that the risk to wastewater treatment plants from the production and use of short chain length chlorinated paraffins is generally low.

Result

For the assessment of surface water for production sites (site specific data) and use in rubber formulations, paints and sealing compounds and textile applications and the assessment of effects on waste water treatment plants for all scenarios:

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

For formulation and use in both metal working fluids and leather finishing:

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

3.3.1.2 Sediment

There are no studies available on sediment-dwelling organisms (information is available on the midge *Chironomus tentans*, but exposure was via water only). The equilibrium partitioning method cannot be used for short chain chlorinated paraffins with log K_{ow} values in excess of 5. However, chlorinated paraffins partition selectively to sediment in aquatic systems. There is no information available on the likely bioavailability of sediment bound residues. Predicted concentrations in sediment range from <0.67 to 153 mg/kg for locally significant sources. These concentrations would represent substantially greater exposure of organisms if they were bioavailable. The Technical Guidance Document suggests that in order

to take into account exposure via ingestion the PEC/PNEC ratio is increased by a factor of 10. Using the tentative PNEC for sediment of 0.88 mg/kg, PEC/PNEC ratios of 1.4 to 1,740 can be estimated. The ratios are summarised in **Table 3.32**. These indicate a risk to sediment dwelling organisms from local sources. The $PEC_{regional}$ for sediment of 1.16 mg/kg gives a PEC/PNEC ratio of 13, indicating possible concern.

Table 3.32 PEC/PNEC ratios for the sediment compartment

Scenario	PEC/PNEC ratio
PEC_{local} Production (2 sites)	<8.1- site specific <9.5 - site specific
PEC_{local} Metal working (formulation)	97
PEC_{local} Metal working (use)	32 or 113
PEC_{local} Rubber formulations	<7.6
PEC_{local} Paints and sealing compounds	negligible
[PEC_{local} Leather (formulation: scenario A)]	[1,400]
PEC_{local} Leather finishing (formulation: scenario B)[1]	1,740
PEC_{local} Leather finishing (use: scenario B)[1]	1,740
PEC_{local} Textile applications	negligible
$PEC_{regional}$	13
$PEC_{continental}$	1.4

[1]Scenario B is more representative of the current usage in this area

The above PEC/PNEC ratios have been determined using a value for K_{oc} of 91,200 estimated from a log K_{ow} of 6.0 using the methods outlined in the Technical Guidance document. Recently, a measured K_{oc} value of 199,500 l/kg has been determined for a C_{10}- and C_{13}-paraffin with around 55% wt Cl content (Thompson *et al.*, 1998). Appendix C considers the effect of this value on the calculated PEC/PNEC ratios and shows that the same conclusions would be reached if this measured value was used in the risk assessment.

Based on the screening assessment, it is recommended that firstly more information on releases (particularly monitoring data near to sources of release) is needed, and then if necessary further toxicity studies, to clarify the risk to sediment-dwelling organisms in aquatic systems. A possible strategy for toxicity testing could be firstly a long-term *Chironomid* toxicity test using spiked sediment with an assessment factor of 100 on the NOEC; secondly a long-term *Oligochaete* toxicity test using spiked sediment, with an assessment factor of 50 on the lowest NOEC; and finally a long-term test with *Gammarus* or *Hyalella* using spiked sediment, with an assessment factor of 10 on the lowest NOEC. The risk reduction measures recommended as a result of the assessment for surface water will also (either directly or indirectly by lowering the $PEC_{regional}$) have some effect on the PECs for sediment. Therefore, any further information gathering or testing should await the outcome of these risk reduction measures on releases to the environment.

Result

For use in paints and sealing compounds and textile applications:

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

For all other scenarios:

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

The need for further information and/or testing should be re-evaluated once the outcome of the risk reduction measures recommended for surface water are known.

3.3.2 Terrestrial compartment

There are no studies available on plants, earthworms or other soil-dwelling organisms.

The equilibrium partitioning method has been used to derive a tentative PNEC for soil organisms of 0.8 mg/kg. However, effects on aquatic species can only be considered as effects on soil-dwelling organisms, which are exposed exclusively to the interstitial water of the soil. The Technical Guidance Document suggests that the PEC/PNEC ratio is increased by a factor of 10 for substances with a log K_{ow} >5 to take into account ingestion of the soil bound substance.

PECs have been derived for agricultural soil and natural soil as 10.8 mg/kg and 11.5 µg/kg respectively in the regional scenario. Thus the tentative PEC/PNEC ratios are 135 and 0.14 for agricultural soil and natural soil. The $PEC_{continental}$ of 0.95 mg/kg for agricultural soil would also indicate concern. When actual sewage sludge concentrations from a German waste water treatment plant are used (PEC = 0.10 mg/kg), the PEC/PNEC ratio is 1.3, again indicating a risk at the regional level. High PECs, and hence PEC/PNEC ratios are also estimated for agricultural soil in the local scenarios. The PEC/PNEC ratios estimated for agricultural soil are summarised in **Table 3.33**.

Table 3.33 PEC/PNEC ratios for the terrestrial compartment

Scenario	PEC/PNEC ratio
PEC_{local} Production (2-sites)	negligible - site specific
PEC_{local} Metal working (formulation)	251
PEC_{local} Metal working (use)	64 or 290
PEC_{local} Rubber formulations	<0.92
PEC_{local} Paints and sealing compounds	negligible
[PEC_{local} Leather (formulation: scenario A)]	[3,875]
PEC_{local} Leather (formulation: scenario B)[1]	4,813
PEC_{local} Leather (use: scenario B)[1]	4,813
PEC_{local} Textile applications	negligible
$PEC_{regional}$	135
$PEC_{continental}$	10.9

[1]Scenario B is more representative of the current usage in this area

Thus, soil organisms could be exposed to short chain length chlorinated paraffins following application of sewage sludge to agricultural soils. There is no information available on the bioavailability of soil-bound residues. There are also no tests on soil organisms which ingest soil particles. It is recommended that more information on releases at a local and regional level (particularly monitoring data near to sources of release) is needed to clarify the risk to the terrestrial compartment. It has already been confirmed that no sewage sludge from the two production sites in the EU is spread onto soil. If this information does not remove the concern further toxicity studies could be performed to refine the PNEC. The following tests are currently recommended in the Technical Guidance Document as being suitable for development of a testing strategy for the terrestrial compartment: plant test involving exposure via soil; test with an annelid; and a test with microorganisms. The risk reduction measures recommended as a result of the assessment for surface water will also (either directly or indirectly by lowering the $PEC_{regional}$) have some effect on the PECs for soil, as the main route to soil is from spreading of sewage sludge. Therefore, any further information gathering or testing should await the outcome of these risk reduction measures on releases to the environment.

The above PEC/PNEC ratios have been determined using a value for K_{oc} of 91,200 estimated from a log K_{ow} of 6.0 using the methods outlined in the Technical Guidance document. Recently, a measured K_{oc} value of 199,500 l/kg has been determined for a C_{10}- and C_{13}-paraffin with around 55% wt Cl content (Thompson *et al.*, 1998). Appendix C considers the effect of this value on the calculated PEC/PNEC ratios and shows that the same conclusions would be reached if this measured value was used in the risk assessment.

Result

For production sites (site specific data), and use in rubber formulations, paints and sealing compounds and textile applications:

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

For all other scenarios:

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

The need for further information and/or testing should be re-evaluated once the outcome of the risk reduction measures recommended for surface water are known.

3.3.3 Atmosphere

Neither biotic nor abiotic effects are likely because of the limited atmospheric release and low volatility of chlorinated short chain chlorinated paraffins.

Short chain length chlorinated paraffins have been raised as a concern with regard to long range atmospheric transport. This is currently being discussed within the appropriate international fora.

Result

ii) There is at present no need for further information and/or testing or 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)

In Section 3.2.4, a PNEC of 16 mg/kg food was derived for the secondary poisoning scenario. The level of short chain length chlorinated paraffins predicted in fish (PEC) is around 2.6 mg/kg in the regional scenario. High concentrations in fish have been predicted for the local scenarios. The PEC/PNEC ratios estimated are shown in **Table 3.34**. On the local scale, these ratios have been estimated assuming that 50% of the dose comes from the local source and 50% comes from the regional sources (as suggested in the Technical Guidance Document).

Table 3.34 PEC/PNEC ratios for secondary poisoning

Scenario	PEC/PNEC ratio
PEC_{local} Production (2 sites)	0.16 - site specific
PEC_{local} Metal working (formulation)	0.96
PEC_{local} Metal working (use)	0.37 or 1.1
PEC_{local} Rubber formulations	<0.17
PEC_{local} Paints and sealing compounds	negligible
[PEC_{local} Leather (formulation: scenario A)]	[1.6]
PEC_{local} Leather (formulation: scenario B)[1]	2.6
PEC_{local} Leather (use scenario B)[1]	2.6
PEC_{local} Textile applications	negligible
$PEC_{regional}$	0.16

[1]Scenario B is more representative of the current usage in this area

Based on the screening approach outlined in the Technical Guidance Document, the PEC/PNEC ratios indicate a risk of secondary poisoning from formulation and use in leather applications, and use in metal working (when the higher release factor is used). Risk reduction measures for use in metal working and leather finishing applications are required based on the aquatic assessment (see Section 3.3.1.1) and these should also reduce the risk from secondary poisoning. The risk of secondary poisoning in birds and mammals, based on the existing information, would appear to be low for the other scenarios considered. Short chain length chlorinated paraffins do bioconcentrate in aquatic organisms and hence have the potential to enter the food chain. If additional information became available indicating that they are more toxic to mammalian or avian species than presently thought, then the risk of secondary poisoning would have to be reassessed.

Result

For production (site specific data), formulation of metal working fluids, and use in rubber formulations, paints and sealing compounds and textile applications:

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

For use in metal working (using the higher release factor), and formulation and use in leather applications:

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

4 HUMAN HEALTH

4.1 HUMAN HEALTH (TOXICITY)

4.1.1 Exposure assessment

4.1.1.0 General discussion

The short chain length chlorinated paraffins are viscous non-volatile liquids and therefore skin contact is the predominant occupational route of exposure. However, there is a potential for significant inhalation exposure in two use areas. Although there is no information available on the extent of absorption of short chain length chlorinated paraffins following their inhalation, toxicokinetic data indicate that they are likely to be poorly absorbed via the dermal route.

4.1.1.1 Occupational exposure

4.1.1.1.1 General discussion

Definitions and limitations

In this document, unless otherwise stated, the term exposure is used to denote personal exposure as measured or otherwise assessed without taking into account the attenuating effect of any respiratory protective equipment (RPE) which might have been worn. The effect of RPE is dealt with separately. This definition permits the effects of controls, other than RPE, to be assessed and avoids the considerable uncertainty associated with attempting to precisely quantify the attenuation of exposure brought about by the proper use of RPE.

Each section considers two routes of exposure, inhalation and dermal. Since there are very few measured data, the exposures are largely predicted from the EASE (Estimation and Assessment of Substance Exposure) model. EASE is a general purpose predictive model for workplace exposure assessments. It is an electronic, knowledge based, expert system which is used where measured exposure data is limited or not available. The model is in widespread use across the European Union for the occupational exposure assessment of new and existing substances.

All models are based upon assumptions. Their outputs are at best approximate and may be wrong. EASE is only intended to give generalised exposure data and works best in an exposure assessment when the relevance of the modelled data can be compared with and evaluated against measured data. Dermal exposure is assessed by EASE as potential exposure rate predominantly to the hands and forearms (approximately 2,000 cm^2).

Overview of exposure

The sections below provide brief descriptions of the processes and sources of occupational exposure for each industry during production, formulation and use. The short chain length chlorinated paraffins are viscous liquids of very low volatility (paraffins with a chlorine content of 50% have a vapour pressure of 0.0213 Pa and 0.7000 Pa at 40^oC and 80^oC respectively). Skin contact is a major route of exposure. However, there is a potential for

inhalation exposure during the formulation of hot melt adhesives, in the use of metal working-fluids and during the spraying of paints, coatings and adhesives containing short chain length chlorinated paraffins.

The number of persons potentially exposed to short chain length chlorinated paraffins within the EU is expected to be in the order of one million, largely in the metal working fluids sector.

Occupational exposure limits

There are no occupational exposure limits for short chain length chlorinated paraffins.

4.1.1.1.2 Manufacture

Introduction

In the manufacture of short chain length chlorinated paraffins it is estimated that about 50-100 employees might be potentially exposed within the EU. The most volatile grades of short chain length chlorinated paraffins (vapour pressure, 0.0213 Pa) are processed at temperatures ranging between 25-45^{o}C. However, the thicker grades, which are less volatile, may be kept at up to 90^{o}C to maintain a suitable viscosity.

Work pattern

The production of short chain length chlorinated paraffins involves the use of closed systems and batch production methods. Exposure is therefore likely to be intermittent and may occur during sampling, plant cleaning, filter cleaning, drumming and tanker loading operations. The main route of potential exposure is considered to be via skin contact.

Inhalation exposure

The EASE Model predicts that airborne concentrations of substances with a vapour pressure of less than 0.001 kPa are negligible (equivalent to an exposure of 0-0.1 ppm 8 hour TWA), regardless of pattern of use and pattern of control. As no aerosol forming activities are anticipated, the inhalation of short chain length chlorinated paraffins during manufacture is considered to be insignificant.

Dermal exposure

Assuming a non-dispersive pattern of use and intermittent skin contact, the EASE Model predicts that exposures to the hand and forearm will be in the range of 0.1-1 mg/cm^2/day. In practice, dermal exposure will be considerably reduced by the use of personal protective equipment.

Summary

For the purposes of risk assessment, an inhalation exposure of 0.1 ppm 8 hour TWA will be used, together with a dermal exposure of 1 mg/cm^2/day.

4.1.1.1.3 Formulation

Introduction

Formulation may be divided into three areas, each involving the preparation of mixtures for further use elsewhere. The first is in the manufacture of metal working fluids, paints, sealants and some adhesives, and fluids used for the treatment of leather or textiles. These are low temperature mixing processes. The second is in the formulation of hot melt adhesives. The third is in the preparation of rubber products where the rubber is mixed with other materials before being formed into sheets. These are cut or moulded into the final product form elsewhere. The numbers of persons potentially exposed to short chain length chlorinated paraffins in the formulation sector is not known but is estimated to be in the region of several thousands within the EU. The processing of short chain length chlorinated paraffins in the various use sectors involves similar procedures. The process temperatures generally range between 40-50^{o}C with the exception of hot melt adhesives and rubber products where temperatures may be in the range 180-200^{o}C.

Work pattern

The blending of the chlorinated paraffins in all three areas generally involves the use of closed systems and batch production methods. Exposure will therefore be intermittent and limited to operations such as charging of mixers, sampling, plant cleaning and loading of tankers, drums and other containers. It is standard practice within the industry to use local exhaust ventilation on mixer charging and, where necessary, decanting points.

Inhalation exposure

The EASE Model predicts negligible airborne concentrations, equivalent to 0-0.1 ppm 8 hour TWA inhalation exposure, from formulation processes operated at between 40-50^{o}C.

However, in the case of hot melt adhesives and rubber products, the higher process temperatures may result in significant airborne vapour concentrations being produced. Assuming a non-dispersive pattern of use, with segregation of the work and the use of local exhaust ventilation, the EASE Model predicts airborne exposures of 0.5-3 ppm 8 hr TWA.

Dermal exposure

Assuming a non-dispersive pattern of use and intermittent skin contact, the EASE Model predicts that exposure to the hands and forearms will be in the range of 0.1-1 mg/cm^2/day.

The exposures predicted above are likely to be at the high end of those experienced. In practice, dermal exposure will be considerably reduced by the use of personal protective equipment and the decontamination of equipment in use. Further, the inhalation exposures arise from batch production, suggesting that the actual exposures are brief and intermittent.

Summary

For the purposes of risk assessment, inhalation exposures of 0.1 ppm 8 hour TWA (low temperature mixing processes) 3 ppm 8 hour TWA (hot melt adhesives and rubber formulation) and 1 mg/cm^2/day (all dermal exposures) will be used.

4.1.1.1.4 Use of formulations

In most formulations the short chain length chlorinated paraffins constitute a small percentage of the products in which they are used. Occupational exposure resulting from the use of the products will therefore be moderated by their low concentration.

Metal working fluids

The number of employees potentially exposed to metal working fluids is estimated to be over a million within the EU.

Work pattern

Metal working fluids are applied by continuous jet, spray, mist or by hand dispenser. Skin contact occurs during preparation or draining of the fluids, handling workpieces, from splashes during machining, changing and setting of tools and during maintenance and cleaning of machines. In addition, inhalable aerosols or oil mist and fumes can be generated during machine operations.

Inhalation exposure

Historical exposure data from machine shops, reported as reflecting worst case situations, indicated exposures ranging from 0.33-3.2 mg/m^3 total mist for operations such as milling, cutting and grinding (Industry supplied data). The chlorinated paraffin content in the fluids used in these exposure surveys ranged from 5-40%. Exposures to chlorinated paraffins were estimated to be from 0.003-1.15 mg/m^3. Exposure data from another study suggested exposures to chlorinated paraffins ranging from 0.003-0.21 mg/m^3.

Dermal exposure

There will be significant potential for skin contact. The nature of this contact, however, will clearly depend upon the activity involved which will determine how often an item is handled and for how long. Assuming non-dispersive use and intermittent (2-10 events per day) skin contact, EASE predicts that exposure to the hands and forearms will be in the range of 0.1-1 mg/cm^2/day. However, the typical content of chlorinated paraffin in metal-working fluids is 2-10% which would approximate to a dermal exposure of 0.002-0.1 mg/cm^2/day. (A separate evaluation for this activity is made for consumers, see Section 4.1.1.2).

It is important to note that, in practice, dermal exposure will be considerably attenuated by the decontamination of equipment and the use of personal protective equipment.

Summary

For the purposes of risk assessment, an inhalation exposure of 1.15 mg/m^3 8 hour TWA will be used, together with a dermal exposure of 0.1 mg/cm^2/day.

Leather and textile treatments

The number of people potentially exposed to short chain length chlorinated paraffin-based textile and leather treatments is not known.

Work pattern

Exposures would arise from handling treatment formulations and treated products and other contact with contaminated surfaces.

Inhalation exposure

The use of these formulations at ambient or slightly raised temperatures, even in unenclosed systems, is not expected to give rise to high airborne concentrations. The EASE Model predicts that inhalation exposure to a substance with a vapour pressure of less than 0.001 kPa is negligible (0-0.1 ppm), regardless of pattern of use and pattern of control. As no aerosol forming activities are anticipated, the inhalation exposure to short chain length chlorinated paraffins during manufacture is considered to be negligible.

Dermal exposure

The pattern of dermal exposure will be intermittent and the concentration of short chain length chlorinated paraffins on the articles will vary depending upon the formulation. Assuming a non-dispersive pattern of use and intermittent skin contact, the EASE Model predicts that exposures to the hand and forearm will be in the range of 0.1-1 mg/cm^2/day. However, it is unlikely that the treatment formulations will contain more than 30% short chain length chlorinated paraffins thus reducing the predicted exposure by a factor equivalent to the concentration in the formulation; the dermal exposure will therefore be in the range 0.03-0.3 mg/cm^2/day. It is important to note that, in practice, dermal exposure will be considerably attenuated by the use of personal protective equipment.

Summary

For the purposes of risk assessment a dermal exposure of 0.3 mg/cm^2/day will be used. Inhalation exposure is considered to be negligible.

Use of treated leather and textiles in protective clothing

The treated textile products described above may be used in industrial protective clothing and tarpaulins. In each of these products, the short chain length chlorinated paraffins are part of a treatment formulation applied to the cloth and the amount on the finished article is likely to be low. Treated leathers would not be used in this kind of application.

Skin contact with some of these products would be very intermittent and in the case of protective clothing (if so used) would be worn over other garments. For the purposes of risk assessment, exposure by both the inhalation and dermal route may be considered to be negligible.

Paints, adhesives and sealants

The number of people potentially exposed to short chain length chlorinated paraffins based paints, adhesives and sealants is not known but is estimated to be in the region of thousands.

Work pattern

No measured data are available and there is scope for widely different use scenarios. In most use scenarios, exposure to vapours is considered insignificant due to the very low vapour pressure of the short chain length chlorinated paraffins. However, spraying is a common method of applying paints, adhesives and certain types of sealant coatings (although not caulk type sealants or grout) and this may result in significant inhalation exposure from the aerosols formed.

Inhalation exposure

EASE predicts an 8-hour TWA inhalation exposure of 100-200 ppm if neat short chain length chlorinated paraffins were sprayed. However, EASE assumes that the short chain length chlorinated paraffins are true vapours; in practice they will be present as a minor constituent of fine droplets; consequently EASE does not provide an appropriate model for this scenario.

Given the lack of comparable information on the levels of fine droplets generated in paint spraying, there is no directly relevant data available for predicting inhalation exposure. The next best approximation is provided by the measured data on metal working fluids, which may be applied by continuous jet or spray, although potentially on a smaller scale than some paint spraying equipment. Using these data as a first approximation, the concentration of total mist in air is 3.2 mg/m^3. Assuming that the formulations are unlikely to contain more than 10% short chain length chlorinated paraffins, gives a concentration of 0.32 mg/m^3.

Dermal exposure

There will also be a potential for dermal exposure to these formulations from splashing and contact with contaminated surfaces. A worst case scenario would be for an operator carrying out manual spraying. Assuming non-dispersive use and intermittent (2-10 events/day) skin contact, EASE estimates dermal exposure to the hands and forearms to be in the range 0.1-1 mg/cm^2/day. As these formulations are unlikely to contain more than 10% short chain length chlorinated paraffins, the predicted dermal exposure range will be reduced to 0.01-0.1 mg/cm^2/day.

It is important to note that, in practice, dermal exposure will be considerably attenuated by the decontamination of equipment and the use of personal protective equipment.

Summary

For the purposes of risk assessment, inhalation exposures of 0.32 mg/m^3 8 hour TWA (all spray processes) and 0.1 mg/cm^2/day (all dermal exposures) will be used.

Further processing and use of rubber products

The further cutting, moulding and shaping of rubber products is unlikely to lead to significant dermal or inhalation exposure, since the short chain length chlorinated paraffins are a minor part of the total formulation and the amount available on the surface for dermal contact is likely to be small. Consequently, for the purposes of risk assessment, dermal and inhalation exposure arising from further *processing* of rubber products is considered to be negligible.

For the reasons stated above, for the purposes of risk assessment it is considered that dermal and inhalation exposure resulting from *use* of these products will be negligible.

4.1.1.1.5 Summary of occupational exposure

Table 4.1 Data to be used for risk assessment

Scenario	Inhalation		Dermal	
	Duration	Concentration	Duration	Concentration
Manufacture	8-hour TWA	0.1 ppm (2.1 mg/m^3)[a]	8-hour day	1 mg/cm^2
Formulation low temperature	8-hour TWA	0.1 ppm (2.1 mg/m^3)	8-hour day	1 mg/cm^2
Formulation high temperature	8-hour TWA	3 ppm (63 mg/m^3)	8-hour day	1 mg/cm^2
Metal working fluids	8-hour TWA	1.15 mg/m^3	8-hour day	0.1 mg/cm^2
Leather and textile treatment	8-hour TWA	negligible	8-hour day	0.3 mg/cm^2
Leather and textile use	8-hour TWA	negligible	8-hour day	negligible
Paints, adhesives & sealants	8-hour TWA	0.32 mg/m^3	8-hour day	0.1 mg/cm^2
Rubber products, processing and use	8-hour TWA	negligible	8-hour day	negligible

[a]mg/m^3 = ppm · Molecular Weight / 24.05526

Molecular weight is assumed to be 500 (the top end of the range) and 24.05526 l/mol is the molar volume of an ideal gas at 20°C and 1 atmosphere pressure (101325 Pa, 760mm mercury, 1.01325 bar)

4.1.1.2 Consumer exposure

Short chain length chlorinated paraffins are used in leather and textile treatments, in metal working fluids, paints, sealants and adhesives and in plastic and rubber products. Consumer exposure may arise from the use of treated finished products or following their application (leather, textiles, plastics and rubber, paints, adhesives and sealants) during the application process (paints, adhesives, sealants) and during the process of use (metal working fluids). The potential exposure scenarios and resulting exposures are considered below. Some exposures are clearly negligible.

4.1.1.2.1 Leather treatment

The production and use section notes that some 390 tonnes of short chain length chlorinated paraffins are used in the leather industry. They are usually mixed with sulphonated oils but it is unlikely that any chemical changes take place in the chlorinated paraffins as a result. They are used to produce a surface sheen to some sorts of leather but also help to impart some tear resistance when used in garments. Worst case exposure scenarios can be estimated as being

when leather garments are worn regularly. The major centres for the leather industry in Europe are in Italy and Spain; the greater proportion of this tonnage is therefore likely to be consumed there. Short chain length chlorinated paraffins are thought to be used infrequently (note the scenario for slippers below) as they are relatively expensive. They are more likely to be used for more expensive products, where flexibility and softness is more important than price (Leather Industry Personal Communication). While a screening level exposure assessment is presented below for leather jackets and trousers, expensive gloves would be a more likely use.

Exposure scenario for the use of chlorinated paraffins in slippers

There is a small use in the UK industry and a possibly larger use in Italy for producing a dark surface sheen to slippers. Short chain length chlorinated paraffins are 1-2% of a 30% solution. The leather is in the treatment for 10 minutes, just after formic acid (to make a pH of 3.5) has fixed the dye. Owing to the short treatment period there is no absorption below the surface of the slipper.

Assuming that the slippers weigh 1000 g there will be a maximum of 3 g of chlorinated paraffins in the slippers. Assuming that all of this migrates out of the slippers over a period of a year the maximum daily exposure will be less than 10 mg/day.

Exposure scenario for the use of chlorinated paraffins in coats and trousers

The maximum concentration of chlorinated paraffins in other leather goods is 1% (UK Leather Industry, Personal Communication). Assuming that leather jackets and trousers are worn next to the skin and weigh a total of 5 kg, there will be a maximum of 50 g of chlorinated paraffins in the clothing. Assuming that all of this migrates out of the leather over a period of a year, then the daily exposure will be a maximum of 50/365 = 137 mg/day.

This assumes that the leather clothing is worn continuously next to the skin, without a lining or other garments and that the migration rate is as high as suggested. However, if the garments are dry-cleaned, then most if not all of the chlorinated paraffins will be removed in this procedure (Leather Industry Personal Communication). Indeed, following dry-cleaning, oils (which are unlikely to contain chlorinated paraffins) are put back into the garments to maintain their suppleness.

Summary

Assuming a consumer wears leather trousers and jacket next to the skin continuously then there will be a maximum daily exposure of 137 mg/day of C_{10}-C_{13} chlorinated paraffins. This value will be taken forward to the risk characterisation section, with the proviso that it is likely to be a large exaggeration. The use of leather slippers is unlikely to be additive.

4.1.1.2.2 Use in textiles

Short chain length chlorinated paraffins may be used in sail cloths and industrial protective clothing and tarpaulins that could be purchased by the public. There was an historical use for chlorinated waxes in military tenting but it is believed that they are no longer used. In each of these products, the short chain length chlorinated paraffins are part of a treatment formulation applied to the cloth.

Consumer contact with these products would be very intermittent; where industrial protective clothing of this type is worn it is very likely to be worn over other clothes, such that skin contact is minimal.

For the purposes of risk assessment, exposure by both the inhalation and dermal route may be considered to be negligible.

4.1.1.2.3 Use in metal working fluids available to consumers

Consumers may have access to (but may not necessarily use) metal working fluids containing short chain length chlorinated paraffins, either for use with lathes at home or in voluntary groups (for example restoring or maintaining old vehicles or engines). No precise information is available.

Exposure scenario for use in metal working fluids

An individual working alone is unlikely to have the same degree of prolonged exposure that would arise from a full working day, nor would they expect to be exposed to mists generated by a number of machines working simultaneously and/or continuously. Similarly, while voluntary groups maintain and use their own machine shops, they may not be in constant use.

Consequently, for consumers as individuals or groups, the exposure information available for the workplace is likely to be an overestimate. The degree of overestimation is uncertain but continuous exposure 8 hours daily for a working week is unlikely. For the purposes of risk assessment, therefore, inhalation and dermal exposure will be treated as individual events, averaged over a day, rather than repeated exposures.

Inhalation exposure

To take account of the factors that are likely to lead to lower exposures for consumers, concentrations in the air will be reduced by a factor of 10 and work duration will be assumed to be 2 hours. Using the workplace value of 1.15 mg/m^3, the concentration in air is calculated to be 0.115 mg/m^3 for 2 hours. Assuming a breathing rate of 1.25 m^3/hour inhalation exposure will be 0.3 mg.

Dermal exposure

Dermal exposure will remain the same, 0.1 mg/cm^2/day. Assuming the surface area of the hands to be 2000 cm^2 (assuming arm and forearm contamination in this case) this amounts to a dermal exposure of 200 mg.

4.1.1.2.4 Use in paints, sealants and adhesives available to consumers

Short chain length chlorinated paraffins are not used in the kinds of paints, sealants or adhesives commonly purchased by consumers. While it is plausible that consumers could obtain the paints from the same sources as professionals, their use as industrial coatings and the container volumes in which they are likely to be supplied suggest that this is likely to be rare. A risk assessment for this potential source of exposure has not, therefore, been carried out.

Similarly, while there may be a consumer use of some of the adhesives sold containing short chain length chlorinated paraffins, the likely short duration of their use, that they form a small proportion of the final product and their physico-chemical properties indicates that consumer exposure from their use, if they are so used, will be negligible.

The short chain length chlorinated paraffins are not used as solvents. They are an integral part of the paint, adhesive or coating and have a very low vapour pressure. Consequently consumer exposure to emissions and hence inhalation and dermal exposure can be considered to be negligible.

4.1.1.2.5 Use in rubber products

Given the nature of the products and their paraffin content, for the purposes of risk assessment, inhalation and dermal exposure arising from the use of finished products can be considered to be negligible.

4.1.1.2.6 Summary of consumer exposure

Table 4.2 Information to be used in the risk assessment

Scenario	Inhalation		Dermal	
	Duration	Concentration (dose)	Duration	Concentration (dose)
Leather slippers		negligible	daily	(<10 mg)
Leather clothing		negligible	daily	(137 mg)
Textiles		negligible		negligible
Metal working fluids	per event, over two hours	0.115 mg/m^3 (0.3 mg)	per event, over two hours	0.1 mg/cm^2 (200 mg)
Paints, sealants & adhesives		negligible		negligible
Rubber products		negligible		negligible

4.1.1.3 Indirect exposure via the environment

Short chain length chlorinated paraffins have several uses that can result in releases into surface water, for instance use in metal working fluids. Short chain length chlorinated paraffins have been shown to bioconcentrate in aquatic organisms and have been detected in some items of food (see Section 3.1.4). Very low levels of chlorinated paraffins are expected to occur in air. The main source of exposure of humans via the environment is therefore likely to be via food and, to a lesser extent, drinking water.

The EUSES model has been used to estimate various concentrations in food, air and drinking water and from these to estimate a daily human intake figure. Some of values are reported in Section 3.1.3 and 3.1.4 and are reproduced again here in **Table 4.3**.

Table 4.3 Estimated concentrations of short chain length chlorinated paraffins in food and human intake media

Scenario	Estimated concentration						
	Drinking water	Air	Fish	Plant roots	Plant leaves	Meat	Milk
Production (default)	0.032 or 0.96 mg/l	11.6 ng/m³	68.5 or 1,980 mg/kg	229 or 6,870 mg/kg	0.013 or 0.085 mg/kg	0.30 or 8.51 mg/kg	0.095 or 2.69 mg/kg
Metal working (formulation)	0.013 mg/l	11.6 ng/m³	28.3 mg/kg	89.3 mg/kg	0.011 mg/kg	0.128 mg/kg	0.041 mg/kg
Metal working (use)	0.003 or 0.014 mg/l	11.6 ng/m³	9.12 or 32.5 mg/kg	22.7 or 103.3 mg/kg	0.011 or 0.011 mg/kg	0.046 or 0.209 mg/kg	0.014 or 0.064 mg/kg
Rubber formulations	<0.09 µg/l	11.6 ng/m³	<2.68 mg/kg	<0.33 mg/kg	<0.010 mg/kg	<0.018 mg/kg	<0.006 mg/kg
Paints and sealing compounds	negligible	negligible	negligible	negligible	negligible	negligible	negligible
Leather (formulation: scenario A)	0.19 mg/l	11.6 ng/m³	48.9 mg/kg	1,380 mg/kg	0.026 mg/kg	1.72 mg/kg	0.55 mg/kg
Leather (formulation: scenario B)	0.24 mg/l	11.6 ng/m³	79.7 mg/kg	1,710 mg/kg	0.045 mg/kg	2.16 mg/kg	0.68 mg/kg
Leather (use: scenario B)	0.24 mg/l	17.8 ng/m³	79.7 mg/kg	1,710 mg/kg	0.045 mg/kg	2.16 mg/kg	0.68 mg/kg
Textile applications	negligible	negligible	negligible	negligible	negligible	negligible	negligible
Regional	6.7 µg/l	11.6 ng/m³	2.6 mg/kg	48 mg/kg	0.011 mg/kg	0.154 mg/kg	0.049 mg/kg

There is considerable uncertainty inherent in the approach EUSES takes for estimating the concentrations of substances with high log K_{ow} values in various parts of the food chain. For instance, the concentrations estimated in drinking water are very high, frequently close to or above the water solubility of the substance, and are much higher than the levels predicted/found in surface waters. This is because in EUSES the drinking water concentrations are taken as the soil pore water concentrations. For highly lipophilic substances such as short chain length chlorinated paraffins, very high concentrations in soil are predicted due to application of sewage sludge containing the substance. This leads to high estimated soil pore water concentrations, which in turn also leads to very high concentrations in plant roots (the estimated plant root - pore water partition coefficient for short chain chlorinated paraffins is around 7,200 kg/l) and hence other parts of the food chain related to plant concentrations e.g. leaves, meat and milk.

The human intake from the various routes can be estimated using the methods given in the Technical Guidance Document using the standard defaults (adult body weight = 70 kg;

bioavailability inhalation = 0.75; bioavailability oral route = 1.0). The estimated figures are shown in **Table 4.4**.

Table 4.4 Estimated human intake from various sources

	Estimated daily human intake (mg/kg body weight/day)							
	Drinking water	**Inhalation**	**Fish**	**Root crops**	**Leaf crops**	**Meat**	**Dairy products**	**Total mg/kg bw/day**
Default intake of crop	2 l/day	20 m^3/day	0.115 kg/day	0.384 kg/day	1.20 kg/day	0.301kg/day	0.561 kg/day	
Production (default)	$9.1 \cdot 10^{-4}$ or 0.027	$2.5 \cdot 10^{-6}$	0.11 or 3.25	1.25 or 37.7	$2.2 \cdot 10^{-4}$ or $1.5 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$ or 0.037	$7.6 \cdot 10^{-4}$ or 0.02	1.4 or 41.0
Metal working (formulation)	$3.7 \cdot 10^{-4}$	$2.5 \cdot 10^{-6}$	0.05	0.49	$1.8 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	0.54
Metal working (use)	$9.0 \cdot 10^{-5}$ or $4 \cdot 10^{-4}$	$2.5 \cdot 10^{-6}$	0.015 or 0.053	0.125 or 0.57	$1.8 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$ or $9.0 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$ or $5.1 \cdot 10^{-4}$	0.14
Rubber (formulation)	$<2.5 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$	$<4.4 \cdot 10^{-3}$	$<1.8 \cdot 10^{-3}$	$<1.8 \cdot 10^{-4}$	$<7.8 \cdot 10^{-5}$	$<4.6 \cdot 10^{-5}$	$<6.5 \cdot 10^{-3}$
Leather (formulation: Scenario A)	$5.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-6}$	0.08	7.56	$4.4 \cdot 10^{-4}$	$7.4 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	7.65
Leather (formulation: Scenario B)	$6.8 \cdot 10^{-3}$	$2.5 \cdot 10^{-6}$	0.13	9.38	$7.7 \cdot 10^{-4}$	$9.3 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	9.53
Leather (use: Scenario B)	$6.8 \cdot 10^{-3}$	$5.1 \cdot 10^{-6}$	0.13	9.38	$7.7 \cdot 10^{-4}$	$9.3 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	9.53
Regional sources	$1.9 \cdot 10^{-4}$	$2.5 \cdot 10^{-6}$	$4.3 \cdot 10^{-3}$	0.26	$1.9 \cdot 10^{-4}$	$6.6 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$	0.27

EUSES calculations and environmental emissions

In the above tables, for "Metal working - use", the first line of the calculation represents 4% emission into the environment from use, the second line 18%. The latter is a default assumption, the former is based upon information gathered from a survey of the industry (UCD 1995). The data based upon the industry survey is considered the most realistic and will be considered further, below.

Releases from actual production sites have been estimated to be <26.7 kg/year to waste water. The higher figures in food given in **Table 4.3** for production have been estimated using the default release figure of 30,000 kg/year to waste water. Thus, based on the actual release data from production sites, the estimated local human intake would be around 1,100 times lower

than the figure of 41.0 mg/kg body weight estimated in **Table 4.4**, i.e. 0.037 mg/kg body weight. Furthermore, one of the sites now no longer sends waste to sewage; these wastes are now incinerated. Since the sewage - sludge - plant chain is the one which (in these calculations) most contributes to human uptake, for this site the calculated uptake via the environment would be further reduced.

EUSES calculations and concentrations in foodstuffs

As can be seen from **Table 4.4**, root crops are predicted to form the major source of human uptake. As mentioned above, there is considerable uncertainty in the derivation of these values. Some surveys of the levels of short chain length chlorinated paraffins in food have been carried out and are reported in Section 3.1.4.2. In one survey (Campbell and McConnell, 1980), the average levels of C_{10-20} chlorinated paraffins found in human foodstuffs were 0.3 mg/kg in dairy products, 0.15 mg/kg in vegetable oils and derivatives, 0.005 mg/kg in fruit and vegetables and not detected (<0.05 mg/l) in drinks. In other surveys, levels of C_{10-20} chlorinated paraffins in shellfish close to sources of discharge of up to 12 mg/kg have been measured and levels of chlorinated paraffins in meat of up to 4.4 mg/kg on a fat weight basis (the sample contained ~2% fat) have been measured. Based on these values, the maximum estimated human intake (ignoring contributions from inhalation) is of the order of 20 µg/kg (body weight)/day, with the major contribution coming from fish/shellfish.

The value of 20 µg/kg/day is in line with the contribution from regional sources without the contribution from root crops (0.27-0.26 = 10 µg/kg/day) from metal working fluid formulation without root crops (0.54-0.49 = 60 µg/kg/day) and from metal working fluid use without root crops (0.140-0.125 = 15 µg/kg/day). The real data above may not include a root crop but does include data from samples taken close to a pollution source and from food probably sourced from elsewhere. Consequently, it does not represent a diet coming only from a polluted source. However, when root crops are removed, fish/shellfish becomes the dominant source in human food for the EUSES calculations, as they are for calculations based on real data.

Summary

The EUSES predictions considerably overestimate human exposure via the environment, specifically in the predictions for root crops. However, real data clearly indicate the potential or human uptake. The value of 20 µg/kg/day is considered to be a reasonable worst case prediction based upon real data and will be used in the risk assessment to represent both local and regional exposure.

4.1.2 Effects assessment: Hazard identification and dose (concentration) - response (effect) assessment

4.1.2.1 Toxico-kinetics, metabolism and distribution

4.1.2.1.1 Studies in animals

***In vivo* studies**

Inhalation

No studies are available.

Oral

Absorption, distribution and excretion were investigated in a study in which groups of 1 to 4 mice were treated with one of three different C_{12} paraffins, differing in degree of chlorination: monochlorododecane (MCDD, 17.4% chlorinated), polychlorododecane I (PCDD I, 55.9% chlorinated) and polychlorododecane II (PCDD II, 68.5% chlorinated) (Darnerud *et al.*, 1982). In the first part of the study, groups of four mice were treated by gavage with terminally labelled-^{14}C PCDD I or II in a fat emulsion (MCDD was not investigated is this part). Sixty two percent of the administered radioactivity was recovered 12 hours after administration of PCDD I; 33% as CO_2 in exhaled air, and 29% in the urine. A further 5% was recovered in the faeces. Only 12% of the administered radioactivity was recovered within 12 hours for the greater chlorinated PCDD II; 8% as carbon dioxide in exhaled air and 4% in the urine. A further 21% was recovered in the faeces.

Distribution of the three radiolabelled chlorinated paraffins was investigated in the second part of the study using whole-body autoradiography techniques in groups of one or two mice per substance. Twenty four hours after administration as above, evidence of radioactivity was apparently seen in tissues with high metabolic activity and/or high rates of cell proliferation (e.g. the intestinal mucosa, bone marrow, brown fat, salivary glands, and thymus). The liver showed the most evidence of radioactivity in PCDD II-treated animals. According to qualitative judgement of the X-ray films by the authors, the evidence of accumulation of radioactivity apparently increased with increasing degree of chlorination. However quantitative investigations were not conducted.

In an unpublished study groups of 18 male and 18 female rats were treated with 10 or 625 mg/kg/day $C_{10\text{-}12}$, 58% chlorinated paraffin, daily in the diet for 13 weeks (unpublished reference 73, 1984). After the 13 weeks, all rats received a single oral (gavage) dose of ^{14}C-radiolabelled $C_{10\text{-}12}$ (position of labelling not stated), 58% chlorinated paraffin, at the same dose level as received daily in the previous weeks. Other groups of 18 males and 18 females, which were not treated previously with chlorinated paraffin, also received a single radioactive dose of 10 or 625 mg/kg/day $C_{10\text{-}13}$, 58% chlorinated paraffin. Urine, faeces and carbon dioxide were collected from groups of animals for either 12 hours or 7 days. Other groups were kept for 24 or 48 hours, or 28 or 90 days at which time tissue distribution studies were conducted. Samples of whole blood were also collected at 12, 24 and 48 hours and 7 days.

Overall there was little difference in excretion between the sexes, dose levels or treatment regimes. Faecal elimination was the principal route of excretion of radioactivity with 54-66% of the administered radioactivity being recovered in 7 days. Most of the recovered radioactivity was obtained within 3-4 days in the naive animals and in 2 days in the animals pretreated for 13 weeks with chlorinated paraffin. Approximately 14% of the administered radioactivity were recovered in the urine in 7 days and less than 1% in exhaled air as carbon dioxide. Blood levels were proportional to dose, and the rates of decline after 7 days were found to be similar. Tissue levels were also proportional to the administered dose and were similar, irrespective of dosing regime, suggesting that the kinetics of absorption, distribution and excretion of the radioactive dose was essentially linear over the range of doses tested and that pre-dosing had no significant influence on this. The highest initial concentrations of radioactivity were found in the liver, kidney, adipose tissue and ovaries. The concentration of radioactivity in all tissues, including the blood, tended to be lower in the pretreated animals than in the naive, although these differences had essentially disappeared by day 7 in males and day 28 in females. The rate of elimination overall was noted to be "somewhat" lower for adipose tissue.

One 90-day and two 14-day studies, which are summarised in more detail in section 4.1.2.6, showed statistically significant increases in liver microsomal activity or levels of cytochrome P450, amino pyrine demethylase and Lowry protein, following oral treatment (by gavage or in the diet) of 300 mg/kg/day and above of a C_{10-12}, 58% chlorinated paraffin (unpublished references 72, 1983; 73, 1984 and 75, 1981).

Dermal

No studies are available on the dermal absorption of short chain length chlorinated paraffins. However very poor dermal absorption has been demonstrated for longer chain chlorinated paraffins. When ^{14}C-labelled C_{18} (50-53% chlorinated) and C_{28} (47% chlorinated) chlorinated paraffins were applied to the dorsal skin of rats, 0.7 and 0.1% of the applied radioactivity, respectively, was absorbed as indicated by that recovered in excreta, expired air and body tissues after 96 hours (Yang *et al.*, 1987). Dermal absorption of short chain chlorinated paraffins may be greater than for the longer chain, but nevertheless will be poor.

Parenteral

Three different ^{14}C-labelled C_{12} paraffins, differing in degree of chlorination (17.4, 55.9 or 68.5% chlorinated) were given intravenously to groups of mice (Darnerud *et al.*, 1982). Results indicated that excretion in urine and as CO_2 in exhaled air was inversely proportional to the degree of chlorination. The distribution of radioactivity was similar at 4 to 24 hours as that seen in the oral administration study. At later times, the adrenal cortex and gonads (on days 4 to 12) and the central nervous system (on days 30-60) were selectively labelled following treatment with the 17.4 and 55.9% chlorinated paraffins (but apparently not with the 68.5% chlorinated paraffin).

Oxidation of chlorinated paraffins by cytochrome P450 was demonstrated following intravenous administration in groups of mice which were pretreated with P450-inducers and inhibitors, before receiving intravenous treatments of four different radiolabelled C_{12} chlorinated paraffins (Darnerud, 1984).

P450-inducers had very little effect on levels of $^{14}CO_2$ collected in exhaled breath, while the inhibitors caused up to 84% depletion of $^{14}CO_2$ collected. It was also noted that the inhibitory effect increased for the paraffins having an increasing degree of chlorination.

***In vitro* studies**

Male rats were treated intraperitoneally with 0 or 1000 mg/kg/day of a C_{10-13}, 49 or 71% chlorinated paraffin for 4 days, after which liver microsomes were pooled and assayed for cytochrome P450 concentrations (Nilsen and Toftgard, 1981). Increases in RLvMc $P450_{54}$ (43 and 87% with the 49 and 71% chlorinated paraffins, respectively) and RLvMc $P450_{50}$ (74% with both paraffins) were observed. There was no increase in the microsomal concentrations of RLvMc $P450_{55}$. Overall, the higher chlorinated paraffin produced a 25% increase in total microsomal P450, while the lower chlorinated paraffin produced only an 8% increase.

In another study by the same group of workers, and using the same protocol, a C_{10-13}, 59% chlorinated paraffin was included in the investigation (Nilsen *et al.*, 1981). Increases in total P450 of 18, 33 and 29% were noted with 49, 59 and 71% chlorinated paraffins respectively.

The activity of microsomal P450, epoxide hydrolase and glutathione S-transferase showed 13, 94-230 and 140% increases, respectively, in male rats which had been treated intraperitoneally with 1000 mg/kg/day C_{10-13}, 70% chlorinated paraffin for 5 days (Meijer *et al.*, 1981). The hydrolase and transferase are unlikely to be involved in the metabolism of chlorinated paraffins and the increase in activity of these enzymes is considered to be due to enzyme induction.

None of the above studies attempted to identify the metabolites of short chain chlorinated paraffins.

4.1.2.1.2 Studies in humans

The only information available on the toxicokinetics of short chain length chlorinated paraffins in humans is from an in vitro study using human skin (Scott, 1989, unpublished reference 108, 1985). A C_{10-13}, 56% chlorinated paraffin (Cereclor 56L) in a cutting oil was held in contact with 12 samples of human epidermal membrane for 56 hours. To facilitate detection of the absorbed material the sample was spiked with ^{14}C-labelled undecane which, according to the unpublished reference, was chlorinated to 58%. The source of skin was not reported. Steady state absorption was reached during 23 to 54 hours, when an extremely slow rate of absorption of 0.04 micrograms/cm^2/hour was determined. Less than 0.01% of the applied dose was absorbed during the 56 hours continuous skin contact.

4.1.2.1.3 Summary of toxicokinetics

In general there is very limited information on the toxicokinetics of short-chain chlorinated paraffins and there is no information with respect to differing chain length and degree of chlorination. No information is available on the toxicokinetics of these substances following inhalation or dermal exposure in animals. However the physicochemical properties and information on longer chain chlorinated paraffins, indicate that dermal absorption is predicted to be minimal.

With respect to oral exposure, only limited studies on short chain chlorinated paraffins are available. Significant absorption (up to about 60% of the administered dose) does occur following oral administration. One study indicated that absorption is greater for short chain chlorinated paraffins with lower chlorination states. Absorbed chlorinated paraffins have been shown to distribute preferentially to tissues of high metabolic activity and/or high rate of cell proliferation, following oral dosing. No attempts have been made to identify any metabolites of chlorinated paraffins, although cytochrome P450 oxidation to CO_2 has been demonstrated. Chlorinated paraffins and/or their metabolites are excreted via exhaled air, urine and faeces, with up to approximately 60% of the administered dose being excreted in the air and urine in 12 hours.

The only information on the toxicokinetics of short chain chlorinated paraffins in humans is from an in vitro study which demonstrated extremely poor absorption across skin samples.

4.1.2.2 Acute Toxicity

4.1.2.2.1 Studies in animals

Inhalation

No signs of toxicity were observed in rats exposed to 3300 mg/m^3 of a C_{12}, 59% chlorinated paraffin (Chlorowax 500C) for 1 hour (Howard *et al.*, 1975). The information was cited in an early review, as personal communication with industry. It has not been possible to locate the original data or find further information on this study.

The only other information available is a very brief unpublished report on a 50% chlorinated short chain paraffin (Cereclor 50HS); although it has not been possible to identify the specific carbon chain length (unpublished reference 55, 1974). Slight eye and nose irritation apparently occurred in rats exposed to 48 g/m^3 paraffin vapour for 1 hour. Recovery apparently occurred "soon" after exposure. No other details were given. Overall, little information is available on the effects of single inhalation exposure to short chain length chlorinated paraffins. There are indications that slight local irritant effects may occur following exposure to very high concentrations.

Oral

No deaths occurred in groups of ten rats treated by gavage with 0.8 to 13.6 g/kg C_{12} paraffin (60% chlorinated) (NTP, 1986). Animals were inactive and ataxic after dosing and showed diarrhoea for 2-6 days after dosing. However no clear evidence of other substance-related toxicity was observed. Macroscopic examination was not performed.

Several unpublished studies have been conducted on C_{10-13} paraffins which were 40 to 70% chlorinated (unpublished references 52, 1969; 55, 1974; 57, 1966; 59, 1968; 60, 1973; 61, 1965; 62, 1971; 64, 1974). In all of these studies groups of three male and three female rats were treated by gavage with a range of maximum doses of 4 to 13 g/kg chlorinated paraffin containing up to 5% epoxy stabilisers with various additives. Rats were observed for 7 days after treatment when macroscopic examinations were conducted. With the exception of one study, no deaths occurred. The death occurred in one rat treated with 13 g/kg 63% chlorinated paraffin (unpublished study 64, 1974). Signs of toxicity in the moribund and surviving

animals were also more extreme in this study and included coma, laboured breathing and tremors. Signs of toxicity in the majority of studies occurred with the lowest doses tested, from approximately 2 g/kg, and included piloerection, urinary incontinence and lethargy. Recovery, when reported, was usually complete by day 7. Macroscopic examination revealed "minimal signs of stress" in the spleen (with a 50% chlorinated paraffin, unpublished reference 59, 1968), blotchy or pale liver with slight fatty changes and inflamed stomach (with 69 and 40% chlorinated paraffin, unpublished references 61, 1965 and 57, 1966). Overall, the chlorinated paraffins tested were of very low oral toxicity following a single dose and the intensity and nature of those effects that were observed were independent of degree of chlorination.

Several or all of these studies have been summarised in a published paper which reported no deaths in rats following a single oral dose of up to 10 g/kg C_{10-13} chlorinated paraffins which were 41-50%, 51-60% or 61-70% chlorinated (Birtley *et al.*, 1980). Signs of toxicity were as above, although focal necrosis in the liver and cloudy swelling of some inner cortical cells of the kidney were also reported to have been noted 14 days after dosing. The severity of these effects was not discussed.

One unpublished study reported an LD_{50} value of 8.2 g/kg in rats. However the carbon chain length and degree of chlorination of the paraffin have not as yet been identified (unpublished reference 34, 1966).

No deaths occurred in groups of ten mice treated by gavage with 1.6 to 27 g/kg C_{12}, 60% chlorinated paraffin (NTP, 1986). Animals were inactive and ataxic after dosing and had ruffled fur on days 2-6 after treatment.

Dermal

In a briefly reported, but apparently well-conducted unpublished study, groups of three rats were treated with 2.5 ml/kg (approximately 2.8 g/kg) undiluted C_{10-13}, 52% chlorinated paraffin (unpublished reference 62, 1971). The substance was applied under an occlusive dressing for 24 hours. Slight erythema and slight desquamation were noted on days three and seven respectively, after the application, but no signs of systemic toxicity were observed.

An LD_{50} value of 10 ml/kg (approximately 13.5 g/kg) was reported in rabbits treated with a C_{12} chlorinated paraffin (Chlorowax 500C; 59% chlorinated). The information was cited in an early review as personal communication with industry; it has not been possible to locate the original data or find further information on this study (Howard *et al.*, 1975).

4.1.2.2.2 Studies in humans

No information is available.

4.1.2.2.3 Summary of single exposure studies

There is no information available on the effects of acute exposure to short chain length chlorinated paraffins in humans. However the limited information available from animal studies clearly demonstrates that short chain length chlorinated paraffins are of very low acute toxicity, with no toxicity occurring in rats following 1-hour exposure to a vapour or aerosol of

3300 mg/m^3 or with a dermal dose of 2.8 g/kg, and some signs of systemic toxicity with oral doses of up to 13 g/kg in rats and 27 g/kg in mice. A very high, unsubstantiated rabbit dermal LD_{50} of approximately 13 g/kg has been reported. The nature and degree of effects were independent of degree of chlorination.

4.1.2.3 Irritation

4.1.2.3.1 Studies in animals

Skin

Two unpublished but well reported skin irritation studies have been conducted according to modern standards. In one study, 0.5 ml of undiluted C_{10-13}, 59% chlorinated paraffin was applied, under a semi-occlusive dressing, to the shaven skin of three rabbits for four hours (unpublished reference, 48, 1986). The skin was examined for signs of irritation for up to 72 hours after the chlorinated paraffin had been removed. No signs of irritation occurred throughout the test.

In the second study, 0.5 ml of C_{10-13}, 70% chlorinated paraffin was tested as above (unpublished reference, 49, 1983). One rabbit showed clearly defined erythema (grade 2 on a 0-4 scale score) at 48 and 72 hours. The other two animals showed "slightly noticeable" erythema (grade 1). Very slight oedema (grade 1) was noted in two animals for up to 24 hours. By day 7, all signs of irritation were completely resolved.

Short chain length chlorinated paraffins were also investigated in several other unpublished studies, although these were not conducted according to modern protocols and were less well, and often only briefly reported. All studies were conducted using rats. In most studies, six 24 hour applications of 0.1 or 0.2 ml of chlorinated paraffin was applied to shaven skin, under occlusive dressings. Treatment periods were separated by 24-hour treatment-free periods. The samples of chlorinated paraffin were usually undiluted but contained low percentages of epoxy stabilisers and/or various additives.

Two studies investigated C_{10-13}, 70% chlorinated paraffin. In the more recent study, no signs of irritation were noted throughout the study following repeated application of the chlorinated paraffin which contained 0.1 or 2% benzoyl peroxide initiator (unpublished reference 64, 1974). In the earlier study the chlorinated paraffin contained 1 or 2% of an epoxised vegetable oil stabiliser with and without additives (0.1% oxalic acid or 0.05% benzotriazole) (unpublished reference 61, 1965). Very mild to mild desquamation was only noted following the applications of chlorinated paraffins which contained the additives. The reactions were described as occasional, transient and inconsistent. It was not stated how many applications were made before these reactions were seen.

Another two studies investigated the effects of three C_{10-13}, 63% chlorinated paraffins, containing up to 3% epoxy soya oil stabilisers or other unspecified additives (unpublished references 64, 1974, and 60, 1965). Erythema was usually noted following 2 to 4 applications of all three paraffins, although on one occasion erythema was noted in 1/3 animals after only one application. The severity of the reactions were not described. Desquamation was also noted following 3 or 4 applications and increased in severity with further treatments. In the

older study (with 0.7% epoxy carboxylate stabiliser) the desquamation was described as severe following the fourth application when the study was terminated.

Several studies have been conducted using C_{10-13} paraffins which were 48, 50, 52 or 55% chlorinated (unpublished references: 52, 1969; 58, 1967; 59, 1968; 62, 1971 & 64, 1974). In most studies the paraffins contained 0.2 or 2% epoxy stabilisers. In one study with 48 or 55% chlorinated paraffins, containing 0.2% epoxy octyl stearate stabiliser, no signs of irritation were noted throughout the study (unpublished reference, 52, 1969). In the other studies results were as above with mild or slight erythema to erythema and mild desquamation usually being noted following the second or third application. In one study, testing a 52% chlorinated paraffin with 2% epoxised octyl oleate stabiliser, erythema was noted following the first application, although the severity of the reactions were not discussed (unpublished reference, 59, 1968). It was noted in 4/5 of the studies that the reactions did not worsen following further applications, although in one study (testing a 52% chlorinated paraffin with unspecified additives), slight erythema, noted after the second application worsened to severe erythema with slight necrosis after the third, when the study was terminated (unpublished reference, 62, 1971).

An unspecified volume of a C_{10-13}, 40% chlorinated paraffin, containing 1% epoxy soya oil stabiliser, produced slight desquamation following the second application and mild erythema after the third (unpublished reference 57, 1966). This condition persisted throughout the remaining applications until the end of the study when small scattered ulcers developed.

Several or all of the above studies have been summarised in less detail in a published report (Birtley *et al.*, 1980).

Two unpublished studies in rats have also been conducted to investigate the potential for skin irritation of two C_{10-11} chlorinated paraffins which were 49 and 60% chlorinated (unpublished references 53, 1980; 54, 1982). The protocols were as above except that single application tests were also conducted. No signs of irritation were noted following a single application of the higher chlorinated paraffin, although slight desquamation was noted in 2/6 rats, three to six hours after the treatment with the lower chlorinated paraffin. As above, both chlorinated paraffins produced slight erythema and/or slight desquamation with repeated applications, although neither study stated when such signs were first observed.

Two studies have also been conducted using rabbits and were reported in very brief unpublished summaries (unpublished references 50, 1975; 51, 1975). A C_{10-13}, 61% chlorinated paraffin and a 50% chlorinated short chain paraffin (Cereclor 50 HS), of unspecified carbon chain length, produced mild or a mild to moderate skin irritation, following a single occlusive application to intact and abraded skin. It was stated that "varying degrees of erythema persisted for 72 hours". No other information was available.

In contrast to the above studies, another two unpublished studies report more severe findings. One of these studies is a very brief summary which states that repeated occlusive application with a 50% chlorinated short chain paraffin (Cereclor 50 HS), of unspecified carbon chain length, resulted in moderately severe irritation with erythema, desquamation, thickening, cracking and scabbing of the skin being observed in rats (unpublished reference 55, 1974). The second study reported slight erythema and desquamation after one twenty four-hour application of the test substance applied under occlusive dressings (unpublished reference, 54,

1982). Following the third application, moderately severe desquamation, intracutaneous oedema with "extensive scratching" were reported and the study was terminated. However it was unclear if the test substance was a chlorinated paraffin or a solvent used in chlorinated paraffin formulations. Overall, due to uncertainties in the identification of the test substances and considering the weight of evidence, neither of these studies is considered to be reliable when assessing the skin irritation potential of the chlorinated paraffins under consideration.

Eye

The eye irritation potential of C_{10-13}, 40 to 63% chlorinated paraffins has been reported in a published study (Birtley *et al.*, 1980), although more detailed information was obtained from unpublished reports of the same studies. Three different C_{10-13} paraffins which were 63% chlorinated and which contained either 2.5 or 2% of two different additives or 0.7% of an epoxy stabiliser were tested in 2 studies (unpublished references 64, 1974; 62, 1973). Both studies were conducted according to modern protocols with either 0.1 ml or "one drop" of the paraffin being instilled into one conjunctival sac of groups of three rabbits. Similar results were reported for all three formulations: "practically no" initial pain (2 on a 6 point scale) was noted. Slight irritation (3 on an 8 point scale), evidenced by redness and chemosis (only noted in the formulation containing the epoxy stabiliser) of the conjunctiva with some discharge, lasted for 24 hours. One drop of 52% or 40% chlorinated paraffins, containing unspecified additives or 1% epoxy stabiliser, were also tested as above (unpublished references 62, 1971, 57, 1966). With the 52% chlorinated paraffin, slight, immediate irritation was followed by slight redness of the conjunctiva which, as above, lasted for 24 hours. With the 40% chlorinated paraffin mild congestion was noted at 1 hour with no effects being seen at 24 hours.

A single application of a C_{12}, 59% chlorinated paraffin (Chlorowax 500C) apparently produced a mild redness in the eyes of 4/6 rabbits (Howard *et al.*, 1975). However the information was cited in an early review as personal communication with industry. It has not been possible to locate the original data or find further information on this study.

Similar results were obtained with another two chlorinated paraffins (Cereclor 50 HS, Hoechst 64 flussig), although the carbon chain length and/or percentage chlorination of these short chain paraffins has not been identified (unpublished references 55, 1974 & 43, 1966). Although little information was provided, the earlier study apparently indicated the severity of the reactions observed did not increase with up to 5 daily instillations of the chlorinated paraffin.

4.1.2.3.2 Studies in humans

C_{10-13}, 50 or 63% chlorinated paraffins were applied, under occlusive dressings, to the upper, outer arm of 26 volunteers (unpublished reference 113, 1975). After 24 hours the applications were removed and 1 hour later skin reactions were examined by two independent assessors. A second application was made and reactions assessed after a further 24 hours contact. Mild erythema and dryness (average scores read at the 24 and 50 hour time points, of less than 2 and 1 respectively on a 4-point scale) were recorded, which were comparable to scores in a liquid paraffin control group.

A review reported industrial information obtained by personal communication that a C_{12} chlorinated paraffin (59% chlorinated) did not produce local irritation when applied to the skin of 200 male and female subjects (Howard *et al.*, 1975). The period of exposure and amount of paraffin applied was apparently not known.
No information was available on the potential to produce eye irritation.

4.1.2.3.3 Summary of irritation

Limited information in humans indicates that short chain length chlorinated paraffins do not cause skin irritation. This view is supported by the information available from studies in animals. Two well-conducted skin irritation studies in animals indicate that C_{10-13}, 59 and 70% chlorinated paraffins have the potential to produce, at most, minimal skin irritation. Several unpublished studies indicate that more pronounced irritation can occur following repeated application of short chain length chlorinated paraffins. This has been demonstrated to be independent of chain length and degree of chlorination and is probably due to a defatting action.

There is no information from humans on the potential for chlorinated paraffins to cause eye irritation. However the information from animals indicates that C_{10-13}, 40 to 63% chlorinated paraffins produce only mild eye irritation in rabbits.

4.1.2.4 Corrosivity

The studies in animals and humans in 4.1.2.3 indicate that short-chain chlorinated paraffins are not corrosive to the skin or eyes.

4.1.2.5 Sensitisation

4.1.2.5.1 Studies in animals

Three unpublished studies are available which have been well-conducted according to modern protocols and using suitable induction regimes.

One study assessed the potential of a C_{10-13} paraffin, which is assumed to be approximately 50% chlorinated, to produce skin sensitisation in guinea pigs using the Magnusson and Kligman method (unpublished reference, 67, 1988). The paraffin used contained 1% stabiliser (Edenol B 74). When challenged with undiluted chlorinated paraffin 2/20 test animals showed marked diffuse redness at 24 hours after challenge and 1/20 showed slight redness and dryness at 24 hours. When the same animals were challenged 1 week later with 50% chlorinated paraffin, no skin reactions were observed. No skin reactions were observed in the control group. The results show that the paraffin tested did not induce skin sensitisation in this study.

The other two studies also used the Magnusson and Kligman method to assess the skin sensitisation potential of a C_{10-13}, 56% chlorinated paraffin in guinea pigs. The chlorinated paraffin used in the earlier study contained 1% epoxide stabiliser (Edenol D 81) and 1% tris-nonylphenyl phosphite (unpublished reference 66, 1983). When challenged with undiluted chlorinated paraffin 1/20 test animals showed "hardly perceptible" erythema at 24 hours after challenge and 1/20 test and 1/10 control animals showed "clearly defined" erythema and

"slight" oedema at 72 hours. The results therefore show that the paraffin tested did not induce skin sensitisation in this study.

The C_{10-13}, 56% chlorinated paraffin tested in the third study contained 1% of a different epoxide stabiliser (Rutapox CY 160) and 1% tris-nonylphenyl phosphite (unpublished reference 65, 1984). When challenged with undiluted chlorinated paraffin 5/20 test animals showed "clearly defined" erythema and another two showed "slight, hardly perceptible" erythema. None of the control animals showed any evidence of a skin reaction. A second challenge was performed two weeks after the first. On this occasion 4/20 test animals showed "clearly defined" erythema and another four showed "slight, hardly perceptible" erythema and slight oedema. The authors concluded that the substance tested was a sensitiser. However, taking into account the fact that less than 30% of the test group showed a clear reaction and the possibility that the epoxide stabiliser was responsible for producing the sensitisation reactions, this study is not considered to provide sufficient evidence that the C_{10-13}, 56% chlorinated paraffin tested should be classified as a skin sensitiser.

Another three briefly reported unpublished studies have been conducted which used similar but not modern protocols. In the first, undiluted C_{10-13}, 52% chlorinated paraffin was applied to the ears of 6 guinea-pigs on three successive days (unpublished reference 62, 1971). Slight erythema was noted when challenged four days later with undiluted paraffin applied to the animal flanks. However it was not stated how many animals showed such a reaction. It was stated that four control animals also showed slight erythema at challenge. Despite the lack of detail it is clear that the paraffin tested did not elicit a sensitisation response in this study. The authors considered that the paraffin was "irritant but not a strong sensitiser". This phrase was used in another unpublished summary when a 50% chlorinated paraffin was tested, apparently using the same protocol (unpublished reference 55, 1974). No details were given, including the carbon chain length of the short chain paraffin (Cereclor 50HS). The only information given was the conclusion which stated that the substance tested was "not a strong sensitiser". In view of use of this phrase it is impossible to draw any conclusions from this study with respect to skin sensitising potential.

The third unpublished study to use the ear/flank protocol apparently found no signs of erythema at challenge with up to 10 % C_{10-13}, 50% chlorinated paraffin (unpublished reference 59, 1968). However there is no information provided in the report to indicate if the challenge concentration was sufficient to stringently test for skin sensitisation. Therefore no conclusions can be drawn from this study.

There is no information available on the potential for short chain length chlorinated paraffins to produce respiratory sensitisation in animals.

4.1.2.5.2 Studies in humans

There are claims in a review cited as a personal communication that allergic reactions were not noted in the subjects dermally treated with the C_{12} chlorinated paraffin (59% chlorinated) (Howard *et al.*, 1975). No further details were given.

In an early study on cutting fluid coolants, 134 non-exposed employees and 75 exposed employees were patch tested with various constituents of the cutting fluids including chlorinated paraffins (Menter *et al.*, 1975). No positive reactions were obtained with any of

the constituents although the authors themselves suggested that the tests were not sufficiently stringent.

A more recent study reported that positive skin reactions to chlorinated paraffin constituents, were obtained in patch tests conducted on 4 employees suffering from scaly eczema, who had had occupational exposure to cutting oils (English *et al.*, 1986). However the paper concluded that the reaction was due to an additive in the cutting oil, rather than to the chlorinated paraffin.

There is no information available on respiratory sensitisation.

4.1.2.5.3 Summary of sensitisation

No conclusions can be drawn from the limited information available on skin sensitisation in humans. However the absence of reports on skin sensitisation, despite the widespread use of these substances, suggests that short chain length chlorinated paraffins do not have the potential to be skin sensitisers. This conclusion is supported with the negative results of two well-conducted skin sensitisation studies in animals which tested C_{10-13}, 50 and 56% chlorinated paraffin. There are no data concerning the effects of varying chain length or higher or lower chlorination states, although one would not predict an effect on sensitisation potential.

No direct information is available from studies in humans or animals on respiratory sensitisation. However, in view of the widespread use of these industrially important substances, the absence of any reports suggests that short chain length chlorinated paraffins are not respiratory sensitisers. Their unreactive nature and the lack of skin sensitisation potential lends added support to this view.

4.1.2.6 Repeated dose toxicity

4.1.2.6.1 Studies in animals

Inhalation

No studies are available.

Oral

Studies in rats

Groups of five rats of each sex were administered 0, 469, 938, 1875, 3750 or 7500 mg/kg/day C_{12}, 60% chlorinated paraffin by gavage, on 12 days over a 16 day period (NTP, 1986). Three deaths occurred in top-dose animals. All top dose animals showed diarrhoea with males and females showing a 22% and 14% inhibition in body weight gain, respectively. Male rats treated with 3750 mg/kg/day showed a 15% inhibition in body weight gain. Enlarged livers were observed in 3-5 animals in every dose group apart from the females treated with 469 mg/kg/day; however the degree of enlargement was not discussed. Histological examinations were not conducted. The liver enlargements are likely to be due to a physiological response to the demand for xenobiotic metabolism or peroxisome proliferation,

neither of which are considered to be of adverse health significance to humans (see Section on Studies on Mechanisms of Toxicity). Other signs of toxicity were noted at doses greater than 1875 mg/kg/day.

In a briefly reported, unpublished study, groups of 10 male rats were administered 0 or approximately 5000 mg/kg/day and 10 females, 0 or approximately 2500 mg/kg/day C_{10-13}, 52% chlorinated paraffin, by gavage, on 14 consecutive days (unpublished reference 62, 1971). All treated animals showed slight piloerection during the experiment and females were "slightly" incontinent. One treated male died after nine doses. Urinalysis showed no changes compared to controls. Evidence of slight anaemia and decreased blood clotting capability were noted in treated males and females. Animals killed 24 hours after the final treatment showed marked hepatocyte enlargement, apparently associated with proliferation of smooth endoplasmic reticulum. An unspecified number of animals, killed 7 days after the final treatment, showed similar but less marked liver changes. Three males and one female also showed slightly increased splenic haemopoiesis. No further details were given.

Groups of five male and five female rats were treated daily, by gavage with 0, 30, 100, 300, 1000 or 3000 mg/kg/day C_{10-12}, 58% chlorinated paraffin, for 14 days (unpublished reference 75, 1981). No treatment-related deaths occurred. Laboured breathing, decreased motor activity, excessive lacrimation and staining around nose, mouth and anogenital region were noted in males and females treated with 3000 mg/kg/day. Laboured breathing was also noted in one animal treated with 1000 mg/kg/day, although this was not considered to be of toxicological significance. Top-dose animals showed reductions in body weight gain (males: 15%, females: 20%) and food consumption (males: 13%, females: 20%), although the decrease in body weight gain was only statistically significant for the females. Haematology and clinical chemistry were not performed. At the end of the study, dose-related, statistically significant increases in absolute and relative liver weights were noted in males and females treated with 100 mg/kg/day (males only: 20% increase), 300 mg/kg/day (20-40% increases), 1000 mg/kg/day (50-80% increases) and 3000 mg/kg/day (60-150% increases). Top dose animals also showed a reduction in relative and absolute thymus (decreases of at least 50%) and ovary (decreases of 35% and greater) weights. The thyroid was not examined. Diffuse, mild hepatocellular hypertrophy was noted with 1000 mg/kg/day and above, and a dose-related increase in hepatic microsomal enzyme activity (aminopyrine demethylase) was noted in females treated with 300 mg/kg/day and above. An increase in microsomal protein content was also seen in top-dose females. Changes in liver histopathology and metabolic enzyme activity appear to reflect xenobiotic metabolism and peroxisome proliferation. Other signs of toxicity were noted at doses greater than 1000 mg/kg/day.

The C_{10-12}, 58% chlorinated paraffin was also administered to groups of 5 male and 5 female rats for 14 days at 0, 900, 2700, 9100 or 27300 ppm in the diet (unpublished reference 72, 1983). These dietary concentrations were calculated to correspond to daily doses of 0, 100, 300, 1000 and 3000 mg/kg/day. No deaths occurred and no clinical signs of toxicity were noted throughout the treatment period. A marked reduction in body weight and food consumption (approximately 50% by day 14) were observed in top dose animals, particularly during the first week of the experiment. Haematological and clinical chemistry studies apparently were not conducted. Statistically significant increases in absolute and relative liver weights were noted with all treatments (100 mg/kg/day: approximately 20%, 300 mg/kg/day: 50%, 1000 mg/kg/day: 110%, 3000 mg/kg/day: 150-240%). Increases in the incidence and degree of hepatocellular hypertrophy were also noted in all treatment groups. Liver enzyme

studies also showed a dose-related increase in activity or microsomal levels for all treatment groups with statistically significant increases in protein content, aminopyrine demethylase and cytochrome P450 occurring in females with 300 mg/kg/day and above. Male rats also showed a statistically significant increase in cytochrome P450 with 1000 mg/kg/day and above. Myocardial atrophy was noted in animals treated with 1000 and 3000 mg/kg/day, although this was considered by the authors to be associated with weight loss, at least in the top dose animals. Also this effect was not reported in any of the other studies and is therefore considered not to be of toxicological significance in relation to chlorinated paraffins. Atrophy of the spleen, thymus and testes in top dose animals were also considered to be secondary to reduced food consumption. The thyroid was not examined. As above, changes in liver histopathology and increases in enzyme activity appear to reflect xenobiotic metabolism and peroxisome proliferation. Other signs of toxicity were noted at doses greater than 1000 mg/kg/day.

In a 13-week study groups of ten rats of each sex were treated with 0, 313, 625, 1250, 2500 or 5000 mg/kg/day C_{12}, 60% chlorinated paraffin, once daily by gavage, 5 days/week (NTP, 1986). No deaths occurred. Males treated with 5,000 and 2,500 mg/kg/day showed a slight inhibition in body weight gain (12 to 11% reductions). Haematology and clinical chemistry does not appear to have been conducted. A dose-related increase (approximately, 25, 38, 55, 100 and 100% with 313, 625, 1250, 2500 and 3000 mg/kg/day respectively) in relative liver weights was observed for males and females. The increase was statistically significant at all dose levels. Hepatocellular hypertrophy was noted in all top-dose animals and in 1 rat treated with 2500 mg/kg/day. Nephropathy was also noted in all top dose males and in 3 top dose females but was also noted in 8/10 control males, although the severity of the effect was greater in the chlorinated paraffin-treated male animals. Interpretation of the kidney findings is difficult. There were apparently no changes in the thyroid, thymus, heart, spleen, or any other organ examined. The increase in liver weight reflects xenobiotic metabolism and peroxisome proliferation. Other signs of toxicity were noted at doses greater than 1250 mg/kg/day.

In a well-conducted unpublished study, which has been summarised in a published review (Serrone *et al.*, 1987), groups of male and female rats were treated with 0, 10, 100 or 625 mg/kg/day $C_{10\text{-}12}$, 58% chlorinated paraffins in the diet for 90 days (unpublished reference 73, 1984). No deaths occurred and no clinical signs of toxicity were observed throughout the study. Top dose males showed a slight reduction in body weight gain (9% less than controls at the end of the study). A decrease in average daily water consumption was observed in top dose males and females (11 and 20% respectively) with corresponding reductions in urine volume and increases in urinary specific gravity. Statistically significant increases in urinary total protein (up to 13%) and cholesterol (up to 54%) in top dose, and glucose levels (up to 20%) in top and mid dose animals were also observed. No changes were observed in haematological parameters. Slight dose-related increases in liver protein content were noted in the treated males with corresponding increases in cytochrome P450 and aminopyrine demethylase, particularly in top-dose males. No changes were observed in enzyme levels or activities in the females. Statistically significant increases in relative and absolute liver (20% and 140%) and kidney weights (10 and 30%) were noted with 100 and 625 mg/kg/day, respectively, and relative and absolute thyroid weights (approximately 32%), with 625 mg/kg/day. Microscopic findings were noted in the top dose males and females and included hepatocellular hypertrophy, mild nephritis (males only), brown pigmentation in the renal tubules (females only) and thyroid hypertrophy. These liver, kidney and thyroid changes were also noted in mid-dose males. The changes in the kidney are of doubtful toxicological

significance and as above liver weight, histopathology and enzyme changes reflect xenobiotic metabolism and peroxisome proliferation and are not considered to be of toxicological significance to humans. Similarly effects seen in the thyroid are not considered to be relevant to humans (see Section on Studies on Mechanisms on Toxicity). Other signs of toxicity were noted at doses greater than 100 mg/kg.

The above review also briefly reports a study in which groups of male and female rats were treated with 0, 10, 100 or 625 mg/kg/day C_{10-12}, 58% chlorinated paraffins by gavage for 90 days (Serrone *et al.*, 1987). Findings are similar to the dietary study, that is, no deaths occurred and no clinical signs of toxicity were observed throughout the study. Top dose males showed a slight reduction in body weight gain and changes in water consumption were noted. Increases in the liver and kidney weights with mid- and high-dose rats and an increase in thyroid weight with the high-dose were reported. No quantitative details were reported for any of these changes. Microscopic findings included hepatocellular hypertrophy in mid and high-dose rats, and thyroid hypertrophy and hyperplasia with the mid- (males only) and high dose. High incidences of trace to mild nephritis were also observed in the kidneys of males at the mid- and high-doses and increased pigmentation in the renal tubules was noted in high-dose females. No further details were given.

A poorly conducted 2-year study (summarised in 4.1.2.8) identified the liver, kidney, thyroid and stomach to be the target organs when rats were treated by gavage with 312 or 625 mg/kg/day C_{12}, 60% chlorinated paraffin for 6 or 12 months or two years (NTP, 1986).

Studies in mice

Groups of five mice of each sex were administered 0, 938, 1875, 3750, 7500 or 15000 mg/kg C_{12} chlorinated paraffin (60% chlorinated) by gavage, on 12 days over a 16 day period (NTP, 1986). Due to the large volume of material to be used, the top two doses were administered in two treatments, 5 hours apart. All mice that received 3750, 7500 and 15000 mg/kg/day and 6/10 receiving 1875 mg/kg/day died before the end of the study. Diarrhoea was noted in all chlorinated paraffin-treated animals apart from the lowest-dose females. Livers appeared enlarged in treated animals which survived until the end of the study. Histological examinations were not conducted.

This study was followed with a 13-week study (NTP, 1986). Groups of ten mice of each sex were treated with 0, 125, 250, 500, 1000, or 2000 mg/kg/day in corn oil once daily by gavage, 5 days/week for 13 weeks. No substance-related deaths occurred although several deaths occurred in each group due to gavage errors. Top dose males showed a slight inhibition (13% reduction) in body weight gain by the end of the study. Relative liver weight showed dose related increases (approximately 17, 40, 80 and 160% with 250, 500, 1000 and 2000 mg/kg/day) which were statistically significant at doses of 250 mg/kg/day and above. The incidence of hepatocellular hypertrophy, observed at 250 mg/kg/day and above, also increased with dose, although the degree of these effects was not reported. Focal hepatocellular necrosis was observed with 500 mg/kg/day and above, although severity was not discussed. There were apparently no changes in the thyroid. The predominant processes underlying the liver effects are likely to be xenobiotic metabolism and peroxisome proliferation. Other signs of toxicity, were observed at doses greater than 1000 mg/kg/day.

A 2-year study (summarised in 4.1.2.8) identified the liver, kidney and thyroid to be the target organs when mice were treated by gavage with 125 or 250 mg/kg/day C_{12}, 60% chlorinated paraffin for two years (NTP, 1986).

Dermal

No standard dermal studies are available. In a poorly reported skin irritation study, no evidence of systemic toxicity was observed in rats which had been treated on alternate days with up to six, 24-hour applications of 0.1 ml of a chlorinated paraffin (41-50%, 51-60% or 61-70% chlorinated) to the shorn backs, under occlusive dressings (Birtley *et al.*, 1980). The number of animals examined and the number of exposures were unclear.

4.1.2.6.2 Studies in humans

Although widely used in various applications there is no information available on the effects of short chain length chlorinated paraffins alone.

4.1.2.6.3 Studies on mechanisms of toxicity

A number of studies are available which have been designed to investigate the possible mechanisms of the toxic effects observed in animals, in order to establish their relevance to humans.

Studies in rats

Male rats were assessed for effects in the liver following treatment by gavage with 0, 10, 50, 100, 250, 500 or 1000 mg/kg/day C_{10-13}, 58 or 56% chlorinated paraffin for 14 days (Wyatt *et al.*, 1993). Livers were removed, weighed, homogenised and an assay was performed for peroxisomal fatty acid *B*-oxidation, which is a marker for peroxisomal proliferation. With the 58% chlorinated paraffin, both absolute and relative liver weights showed a dose-related increase (from 28 to 60%) with increases being statistically significant with 250 mg/kg/day and above. Oxidase activity also showed a statistically significant increase with 250 mg/kg/day and above, reaching an almost 3-fold increase with the top-dose. With the 56% chlorinated paraffin, absolute and relative liver weights showed a dose-related increase (from 20 to 77%) with increases being statistically significant with 100 mg/kg/day and above. Oxidase activity again showed a statistically significant increase with 250 mg/kg/day and above, reaching an almost 3-fold increase with the top-dose.

Top-dose animals in this study were also assessed for effects on the thyroid, by analysing blood samples for thyroid stimulating hormone (TSH), and total and free T_3 and T_4. Uridine diphosphate glucuronosyl (UDPG) -transferase activity, a liver enzyme involved in the excretion of T_4, was measured in liver microsomes. With both chlorinated paraffins, free and total T_4 levels were decreased by 30-40% and 2-fold increases were noted in liver microsomal UDPG-transferase activity and plasma TSH levels. There were no changes in T_3 levels.

In a similar study, male and female rats were treated by gavage with 0, 313, 625 or 1000 mg/kg/day 58% chlorinated paraffin for 0, 15, 29, 57 or 91 days (Elcombe *et al.*, 1994). The liver, thyroid and kidney were examined histologically and as above, blood samples were analysed for total

and free T_4 and TSH and liver homogenates for UDPG-transferase activity. Seven days before sacrifice on days 29 and 91, animals were subcutaneously implanted with minipumps containing bromodeoxyuridine. Statistically significant increases in relative liver weight, of approximately 50 and 75% were noted with doses of 313 and 625 mg/kg/day, respectively. These increases were noted at the first kill (15 days) and did not continue to increase further at the later sacrifice times (absolute liver weights were not reported). Peroxisomal *B*-oxidation was also noted to show a dose-related and statistically significant increase with doses of 313 and 625 mg/kg/day from day 15, and like the relative liver weights, did not continue to increase at later sacrifice times. Liver weights and *B*-oxidation were apparently not recorded in the top-dose animals. It was claimed that hepatic peroxisome proliferation was also evidenced ultrastructurally, although no details were presented.

UDPG-transferase activity also showed a dose-related and statistically significant increase of at least 150%, with doses of 313 and 625 mg/kg/day from day 15. As with the liver weights and *B*-oxidation, the UDPG-transferase activity did not continue to increase further at the later sacrifice times. Statistically significant decreases (up to approximately 50%) in total and free plasma T_4 were noted with 1000 mg/kg/day, at all time points. Decreases in total and free plasma T_4 were also noted with doses of 625 and 313 mg/kg/day, although these decreases were not always statistically significant (generally only significant on days 15 and 57). With 1000 mg/kg/day, "marked" increases in plasma TSH were observed from day 8 to 15, with non-statistically significant increases being noted at the later time points. Thyroid follicular cell hypertrophy was also apparently noted with 313 mg/kg/day and above at all time points and hyperplasia at days 56 and 91, although no further details were given. A statistically significant increase in replicative DNA synthesis in thyroid cells was also noted on day 91 with 313 mg/kg/day and above.

Renal tubular eosinophilia, increasing in intensity with time, was noted from day 15 in male rats treated with 313 and 625 mg/kg. From day 29 increasing numbers of males showed initially focal and then multifocal areas of basophilia. No kidney effects were noted in the female rats. Hyaline droplet formation was not confirmed by immunocytochemical techniques (personal communication, ICI, 1995), however the response was indicative of this male rat specific phenomenum.

Male and female rats were treated by gavage with 0 or 1000 mg/kg/day C_{10-13}, 56 or 58% chlorinated paraffins for 14 days (Elcombe *et al.*, 1995). Microscopic examination of the liver showed hepatocyte hypertrophy and proliferation of peroxisomes and smooth endoplasmic reticulum. Morphometric analysis confirmed "marked" peroxisome proliferation with both chlorinated paraffins, with statistically significant increases being noted in peroxisome volume density. Absolute liver weights were not reported. Relative liver weights and total cytochrome P450 levels showed at least 2-fold increases compare to controls and peroxisomal *B*-oxidation showed 3 to 8-fold increases with the effect being greater in males.

Another two studies investigated the early changes in the liver and thyroid when male and female rats were treated by gavage with 0 or 1000 mg/kg/day C_{10-13}, 58% chlorinated paraffin for 1, 2, 4, 7, 15 or 28 days (ICI Draft paper 1 and 2). Histopathological examination revealed hepatocyte eosinophilia on day 1, which was followed by centrilobular and pan-lobular hypertrophy which is taken to be indicative of an increase in the number of peroxisomes. The first biochemical change to be detected was a statistically significant increase in hepatic peroxisomal *B*-oxidation on day 2 in the males and day 4 in the females, which reached a

maximum by days 7 and 15 in the males (approximately 3-fold increase) and females (approximately 9-fold increase) respectively. This was accompanied by a progressive increase in absolute and relative liver weight which was small but statistically significant from day 2 in the males and day 4 in the females (increases of approximately 10% on day 2, 60% on day 4). Thyroid follicular cell hypertrophy was noted on day 4 in both sexes and increased with time. In the males liver UDPG-transferase activity was consistently higher than control values from day 2 onwards, although not statistically significant until day 4. The activity in the females showed small non-statistically significant increases on days 4 to 15. Free and total T_4 was reduced by up to approximately 50% in both sexes throughout the study from day 1. Reductions of approximately 30% in plasma concentrations of free and total T_3 were seen in the males, during the first 4 days of the study. T_3 levels were not measured in the females. The changes in the T_4 levels noted to occur before changes in UDPG-transferase activity, may be a reflection of the sensitivity of the respective assays used. TSH levels were elevated in males and females throughout the study, although the increases were not always statistically significant.

In a poorly reported intraperitoneal study, rats were administered 0 or 1000 mg/kg/day C_{10-13}, 49, 59 or 71% chlorinated paraffin on days 1 and 4 or days 1, 4 and 6 (Nilsen *et al.*, 1981). With all three chlorinated paraffins, an increase in the occurrence and size of hepatocellular cytoplasmic lipid droplets was noted. The 49% chlorinated paraffin also produced a 20 to 30% increase in the size of the hepatocytes on days 5 and 7, a proliferation of smooth endoplasmic reticulum, a "moderate" increase in the numbers of mitochondria and an increase in the size and number of peroxisomes. It is not clear whether these effects, including the peroxisome proliferation, were not noted with the higher chlorinated paraffins or if such effects were not investigated.

Studies in mice

Male mice were assessed for effects in the liver following treatment by gavage with 0, 10, 50, 100, 250, 500 or 1000 mg/kg/day C_{10-13}, 58 or 56% chlorinated paraffin for 14 days (Wyatt *et al.*, 1993). Livers were removed, weighed, homogenised and assays performed for peroxisomal fatty acid *B*-oxidation. With the 58% chlorinated paraffin, absolute and relative liver weights showed a dose-related increase, with increases (from 23 to 89%) being statistically significant from 500 and 250 mg/kg/day, respectively. The oxidase activity showed a statistically significant increase with 250 mg/kg/day and above, although a non-statistically significant increase of 67% above the control value was noted with 100 mg/kg/day. Increases in oxidase activity reached a 7-fold increase with the top dose. With the 56% chlorinated paraffin, absolute and relative liver weights showed a dose-related increase, with increases (from 26 to 85%) being statistically significant with 100 mg/kg/day and above. Oxidase activity showed a statistically significant increase with 250 mg/kg/day and above, reaching a 10-fold increase with the top-dose.

Male and female mice were treated by gavage with 0 or 1000 mg/kg/day C_{10-13}, 56 or 58% chlorinated paraffins for 14 days (Elcombe *et al.*, 1995). Microscopic examination of the liver showed hepatocyte hypertrophy and smooth endoplamsic reticulum and peroxisome proliferation. Morphometric analysis confirmed "marked" peroxisome proliferation with both chlorinated paraffins, with statistically significant increases being noted in peroxisome volume density. Compared to controls, relative liver weights and total cytochrome P450 levels were

increased by 40 to 80% respectively. Absolute liver weights were not reported. Peroxisomal *B*-oxidation showed 4 to 6-fold increases.

Studies in guinea-pigs

Male guinea-pigs were treated by gavage with 0, 500 or 1000 mg/kg/day 58% chlorinated paraffin for 14 days (Elcombe *et al.*, 1994). The liver and thyroid were examined histologically and as above, blood samples subjected to analysis for total and free thyroxine and TSH. No effects on thyroid homeostasis (that is, changes in thyroid hormones) were seen and no evidence of hepatic peroxisome proliferation or renal changes were noted. Liver weights were not reported.

Male guinea-pigs were treated by gavage with 0 or 1000 mg/kg/day C_{10-13}, 56 or 58% chlorinated paraffins for 14 days (Elcombe *et al.*, 1995). No treatment-related changes were observed by electron microscopy of the liver and morphometry showed no evidence of peroxisome proliferation. Absolute liver weights were not reported. Relative liver weights showed increases of 36 to 50%; however no changes in total cytochrome P450 levels or peroxisomal *B*-oxidation were noted.

In a briefly reported study, guinea pigs were treated by gavage with 0, 500 or 1000 mg/kg/day C_{10-13}, 58% chlorinated paraffin for 14 days (ICI Draft paper 3). This study formed part of the above study (personal communication, ICI, 1995). A statistically significant decrease in body weight gain of approximately 12% with both doses was noted at the end of the study. No change was noted in absolute liver weight although there was a statistically significant increase in relative liver weight (of approximately 18% with both doses). A dose-dependent loss of glycogen was detected in the livers of treated animals. There were no other histological changes in the liver, thyroid or kidney. Nor were there any changes in plasma levels of T_3, T_4 or TSH.

<u>Overall assessment of mechanistic studies</u>

The results of these mechanistic studies indicate that short chain length chlorinated paraffins produce peroxisome proliferation in rats and mice which probably underlies the liver damage observed in some prolonged exposure studies. Peroxisome proliferation has been evidenced by microscopy, morphometric analysis and marker enzyme activity. Fourteen-day studies in rats and mice have indicated a no effect level for peroxisome proliferation of 100 mg/kg/day. Although the threshold for the effect is the same in rats and mice, mice show a much greater peroxisome proliferation with higher doses. Peroxisome proliferation was not observed in studies in guinea pigs which are known to be insensitive to such an effect. Similarly, humans are also recognised to be insensitive to the effects of peroxisomal proliferating agents (Bentley *et al.*, 1993, Ashby *et al.*, 1994). Consequently, it can be concluded that the liver damage observed in studies in rats and mice is not relevant to human health. The only effect on the liver at doses below those producing peroxisome proliferation is small but statistically significant increases in liver weight. Such increases probably reflect increases in xenobiotic metabolism and are not considered to be of toxicological significance.

Short chain length chlorinated paraffins also cause effects in the thyroid in rats and mice but not the guinea-pig. From the hepatic enzyme and hormone studies considered above, these effects appear to be due to stimulation of the thyroid via negative feed back mechanisms. The

chain of events starts with a liver effect, namely an increase in UDPG-transferase. The UDPG transferase activity results in an increase in excretion of T_4 and a resultant decrease in plasma T_4 levels. The decrease in plasma T_4 produces an increase in the release of pituitary TSH which in turn triggers a compensatory increase in the production of T_4 by the thyroid. Since T_4 is continually excreted and the thyroid stimulated, the increased activity in the thyroid eventually leads to hypertrophy, hyperplasia and as a consequence, a tendency to develop thyroid tumours.

It is possible that the increase in UDPG-transferase activity is a direct consequence of peroxisome proliferation or alternatively that it is triggered by the same mechanism as that producing peroxisome proliferation. However, from the evidence available, it is not clear whether or not the two are linked, although neither peroxisome proliferation nor thyroid effects (including changes in plasma T_4 and TSH) were seen in studies in guinea pigs at high doses of 1000 mg/kg/day.

In addition, it has been suggested that rodents are particularly susceptible to changes in the thyroid due to the absence of a T_4-binding globulin which is present in humans and which has a very high affinity for T_4 (Dohler *et al.*, 1979). Other binding proteins are present in rodents, however their binding efficiency is considerably less than T_4-binding globulin. In rodents, in the absence of T_4-binding globulin, more free T_4 is available for metabolism and thus excretion from the body. This would be potentiated by increased UDPG-transferase activity. Hence humans are likely to be less susceptible to changes in plasma levels of T_4 and to the subsequent thyroid stimulation, seen in rats and mice in the studies above. Overall, taking into account the probable mechanisms indicated above, the apparent association with the hepatic effects observed and the difference in T_4 binding between humans and rats, the effects seen in the thyroid in rats and mice are considered unlikely to be relevant to human health.

4.1.2.6.4 Summary of repeated exposure studies

There is no information available on the effects of repeated exposure to short chain length chlorinated paraffins in humans. No standard inhalation or dermal studies in animals are available, although short chain length chlorinated paraffins are likely to exert minimal systemic toxicity following dermal exposure. All available oral studies in animals were conducted using 52 to 60% chlorinated short chain length paraffins, and therefore it is not possible to observe directly from data whether different degrees of chlorination would alter the toxicity.

The liver and thyroid were identified as target organs in the oral studies in rats and mice. Small increases in liver weight are likely to be due to a response to xenobiotic metabolism which is not of toxicological significance. Larger increases in liver weight and hepatocelluar hypertrophy have been shown to be a reflection of peroxisome proliferation. Humans are not susceptible to peroxisome proliferation and hence the liver effects are considered not to be relevant to human health (Bentley *et al.*, 1993, Ashby *et al.*, 1994). Increases in thyroid weight and follicular cell hypertrophy have been shown to be caused by stimulation of the thyroid via a negative feedback mechanism, initiated by increased excretion and plasma depletion of T_4. The depletion of T_4 is a result of increased liver enzyme activity (UDPG-transferase) which may be related to peroxisome proliferation. Also humans and rodents show different T_4-globulin binding characteristics which results in humans being less susceptible to plasma T_4 depletion

and hence to thyroid stimulation. Overall the thyroid effects seen in rats and mice are considered unlikely to be relevant to human health.

Other signs of toxicity, such as reductions in body weight gain and increases in kidney weight, were observed in several 14- and 90-day studies in rats with doses greater than 100 mg/kg/day. In mice general signs of toxicity were observed in a 90-day study at doses greater than 1000 mg/kg/day. Therefore NOAELs, for effects which are considered to be relevant to human health, of 100 and 1000 mg/kg/day were observed rats and mice respectively.

4.1.2.7 Mutagenicity

4.1.2.7.1 In *vitro* studies

Bacterial studies

In a well-conducted unpublished study a C_{12}, 57% chlorinated paraffin, did not produce an increase in revertants in *Salmonella typhimurium* strains TA 98, TA 100, TA 1535, TA 1537 and TA 1538, and *Escherichia coli* WP2uvrA, in the absence or presence of Aroclor-induced rat liver S9 (unpublished reference 86, 1988). The chlorinated paraffin was tested up to 5000 micrograms per plate.

Negative results were also obtained in an Ames test using *Salmonella typhimurium* strains TA 97, TA 98, TA 100 and TA 1535, when a slightly higher chlorinated (60%) C_{12} paraffin was tested up to 3333 micrograms/plate, in the presence and absence of Aroclor-induced rat or hamster liver S9 (NTP, 1986). This study employed a 20 minute preincubation period. However cytotoxicity was not observed and precipitation was not reported; it is possible that the maximum concentration tested could have been increased further (up to 5000 micrograms/plate).

Similarly, a C_{10-13}, 50% chlorinated paraffin, did not produce an increase in revertants in *Salmonella typhimurium* strains TA 98, TA 100, TA 1535 and TA 1538, in the absence or presence of Aroclor-induced rat liver S9, when tested up to 2500 micrograms per plate (Birtley *et al.*, 1980; unpublished study 89). As above, cytotoxicity was not observed and precipitation was not reported and hence the maximum concentration tested could have been increased.

Negative results were also claimed in another two unpublished Ames test studies; however these reports were little more than statements with no experimental details and therefore their reliability is unknown (unpublished references 90, 1989 and 94, 1977).

One unpublished study reported positive findings (unpublished reference 85, 1986). A C_{10-13}, 50% chlorinated paraffin, containing 1% epoxy stabiliser, was tested with up to 10,000 micrograms/plate, in *Salmonella typhimurium* strains TA 98, TA 100, TA 1535, TA 1537 and TA 1538, and *Eschericha coli* WP2uvrA, in the absence or presence of Aroclor-induced rat liver S9. No toxicity was observed. Dose-related increases in the number of revertants occurred with S9 in strains TA 100 and without activation in strains TA 100 and TA 98 (with 500 micrograms/plate and above). However the increase in TA 100, in the presence of activation was just less than two fold, and in TA 98, in the absence of activation only just reached a two fold increase. Also the possibility that the epoxy stabiliser was responsible for

the increase in revertants can not be discounted. Overall it is not possible to draw firm conclusions from this study.

Mammalian cell studies

No standard cytogenetics studies in mammalian cells are available. A well-conducted gene-mutation (HPRT) study in Chinese hamster V79 cells, performed to modern protocols was available (unpublished reference 92, 1987). When tested up to cytotoxic concentrations, a C_{10-13}, 56% chlorinated paraffin did not induce a significant, reproducible increase in the number of mutant colonies, in the presence or absence of Aroclor-induced rat liver metabolic activation.

Although not mutagenicity assays, the results of two cell transformation assays, using BHK21/C13 cells, have been summarised here for convenience. In the first, cells were treated, in the presence of Aroclor-induced rat liver metabolic activation, with up to toxic concentrations of a C_{10-13}, 50% chlorinated paraffin (Birtley *et al.*, 1980, unpublished reference 95, 1981 & 94, 1977). There was no evidence of an increase in cell transformation frequency. The test was not conducted in the absence of metabolic activation mix.

In contrast, increases in transformation frequency were obtained in the presence and absence of Aroclor-induced rat liver activation mix when cells were treated with a C_{12}, 58% chlorinated paraffin (Chlorowax 500C) (unpublished reference 96, 1982). Large increases (5 to 1000-fold) in the transformation frequency were obtained at both cytotoxic and nontoxic concentrations. The relationship between this effect and neoplastic activity of chlorinated paraffins *in vivo* (see later) is not clear.

4.1.2.7.2 *In vivo* studies

A C_{10-12}, 58% chlorinated paraffin was tested in a rat bone-marrow cell chromosomal aberration study (unpublished reference 97, 1982; Serrone *et al.*, 1987). Groups of 8 male rats were treated with 0, 250, 750 and 2500 mg/kg/day chlorinated paraffin, by gavage, daily for five days. Reduced body weight was noted with the mid dose and 7 deaths occurred with the top dose. Sampling was conducted on day 6 and 100 metaphase spreads per animal were analysed. There was no increase in the frequency of chromosomal aberrations, excluding gaps, at 250 or 750 mg/kg/day, or in the one surviving animal treated with 2500 mg/kg/day. The incidence of chromosomal gaps was not assessed and no other sampling times were conducted. Cytotoxicity was not assessed and therefore there is no direct measure of whether or not the test substance reached the target tissue. However, consideration of the toxicokinetics of these paraffins indicates significant absorption by the oral route and the limited distribution data available indicate distribution to the bone-marrow to be anticipated. Therefore, it would be reasonable to conclude that a significant amount of the test substance would have reached the target tissue in this study.

A germ cell mutagenicity study on the above chlorinated paraffin has also been conducted (unpublished study 99, 1983; Serrone *et al.*, 1987). Dominant lethality was assessed when groups of 15 male rats were treated with 0, 250, 750 or 2000 mg/kg/day chlorinated paraffin, by gavage, on five consecutive days. Two days after the final treatment, males were paired with two females for 5 days, and after a 2-day break with another two females, until each male had been paired with 20 females. Uterine examinations were conducted in females 15 days

after the introduction of the male. During treatment top-dose males showed a slight decrease in body weight and mid-dose males a slight decrease in body weight gain. Mean body weights were then comparable through out the remainder of the study. There was no difference in the number or location of viable embryos, nonviable embryos, early resorptions or pre-implantation losses.

4.1.2.7.3 Studies in humans

There is no information available.

4.1.2.7.4 Summary of mutagenicity

There are relatively few data available on the genotoxicity of these substances, particularly considering the varying chain-length and degree of chlorination of the different compounds in this family. However the limited information in bacteria indicate that short-chain 50-60% chlorinated paraffins are not mutagenic in these systems. No standard in vitro cytogenetic studies are available but a gene-mutation assay was negative for a C_{10-13}, 56% chlorinated paraffin. Two well-conducted in vivo studies suggest that short-chain chlorinated paraffins do not produce mutagenicity in somatic (bone marrow) or germ cells.

Overall, the data available and a consideration of the generally unreactive nature of these substances indicate that short chain chlorinated paraffins (as a group) are not mutagenic.

4.1.2.8 Carcinogenicity

4.1.2.8.1 Studies in animals

Inhalation

No studies are available.

Oral

Studies in rats

In a poorly-conducted study with low survival rates, groups of 50 male and 50 female F344/N rats were administered 0, 312 or 625 mg/kg/day C_{12}, 60% chlorinated paraffin in corn oil by gavage, 5 days/week for 104 weeks (NTP, 1986). Additional groups of 20 male and 20 female rats were included in each treatment group for concurrent 6- and 12-month studies (limited pathology was performed in these shorter duration studies). In the 2 year study, all animals were observed daily and body weights recorded at least monthly. Necropsy and complete histopathological examinations were performed on all animals either at death, following sacrifice when moribund, or at the end of the study, unless excessively autolysed or cannibalised.

At the end of the 6- and 12-month studies, high-dose male rats showed a slight inhibition (12% reduction) in body weight gain. A statistically significant, dose-related increase in absolute and relative liver weight, of up to 124%, was observed at 6 and 12 months. The effect

was greater in the females but was no greater in either sex at 12 months than at 6. The increase in liver weights was accompanied by hypertrophy of the hepatocytes. A statistically significant, dose-related increase in absolute and relative kidney weight, of 24 to 46%, was also observed at 6 and 12 months. As with the liver, the effect was no greater at 12 months than at 6. The kidneys also showed a dose-related increase in the incidence and severity (minimal to mild in controls and low-dose animals, and mild to moderate in top-dose animals) of damage in the tubules and of interstitial inflammation. It was noted that nephropathy in the male rats was more severe than that in the females. No other changes were observed.

In the two year study, survival of treated male animals beyond week 89 was extremely poor with 27/50, 6/50 and 3/50 control, low- and high-dose males surviving to the end of the study. Survival in the females was reasonable; the corresponding rates were 34/50, 23/50 and 29/50. Mean body weights of top-dose males were at least 10% lower than controls after week 37 and were 23% lower by the end of the study. All other body weights were similar to control values. Clinical observation revealed no treatment-related changes until approximately week 90 when males and females of both treated groups showed non-specific signs of toxicity such as decreased activity, pale eyes and skin, emaciation and abnormal breathing. Several high dose females also showed distended or firm abdomens, possibly due to liver enlargement.

There were significant increases in a number of specific neoplasias in treated rats. A slight but statistically significant increase in hepatocellular carcinomas was noted in the low dose males. Incidence rates in control, low and high dose males which survived to the end of the study were; 0/27, 2/6 (33%) and 0/3 respectively. Overall rates, that is, the incidence in all male rats examined, irrespective of survival time, were 0/50, 3/50 (6%) and 2/48 (4%) respectively. The corresponding overall rates in the females were; 0/50, 1/50 (2%) and 1/50 (2%). A statistically significant increase in the incidence of liver neoplastic nodules was also noted in both male and female rats, with incidence of 0/50, 10/50 (20%) and 16/48 (33%) being reported in control, low and high dose males and in 0/50, 4/50 (8%) and 7/50 (14%) females, respectively.

Low-dose female rats showed a statistically significant increase in thyroid follicular cell adenomas [control: 0/50, low dose: 6/50 (12%), high dose: 3/50 (6%)], while high dose females showed a non statistically significant increase in follicular cell carcinomas [control: 0/50, low dose: 0/50, high dose: 3/50 (6%)]. The incidence in all male groups, including the controls was 3/50 (6%). The historical incidence (from in-house data and from all NTP studies) for follicular cellular adenomas and carcinomas is 0.8 and 0.4% respectively.

A statistically significant increase in kidney tubular cell adenomas was noted in low dose male rats. The terminal incidence rates in control, low and high dose males surviving to the end of the study were; 0/27, 2/6 (33%) and 0/3, respectively. Overall rates were 0/50, 7/50 (14%) and 3/49 (6%). Adenocarcinomas were also noted in 2/50 (2%) low dose males but were not noted in high dose or control animals. There were no dose-related increases in kidney tumours in female rats.

Male rats also showed increases in mononuclear cell leukaemia. Terminal and overall incidence rates in control, low and high dose animals were; 3/27(11%), 2/6 (33%) and 0/3, and 7/50 (14%), 12/50 (24%) and 14/50 (28%), respectively. The incidences in females were: controls; 11/50 (22%), low dose: 22/50 (44%), high dose: 16/50 (32%). No significance can be read into this pattern of results, in view of the poor survival in males and the high incidence in all groups in the females.

High dose males also showed slight increases in the incidence of squamous cell papillomas in the forestomach (control: 0/50, low dose: 0/50, high dose: 2/49, historical control incidence was not given), probably a reflection of chronic irritation from repeated gavage dosing. Also in high dose males pancreatic acinar cell carcinomas were increased (controls: 0/50, low dose: 0/50, high dose: 2/49 (4%, historical control incidence: 0.2%). Treated male rats also showed an increase in acinar adenoma (controls: 11/50 (22%), low dose: 22/50 (44%), high dose: 15/49 (31%), historical control incidence: 4.2%). In view of the atypically high incidence in the controls and the pattern of results seen, no significance can be read into these results.

Non-neoplastic changes were mainly observed in the liver, kidney and stomach. Minimal to slight necrosis, focal cellular change, minimal hypertrophy and gross dilation of the blood vessels, were noted in the livers of both treatment groups. Liver weights were not reported. Multiple cysts were observed in the kidney cortex in low (26/49) and high (27/50) dose males but not in controls. The incidence of kidney nephropathy was increased in females (control: 33/50, low dose: 50/50 and high dose: 48/50) but was not increased in treated males although the severity of the nephthropathy was judged to be greater in treated males compared to controls. Kidney weights were not reported. Males also showed a dose-related increase in the incidence of kidney tubular cell hyperplasia (controls: 1/50, low dose: 9/50, high dose: 12/49). Oedema and erosion of the glandular stomach and ulcers, inflammation, epithelial hyperplasia and hyperkeratosis of the forestomach were observed in a dose-related fashion in male rats. Hyperplasia of the parathyroid and fibrous osteodystrophy were also observed in treated males.

Overall, this was a poor quality study which provided suggestive, but not definitive evidence of significant carcinogenic activity in the liver, thyroid and kidney.

Studies in mice

Groups of 50 male and 50 female $B6C3F_1$ mice were administered 0, 125 or 250 mg/kg/day C_{12}, 60% chlorinated paraffin in corn oil by gavage, 5 days/week for 104 weeks (NTP, 1986). All animals were observed daily and body weights recorded at least monthly. Necropsy and complete histopathological examinations were performed on all animals either at death, following sacrifice when moribund, or at the end of the study, unless excessively autolysed or cannibalised.

Survival of high dose females was significantly lower than controls after week 100. Survival rates at the end of the study in control, low and high dose females were 35/50, 31/50 and 25/50 respectively. The corresponding rates in the males were 34/50, 30/50 and 30/50 respectively. In general, survival was adequate in this study. No significant differences were noted in mean body weights of the treated animals compared to control animals. Treatment-related clinical observations were noted in males and females of both dose groups beyond week 86 and included decreased activity, prominent backbones and abnormal breathing.

Dose-related increases in the incidence of hepatocellular carcinomas were noted in male and female mice although the increases only reached statistical significance in the high dose females. The overall rates in females (control, low and high) were 3/50 (6%), 4/50 (8%) and 9/50 (18%), respectively (the historical incidence for hepatocellular carcinomas in female mice, from in-house data and from all NTP studies, is 2-3%). Overall rates in males were 11/50 (22%), 15/50 (30%) and 17/50 (34%), respectively (the historical incidence for hepatocellular

carcinomas in male mice, from in-house data and from all NTP studies, is 22-27%). Statistically significant dose-related increases in the incidence of hepatocellular adenomas were also noted in both male and female mice. Overall rates in control, low and high dose males were 11/50 (22%), 20/50 (40%) and 29/50 (58%), respectively. Corresponding rates in the females were 0/50, 18/50 (36%) and 22/50 (44%), respectively (the historical incidences for hepatocellular adenomas in male and female mice, from in-house data and from all NTP studies, are 12 and 4%, respectively).

Female mice showed a statistically significant dose-related increase in the incidence of thyroid follicular cell adenomas. Overall rates in control, low and high dose females were 8/50 (16%), 12/49 (24%) and 13/49 (27%), respectively. Top dose females also showed an increase in follicular cell carcinomas: 0/50, 0/49 and 2/49 (4%) in control, low and high dose mice respectively (the incidence of follicular cell adenomas or carcinomas combined in historical control female mice is approximately 0.5%). There were no increases in thyroid tumour incidence in males.

Female mice also showed a statistically significant, but not dose-related, increase in Harderian gland carcinomas with overall rates in control, low and high dose females being 1/50 (2%), 6/50 (12%) and 2/50 (4%), respectively. The historical control incidence of Harderian gland carcinomas in female mice is 1.9. No such effects were seen in the males. These findings are not considered to be of significance for human health.

Male mice showed a statistically significant, dose-related increase in alveolar/bronchiolar carcinomas with overall incidence rates in control, low and high dose males being 0/50, 3/50 (6%) and 6/50 (12%), respectively. However, the incidence of alveolar/bronchiolar carcinomas in historical control male mice is 5.8%. An increase in adenomas did not occur. There were no increases in lung tumour incidence in females. No significance for human health can be read into this pattern of results.

The thyroid showed a spectrum of follicular cell lesions in all groups ranging from early hyperplasia to multi-layered projections that extended into the lumen (overall rates: 32%, 55% and 45% in control, low and high dose females and in 10%, 12% and 24% in males, respectively). An increased incidence of kidney nephrosis was noted in high dose female mice. Nonneoplastic lesions were not noted in the liver. Liver weights were not recorded.

The most significant findings in this study were the increased incidences of carcinoma and adenoma in the thyroid in female mice and the liver in male and female mice.

Dermal

No studies are available.

4.1.2.8.2 Studies in humans

There is no information available.

4.1.2.8.3 Discussion at Technical Meetings and by the Specialised Experts

The paragraphs below outline the discussion at the Technical Meetings and present the conclusions of the Specialised Experts. Words in square brackets [ ] have been added for clarity.

The carcinogenicity of short chain length chlorinated paraffins was discussed at Technical Meetings on October 1st - 3rd 1996 and February 19th - 21st 1997. Member States agreed that the substance was not genotoxic but could not agree further on the significance of the tumours seen nor on their relevance to man.

The Commission Group of Specialised Experts in the fields of Carcinogenicity, Mutagenicity and Reprotoxicity met on 4th - 6th June 1997. The Specialised Experts considered the NTP cancer bioassays to be of poor quality and that no significance should be attributed to the slight excess of tumours seen in the lung, pancreas, stomach, [to the] leukaemia[s] or Haderian gland. The Specialised Experts agreed that of the tumours observed, only those in the liver, thyroid and kidney should be considered significant. Mechanisms for two of these had been suggested [see above]. Peroxisome proliferation for the liver tumours and hormonal imbalance for the thyroid. These mechanisms were accepted by the Specialised Experts.

[The Specialised Experts considered that] no plausible mechanism was suggested for the kidney tumours. It had been noted that α2u globulin might be responsible, but studies had failed to show significant levels of the protein. Other evidence had shown that there was chronic nephropathy which might be a contributing factor in the tumour development. [The Specialised Experts considered that] as there was still insufficient evidence to conclude a male rat specific event, the consequences for humans could not be ruled out.

4.1.2.8.4 Summary of carcinogenicity

No information is available on studies in human populations potentially exposed to short chain length chlorinated paraffins. The only studies available in animals investigated the effects of a C_{12}, 60% chlorinated paraffin.

Short chain length chlorinated paraffins are not mutagenic. In rodent carcinogenicity studies, the chlorinated paraffin tested produced toxicologically significant, dose-related increases in the incidence of several tumour types. Dose-related increased incidence of adenomas and carcinomas of the liver and thyroid were observed in mice. There was an indication of similar effects in a poor quality study in rats. These findings reflect, in the case of the liver, chronic tissue damage caused by peroxisome proliferation and for the thyroid, long-term hormonal stimulation. From consideration of the probable underlying mechanisms involved (see 4.1.2.6. Repeated dose toxicity) it is likely that these carcinogenicity observations are not relevant to human health. Male rats also showed an increased incidence of kidney tubular cell adenomas. This was not seen in female rats or in mice of either sex. Although hyaline droplets were not directly observed, the pattern of results in male rats is consistent with tumour formation following kidney damage caused by hyaline droplet formation, which is a male rat-specific phenomenon. This is suggestive that the benign tumours observed in the kidney of males rats are not likely to be relevant for human health.

<u>Discussion at Technical Meetings and by the Specialised Experts</u>

There was no agreement on the significance of the tumours nor their relevance to man between Member States. The issue was subsequently referred to the Specialised Experts. In their view only three were considered significant and of these two were considered not to be relevant to man. In their view, there was insufficient evidence to conclude that the kidney

tumours were a male rat specific event and consequently the concern for humans could not be ruled out.

Conclusion

It is recognised that the current evidence on the mechanism underlying the development of the kidney tumours is not definitive. Given that the short chain length chlorinated paraffins are not genotoxic, it is considered that there would be no risk of kidney tumour development associated with exposures lower than those required to produce chronic toxicity in this target organ. A NOAEL for kidney toxicity in male rats has been previously identified at 100 mg/kg/day. This value will be used in the risk assessment.

4.1.2.9 Toxicity for reproduction

4.1.2.9.1 Studies in animals

Effects on fertility

No studies specifically investigating effects on fertility are available. However in a repeat toxicity study female rats showed a decrease of 35 to 48% in relative and absolute ovary weight, respectively, following administration by gavage of 3000 mg/kg/day for 14 days, of a C_{10-12}, 58% chlorinated paraffin (unpublished reference 75, 1981). Other signs of toxicity including a 20% decrease in body weight gain were also noted with this dose and the effect on the ovaries is likely to be secondary to this. No changes were seen in the ovary with 1000 mg/kg/day.

No changes were seen in the seminal vesicles, prostate, testes, ovaries or uterus when rats and mice were treated for 13 weeks with up to 5000 and 2000 mg/kg/day, respectively, of a C_{12}, 60% chlorinated paraffin (NTP, 1986).

Developmental studies

In a well-conducted study, rats were treated by gavage with 0, 100, 500 or 2000 mg/kg C_{10-13}, 58% chlorinated paraffin, on days 6 to 19 of gestation (unpublished reference 102, 1982; Serrone *et al.*, 1987). Caesarean sections were performed on day 20. Eight of 25 pregnant rats died in the top-dose group. No deaths occurred in the other groups. General signs of maternal toxicity, such as emaciated appearance, excessive salivation and decreased activity, were observed in both the mid- and top-dose groups. Top-dose females also showed a decrease (by 35%) in body weight gain. Statistically significant increases in the number of post-implantation losses, due to both early and late resorptions, and a statistically significant decrease in viable foetuses per dam were noted with 2000 mg/kg/day. Adactyly and/or shortened digits were also observed in 19 foetuses from 3/15 litters examined with 2000 mg/kg/day only.
There were no changes in any developmental parameters with 500 mg/kg/day. No effects on dams or foetuses were observed with 100 mg/kg/day. Overall, developmental effects were only noted at concentrations causing severe maternal toxicity in rats.

In a less well-conducted study in rabbits, groups of 16 pregnant females were treated by gavage with 0, 10, 30 or 100 mg/kg C_{10-12}, 58% chlorinated paraffin in corn oil, on days 6 to

27 of gestation (unpublished reference 100, 1983; Serrone *et al.*, 1987). Caesarean sections were carried out on day 28. No maternal deaths occurred and no signs of toxicity were noted in any of the groups. No malformations were noted at any dose level. At 100 mg/kg/day, whole litter resorptions occurred in 2/14 pregnant dams and at 30 mg/kg/day, in 1/15. This did not occur in the control or low dose groups. The historical control incidence for this effect was given as 13/277, indicating that the appearance of one or two dams with whole litter resorption in a treatment group could arise by chance alone. Consequently these observations are considered not to provide convincing evidence of a treatment related effect. The potential to produce developmental effects at maternally toxic doses was not assessed in this study.

The dose levels used in this study were derived from two range-finding studies (unpublished references 103 and 104, 1982). Due to either excessive maternal toxicity or a reduction in sample sizes in all groups, including controls (due to rabbits which aborted or were non gravid) and a corresponding reduction in study sensitivity, it is not possible to draw any conclusions from these studies.

4.1.2.9.2 Studies in humans

No data are available.

4.1.2.9.3 Summary of toxicity for reproduction

In relation to fertility, there is no information available in humans and there are no animal studies specifically investigating such effects. However no changes were seen in the reproductive organs in rats and mice treated for 13 weeks with up to 5000 and 2000 mg/kg/day, respectively, of a C_{12} 60% chlorinated paraffin.

In terms of developmental effects, there is no information available in humans, although in a well-conducted study in rats a C_{10-13}, 58% chlorinated paraffin produced developmental effects at a dose which also caused severe maternal toxicity (2000 mg/kg), but no developmental effects at lower doses (500 mg/kg and below). No developmental effects were observed in a study in rabbits, although maternally toxic doses were not tested.

There is no information on short chain length chlorinated paraffins with higher and lower chlorine content.

4.1.3 Risk characterisation

The section below, titled "General aspects" provides a brief toxicological profile of short chain length chlorinated paraffins, identifying the lead effects and, where appropriate, identifying NOAELs and LOAELs. The rest of the section compares this information with exposure information for workers, consumers and man exposed via the environment. Where appropriate Margins of Safety (MoS) are calculated.

4.1.3.0 General aspects

Very little toxicological information is available from studies in humans, although there is a reasonable database for short chain length chlorinated paraffins as a group from animal studies. The available animal data do not allow a direct comparison, for every toxicological

endpoint, of the effects of short chain length chlorinated paraffins with differing chain length and degree of chlorination. However the information available from acute studies and skin irritation studies indicates that the intensity and nature of effects for these endpoints are independent of chain length and degree of chlorination.

There is very limited information on toxicokinetics. No information is available on absorption via the inhalation route. A study in animals via the oral route indicates that significant absorption (60%) does occur. Studies in animals (on a longer chain substance) and humans indicate that absorption via the dermal route will be low .

For the purposes of risk assessment, when calculating the systemic dose absorption via the inhalation route will be assumed to be 100% of the inhaled amount, via the oral route 100% of the swallowed amount and via the dermal route 1% of the amount applied to the skin. These are considered to be very conservative assumptions.

Assessment of the available data clearly indicates that short chain length chlorinated paraffins are of low acute toxicity in animals. Limited information indicates that short chain length chlorinated paraffins do not cause skin irritation in humans and in animal studies, at most, minimal skin and mild eye irritation were reported. More pronounced skin irritation was observed in animals following repeated exposure presumably because of defatting. No conclusions can be drawn from the information available on skin sensitisation in humans. However well conducted studies in animals have shown that short chain length chlorinated paraffins do not have the potential to produce skin sensitisation. Although there is no information on respiratory sensitisation in humans or animals, it is significant that no such effects have been reported in humans despite their widespread use. There is no information on the health effects in humans of repeated exposure to short chain length chlorinated paraffins. The principal signs of toxicity in animals were effects in the liver and thyroid. However mechanistic information has indicated that these effects are probably not relevant to human health. NOAELs of 100 and 1000 mg/kg/day were identified in rats and mice respectively for other signs of toxicity, such as decreased body weight gain and increased kidney weight, which may be relevant to human health.

Short chain length chlorinated paraffins were not mutagenic in bacterial cell systems. No standard *in vitro* cytogenetics studies were available but a gene-mutation assay was negative. Well conducted *in vivo* studies indicate that short chain length chlorinated paraffins do not produce mutagenicity in somatic or germ cells. Overall the evidence indicates that short chain length chlorinated paraffins are not mutagenic.

No information is available on carcinogenicity studies in human populations potentially exposed to exclusively short chain length chlorinated paraffins. In rodent carcinogenicity studies, dose-related increases in the incidence of adenomas and carcinomas were observed in the liver, thyroid and kidney. Other cancers seen were dismissed as not significant. Consideration of the characteristic patterns in the results and the probable underlying mechanisms involved, indicate that the findings reflect, in the case of the liver, chronic tissue damage caused by peroxisome proliferation and for the thyroid, long term hormonal stimulation, potentially consequent to the liver effects. Consideration of the likely underlying mechanisms for these tumours suggests that they are not relevant to human health.

The kidney adenomas (benign) were seen exclusively in male rats. It is considered likely that the underlying mechanism is the male rat-specific phenomenon of hyaline droplet nephropathy, although this has not been clearly demonstrated. It is noted that Industry are undertaking further research to address the mechanism(s) underlying the formation of kidney tumours. The Specialised Experts concluded (see Section 4.1.2.8.3) that there was insufficient evidence to conclude a male rat specific event and that the consequences for humans could not be ruled out. Given that the short chain length chlorinated paraffins are not genotoxic, it is considered that there would be no risk of kidney tumour development associated with exposures lower than those required to produce chronic toxicity in this target organ. The NOAEL for kidney toxicity in male rats, identified at 100 mg/kg/day will therefore be used as the NOAEL for kidney carcinogenicity.

There are no data available in humans or animals on fertility although no changes were seen in the reproductive organs in rats and mice treated for 13 weeks with up to 5000 and 2000 mg/kg/day, respectively, of a short chain length chlorinated paraffin. There are no data available on developmental effects in humans. A short chain length chlorinated paraffin produced developmental effects in rats at a dose which also caused maternal toxicity (2000 mg/kg), but no developmental effects at lower doses (500 mg/kg and below). No developmental effects were observed in a study in rabbits, although maternally toxic doses were not tested. For the purposes of risk assessment, an NOAEL of 500 mg/kg/day will be used for developmental effects.

Overall, short chain length chlorinated paraffins are of low toxicity with the principal toxicological issue being for general non-specific toxicity following repeated exposure. NOAELs for general toxicity of 100 and 1000 mg/kg/day were identified in rats and mice respectively.

There are several gaps in the database, particularly with regard to differing chain length and degree of chlorination. However, taking into account the low toxicity observed in all available studies and the generally unreactive nature of short chain length chlorinated paraffins, it would appear unnecessary to attempt to fill these gaps with further testing.

4.1.3.1 Workers

4.1.3.1.1 Introduction

For the purpose of risk characterisation it is assumed that good personal hygiene is practised in the workplace and that no oral uptake of short chain length chlorinated paraffins will occur. Short chain length chlorinated paraffins are principally used in metal working fluids, although they are also used in textile and leather treatment formulations, paints, adhesives and certain rubber products. They are produced in batches in closed systems, occupational exposures are consequently intermittent, occurring during sampling, plant and filter cleaning, drumming and tanker loading. Formulation involves a similar work pattern, but may be divided into high and low temperature processes, the former giving rise to greater potential for inhalation exposure. Inhalation and dermal exposures arising from production, formulation and the various uses are presented in **Table 4.5** below, summarised from Section 4.1.1.1. The exposures are largely derived from model predictions and neither they, nor the doses calculated from them, take account of the attenuating effects of PPE.

At the exposure levels presented in **Table 4.5**, the only effects that are likely to be of concern are those arising from repeated exposures (doses), that is general toxicity, kidney carcinogenicity and developmental effects. It is very unlikely that workers would be exposed to levels likely to lead to effects from single exposure. Furthermore, as short chain length chlorinated paraffins, have only minimal irritant effects, these are also unlikely to be expressed, particularly if appropriate PPE is worn where dermal contact might be expected.

For the purposes of risk assessment, NOAELs can be identified for the repeated dose study (100 mg/kg/day) and for carcinogenicity (100 mg/kg/day, based upon the NOAEL for the repeated dose study). There is no data on fertility but no changes were seen in reproductive organs at 5000 and 2000 mg/kg/day respectively for rats and mice. While developmental effects were only seen at a maternally toxic dose in rats (2000 mg/kg/day) they were not seen at lower doses (500 and 100 mg/kg/day). A NOAEL of 500 mg/kg/day will be used for developmental effects.

In the Tables below, no attempt has been made to predict a MoS for local effects, nor for a single route of exposure. Short chain length chlorinated paraffins are absorbed to a degree by the inhalation and dermal routes and there is no reason to assume a route specific toxicity. Consequently, to calculate a MoS, the NOAELs identified above are compared with a systemic dose, summing the contributions from the two relevant routes. These calculations assume (unless stated otherwise) 100% absorption via the oral and inhalation routes, 1% via the dermal route, that an individual weighs 70 kg, breathes in 10 m^3 of air in an 8 hour working day and has a surface area on skin and forearms of 2000 cm^2. The total systemic doses are presented in **Table 4.5**, the MoS in **Table 4.6**.

Table 4.5 Inhalation and dermal exposures and doses and total systemic doses for the manufacture and use of short chain length chlorinated paraffins

Scenario	Inhalation		Dermal		Total Systemic
	Concentration	Dose mg/kg/day	Concentration	Dose mg/kg/day	Dose mg/kg/day
Manufacture	0.1 ppm (2.1 mg/m³)[a]	0.3	1 mg/cm²	0.29	0.6
Formulation low temperature	0.1 ppm (2.1 mg/m³)[a]	0.3	1 mg/cm²	0.29	0.6
Formulation high temperature	3 ppm (63 mg/m³)[a]	9	1 mg/cm²	0.29	9.3
Metal working fluids	1.15 mg/m³	0.2	0.1 mg/cm²	0.03	0.23
Leather and textile treatment	negligible	negligible	0.3 mg/cm²	0.09	0.1
Leather and textile use	negligible	negligible	negligible	negligible	
Paints, adhesives & sealants	0.32 mg/m³	0.05	0.1 mg/cm²	0.03	0.1
Rubber products, processing and use	negligible	negligible	negligible	negligible	negligible

[a] mg/m³ = ppm x Molecular Weight / 24.05526

Molecular weight is assumed to be 500 (the top end of the range) and 24.05526 l/mol is the molar volume of an ideal gas at 20°C and 1 atmosphere pressure (101325 Pa, 760mm mercury, 1.01325 bar)

Table 4.6 Total systemic doses, NOAELs and margins of safety for the manufacture and use of short chain length chlorinated paraffins

Scenario	Total Systemic Dose mg/kg/day	NOAEL [Repeat dose and carcinogenicity mg/kg/day]	Margin of Safety	NOAEL [Developmental effects mg/kg/day]	Margin of Safety
Manufacture	0.60	100	166	500	830
Formulation low temperature	0.60	100	166	500	830
Formulation high temperature	9.30	100	10.8	500	54
Metal working fluids	0.23	100	435	500	2175
Leather and textile treatment	0.10	100	1000	500	5000
Leather and textile use					
Paints, adhesives & sealants	0.10	100	1000	500	5000
Rubber products, processing and use					

None of the above calculations take account of personal protective equipment, which may considerably reduce individual exposures

4.1.3.1.2 Risk characterisation for workers

The manufacture and use of short chain length chlorinated paraffins gives rise to a range of systemic doses. At the exposure levels presented in **Table 4.5**, the only effects that are likely to be of concern are those arising from repeated exposures (doses), that is general toxicity, kidney carcinogenicity and developmental effects. When compared to the relevant NOAELs, in all but one case, the margin of safety is well over 100. While it is important not to read too much into simple ratios, this does suggest that, in general, the use of the substance is appropriately controlled.

The clear exception is high temperature formulation of hot melt adhesives and rubber products where the margin of safety is narrower. In this particular case it is important to recognise that the high end of the EASE predictions has been used. Further, because these are batch production processes, the time for which an individual is likely to be exposed will be considerably reduced. If as is probable, operators are exposed for a shorter time, perhaps one hour, the inhaled dose reduces by 7/8 and the total systemic dose to approximately 2 mg/kg/day. Assuming an absorption of 75% of the inhaled dose would reduce the systemic dose further still. Noting the inherent conservatism of these calculations, it is considered that the likely exposures arising from high temperature formulation are appropriately controlled and that there is no further cause for concern.

Some users of metal working fluids may use fluids with a chlorinated paraffin content of up to 80% for specific purposes. In those circumstances, assuming that the duration and other assumptions hold true, the inhaled and dermal doses will increase to 1.6 and 0.24 mg/kg/day respectively, and the total systemic dose to 1.84 mg/kg/day. The margins of safety then narrow to approximately 54 and 250. These are not considered to be a cause for additional concern.

Conclusion

At the exposure levels presented, the only effects that are likely to be of concern are those arising from repeated exposures (doses), i.e. general toxicity, kidney carcinogenicity and developmental effects. When compared to the relevant NOAELs, in all but one case, the margin of safety is considered to be adequate, that is at least two orders of magnitude. While it is important not to read too much into simple ratios, this does suggest that, in general, the use of the substance is appropriately controlled. While certain uses imply a narrower margin of safety, these are not considered to be a cause for concern.

Result

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

4.1.3.2 Consumers

4.1.3.2.1 Introduction

Short chain length chlorinated paraffins may be used in a number of consumer products, including leather clothing, metal working fluids and on textiles, in certain industrial paints, sealants and adhesives and in rubber products. Aside from leather clothing and metal working fluids, the consumer exposures are considered to be negligible. Inhalation exposure is only considered to be significant for metal working fluids.

Inhalation and dermal exposures arising for consumers are presented in **Table 4.7** below, summarised from Section 4.1.1.2. The exposures are largely derived from simple calculations.

At the exposure levels presented in **Table 4.7**, the only effects that are likely to be of concern are those arising from repeated exposures (doses), that is general toxicity, kidney carcinogenicity and developmental effects. It is very unlikely that consumers would be exposed to levels likely to lead to effects from single exposure, nor to irritant effects.

For the purposes of risk assessment, NOAELs can be identified for the repeated dose study (100 mg/kg/day) and for carcinogenicity (100 mg/kg/day, based upon the NOAEL for the repeated dose study). There is no data on fertility but no changes were seen in reproductive organs at 5000 and 2000 mg/kg/day respectively for rats and mice. While developmental effects were only seen at a maternally toxic dose in rats (2000 mg/kg/day) they were not seen at lower doses (500 and 100 mg/kg/day). A NOAEL of 500 mg/kg/day will be used for developmental effects.

In the Tables below, no attempt has been made to predict a MoS for local effects, nor for a single route of exposure. Short chain length chlorinated paraffins are absorbed to a degree by the inhalation and dermal routes and there is no reason to assume a route specific toxicity.

Consequently, to calculate a MoS, the NOAELs identified above are compared with a systemic dose, summing the contributions from the two relevant routes. These calculations assume (unless stated otherwise) 100% absorption via the oral and inhalation routes, 1% via the dermal route and that an individual weighs 70 kg. For the metal working fluids scenario, the assumption is made that an individual breathes in 2.5 m^3 of air in a 2 hour working day and has a surface area on skin and forearms of 2000 cm^2. The total systemic doses are presented in **Table 4.7**, the MoSs in **Table 4.8** below.

Table 4.7 Inhalation and dermal exposures and doses and total systemic doses for consumers exposed to short chain length chlorinated paraffins

Scenario	Inhalation		Dermal		Total Systemic Dose mg/kg/day
	Concentration	Dose mg/kg/day	Concentration	Dose mg/kg/day	
Metal working fluids	0.115 mg/m^3	over 2 hours, 0.004	0.1 mg/cm^2	0.03	0.03
Leather and textile use	negligible	negligible	37 mg over the body	0.02	0.02

Table 4.8 Total systemic doses, NOAELs and margins of safety for consumers exposed to short chain length chlorinated paraffins

Scenario	Total Systemic Dose mg/kg/day	NOAEL [Repeat dose and carcinogenicity mg/kg/day]	Margin of Safety	NOAEL [Developmental effects mg/kg/day]	Margin of Safety
Metal working fluids	0.03	100	3333	500	16,666
Leather and textile use	0.02	100	5000	500	25,000

4.1.3.2.2 Risk characterisation for consumers

At the exposure levels presented in **Table 4.7**, the only effects that are likely to be of concern are those arising from repeated exposures (doses), that is general toxicity, kidney carcinogenicity and developmental effects. When compared to the relevant NOAELs, the margins of safety presented in **Table 4.8** are well over three orders of magnitude and, given the conservative nature of the exposure calculations, in all probability considerably more. While it is important not to read too much into simple ratios, this does suggest that the use of the substance poses no significant risk for consumers.

Conclusion

The use of the substance poses no significant risk for consumers.

Result

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

4.1.3.3 Man exposed indirectly via the environment

4.1.3.3.1 Introduction

The EUSES predictions considerably overestimate human exposure via the environment, specifically in the predictions for root crops. However, real data clearly indicate the potential for human uptake. The value of 20 µg/kg/day (assuming 100% adsorption via the oral and inhalation routes) is considered to be a reasonable worst case prediction based upon real data and will be used in the risk assessment to represent both local and regional exposure.

At this dose level, the only effects that are likely to be of concern are those arising from repeated exposures (doses), that is general toxicity, kidney carcinogenicity and developmental effects. It is very unlikely that man exposed via the environment would be exposed to levels likely to lead to effects from single exposure, nor to irritant effects.

For the purposes of risk assessment, NOAELs can be identified for the repeated dose study (100 mg/kg/day) and for carcinogenicity (100 mg/kg/day, based upon the NOAEL for the repeated dose study). There are no data on fertility but no changes were seen in reproductive organs at 5000 and 2000 mg/kg/day respectively for rats and mice. While developmental effects were only seen at a maternally toxic dose in rats (2000 mg/kg/day) they were not seen at lower doses (500 and 100 mg/kg/day). A NOAEL of 500 mg/kg/day will be used for developmental effects.

In comparing the exposure and effects data, no attempt has been made to predict MoS for local effects, nor for a single route of exposure. Short chain length chlorinated paraffins are absorbed to a degree by the inhalation and oral routes and there is no reason to assume a route specific toxicity. Consequently, to calculate MoS, the NOAELs identified above are compared with a systemic dose, summing the contributions from the two relevant routes.

4.1.3.3.2 Risk characterisation for man exposed indirectly via the environment

At the predicted level of exposure, the Margins of Safety are 5000 and 25000 for repeat dose/carcinogenicity and developmental effects respectively. While it is important not to read too much into simple ratios, this does suggest that the use of the substance poses no significant risk for man exposed via the environment.

Conclusion

There is no significant risk to man exposed via the environment.

Result

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

4.1.3.4 Combined exposure

During occupational exposure to short chain length chlorinated paraffins, the highest potential uptake is estimated to occur during their formulation in hot melt adhesives (up to 9.3 mg/kg/day). An individual formulating hot melt adhesives may also be exposed as a consumer (0.02 mg/kg/day) and via the environment (0.02 mg/kg/day). A combined uptake of up to 9.3 mg/kg/day is therefore estimated for a very conservative worst case situation. Other occupational sources of exposure contribute to much lower systemic doses. This indicates that the risk from combined exposure is low.

Result

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

4.2 HUMAN HEALTH (PHYSICO CHEMICAL PROPERTIES)

(risk assessment concerning the properties listed in Annex IIA of Regulation 1488/94)

Short chain length chlorinated paraffins have a very low vapour pressure, no explosive or oxidising properties and are not flammable. The flash point is in excess of 150 °C. Therefore it can be concluded that there is no concern for human health arising out of the physico-chemical properties.

5 RESULTS

5.1 INTRODUCTION

Short chain length chlorinated paraffins are viscous liquids of very low volatility. They are principally used in metal working fluids, although they are also used in textile and leather treatment formulations, paints, sealants and certain rubber products. They are produced in batches in closed systems.

5.2 ENVIRONMENT

The use of short chain length chlorinated paraffins in sealants, rubber, backcoating of textiles and paints is not thought to present a risk to the environment. Secondary poisoning is not thought to be of concern, except for leather treatment formulation and use and possibly for use in metal finishing. No risks to the function of sewage treatment plants were identified from either production or any use. For the atmospheric compartment, neither biotic or abiotic effects are considered likely to occur as a result of production or any use. Short chain length chlorinated paraffins have been raised as a possible concern with regard to long range atmospheric transport. This area is currently being discussed within the appropriate international fora.

The use of short chain length chlorinated paraffins in metal working fluids and in leather finishing has been found to present a risk to aquatic organisms in surface water due to local exposures. Possible risks to sediment-dwelling organisms were identified as a result of production of short chain length chlorinated paraffins, formulation and use of metal cutting fluids and formulation and use of leather finishing products, use in rubber formulations, and at a regional level. There is a possible risk to soil-dwelling organisms in agricultural soils at a local level (for metal working fluid formulation and use, and leather finishing formulation and use) and at a regional level due to spreading of sewage sludge. Further information for the soil and sediment compartments could be gathered to clarify the risk. However, risk reduction methods should be considered for metal working since further information (either exposure or aquatic toxicity) is unlikely to change significantly the PEC/PNEC ratios calculated for aquatic organisms. Based on the available data, a risk to aquatic organisms cannot be excluded for leather finishing applications either and so risk reduction measures should also be considered for this use.

Results

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

The PECs and PNECs for the sediment and soil compartments can all be revised. For soil, better information on releases of short chain length chlorinated paraffins to this compartment would revise the PEC. Monitoring data for soil and sediment near to sources of release would also be useful in this respect. Finally, since the PNECs for soil and sediment are based on the equilibrium partitioning method, the PNECs could be revised through toxicity testing on sediment- and soil-dwelling organisms if the revision of the PECs does not remove the concern. For sediment, the basis for any further toxicity testing could be firstly a long-term *Chironomid* test; secondly a long-term *Oligochaetes* test; and finally a long-term test with

Gammarus or *Hyalella* (all using spiked sediment). For soil, the test strategy could be based on the tests recommended in the Technical Guidance Document (currently a plant test involving exposure via soil; a test with an annelid; and a test with microorganisms).

The risk reduction measures recommended as a result of the assessment of aquatic effects from metal working and leather finishing will also (either directly or indirectly) have some effect on the PECs for sediment and soil. Any further information and/or testing requirements should therefore await the outcome of these risk reduction measures on releases to the environment.*

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

This applies to the assessment of
- atmospheric risks;
- risks to waste water treatment plants from production and all uses of short chain length chlorinated paraffins;
- the risk of secondary poisoning arising from production, formulation of metal working fluids and use in rubber formulations, paints and sealing compounds and textile applications;
- aquatic, sediment and terrestrial risks from use in sealants, backcoating of textiles and paints;
- aquatic and terrestrial risks from use in rubber formulations and from production sites (using site specific data); and
- aquatic risks at the regional level.

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

A risk to aquatic organisms exists arising from the local emission of short chain length chlorinated paraffins from metal working applications and leather finishing and from the formulation of products for these uses. This conclusion also applies to secondary poisoning arising from formulation and use in leather finishing, and use in metal working applications.

5.3 HUMAN HEALTH

Assessment of the available data clearly indicates that short chain length chlorinated paraffins are of low acute toxicity in animals. Limited information indicates that they do not cause skin irritation in humans and in animal studies, at most, minimal skin and mild eye irritation. Overall the evidence indicates that they are not mutagenic.

Kidney adenomas (benign) were seen exclusively in male rats. It is considered likely that the underlying mechanism is the male rat-specific phenomenon of hyaline droplet nephropathy, although this has not been clearly demonstrated. The Commissioned Group of Specialised Experts concluded that there was insufficient evidence to conclude a male rat specific event and that the consequences for humans could not be ruled out. Given that the short chain length chlorinated paraffins are not genotoxic, it is considered that there would be no risk of kidney

* See Appendix D

tumour development associated with exposures lower than those required to produce chronic toxicity in this target organ.

A short chain length chlorinated paraffin produced developmental effects in rats at a dose which also caused maternal toxicity.

5.3.1 Risk to workers

At the exposure levels calculated, the only effects that are likely to be of concern are those arising from repeated exposures (doses), that is general toxicity, kidney carcinogenicity and developmental effects. When compared to the relevant NOAELs, in all but one case, the margin of safety is considered to be adequate, that is at least two orders of magnitude. While it is important not to read too much into simple ratios, this does suggest that, in general, the use of the substance is appropriately controlled. While certain uses imply a narrower margin of safety, these are not considered to be a cause for concern.

Result

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

5.3.2 Risk to consumers

At the exposure levels calculated, the only effects that are likely to be of concern are those arising from repeated exposures (doses), that is general toxicity, kidney carcinogenicity and developmental effects. When compared to the relevant NOAELs, the margins of safety are well over three orders of magnitude and, given the conservative nature of the exposure calculations, in all probability considerably more. While it is important not to read too much into simple ratios, this suggests that the use of the substance poses no significant risk for consumers.

Result

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

5.4 MAN EXPOSED INDIRECTLY VIA THE ENVIRONMENT

At the predicted level of exposure, the Margins of Safety are three and six orders of magnitude for repeat dose/carcinogenicity and developmental effects respectively. While it is important not to read too much into simple ratios, this does suggest that the use of the substance poses no significant risk for man exposed via the environment.

Result

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

5.5 HUMAN HEALTH (PHYSICO CHEMICAL PROPERTIES)

There are no risks from physico chemical properties arising out of the use of SCCPs.

Overall risk assessment conclusion for Human Health (Physico chemical properties):

Result

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

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GLOSSARY

Standard term / Abbreviation	Explanation/Remarks and Alternative Abbreviation(s)
Ann.	Annex
AF	assessment factor
BCF	bioconcentration factor
bw	body weight / *Bw*, *b.w.*
°C	degrees Celsius (centigrade)
CAS	Chemical Abstract System
CEC	Commission of the European Communities
CEN	European Committee for Normalisation
CEPE	European Committee for Paints and Inks
d	day(s)
d.wt	dry weight / dw
DG	Directorate General
DT_{50}	period required for 50 percent dissipation (define method of estimation)
DT_{50lab}	period required for 50 percent dissipation under laboratory conditions (define method of estimation)
DT_{90}	period required for 90 percent dissipation (define method of estimation)
$DT_{90field}$	period required for 90 percent dissipation under field conditions (define method of estimation)
EC	European Communities
EC	European Commission
EC_{50}	median effective concentration
EEC	European Economic Community
EINECS	European Inventory of Existing Commercial Chemical Substances
EU	European Union
EUSES	European Union System for the Evaluation of Substances
f_{oc}	organic carbon factor (compartment depending)
g	gram(s)

gw	gram weight
GLP	good laboratory practice
h	hour(s)
ha	Hectares / *h*
HPLC	high pressure liquid chromatography
IARC	International Agency for Research on Cancer
C_{50}	median immobilisation concentration or median inhibitory concentration 1 / *explained by a footnote if necessary*
ISO	International Standards Organisation
IUPAC	International Union for Pure Applied Chemistry
kg	kilogram(s)
kPa	kilo Pascals
K_{oc}	organic carbon adsorption coefficient
K_{ow}	octanol-water partition coefficient
Kp	solid-water partitioning coefficient of suspended matter
l	litre(s)
log	logarithm to the basis 10
$L(E)C_{50}$	lethal concentration, median
m	Meter
µg	microgram(s)
mg	milligram(s)
MOS	margins of safety
NOAEL	no observed adverse effect level
NOEC	no observed effect concentration
NOEL	no observed effect level
OECD	Organisation for Economic Co-operation and Development
OJ	Official Journal
pH	potential hydrogen -*logarithm* (to the base 10) of he 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
Pa	Pascal unit(s)
PEC	predicted environmental concentration

PNEC(s)	predicted no effect concentration(s)
$PNEC_{water}$	predicted no effect concentration in water
(Q)SAR	quantitative structure activity relation
STP	sewage treatment plant
TGD	Technical Guidance Document[4]
UV	ultraviolet region of spectrum
UVCB	Unknown or Variable composition, Complex reaction products or Biological material
v/v	volume per volume ratio
w/w	weight per weight ratio

[4] Commission of the European Communities, 1996. Technical Guidance Documents in Support of the Commission Directive 93/67/EEC on risk assessment for new substances and the Commission Regulation (EC) No 1488/94 on risk assessment for existing substances. Commission of the European Communities, Brussels, Belgium. ISBN 92-827-801[1234]

Appendix A Quality of aquatic toxicity tests

All of the studies for which experimental detail are available are adequate for risk assessment. Where possible, the method used has been related to the nearest equivalent OECD test method. However, several of the studies appear to have been generated for submission to the US EPA using methods for which there is no OECD equivalent.

It should be noted that in many studies, every effort has been made to try to test the chlorinated paraffin meaningfully at the highest concentration possible. This has involved the use of co-solvents (usually acetone or emulsifiers). EG and G Bionomics found that stable solutions of chlorinated paraffins of 300-500 µg/l could be maintained in test solutions containing 0.5 ml/l of acetone. This is confirmed in the many tests carried out by ICI, where difficulties in maintaining concentrations (i.e. a suspension was formed) above c.a. 500 µg/l is frequently reported. This has not significantly affected the overall conclusions from these tests, since effects were often seen at much lower concentrations, where a true solution could be maintained.

The majority of these tests use acetone as cosolvent (generally at concentrations of 100-500 µl/l). In all cases acetone controls were run, but in some experiments differences were seen in some endpoints between acetone controls and controls, possibly due to growth of microorganisms in the acetone controls, as has been seen in some studies. The OECD test guidelines generally recommend that the co-solvent should be less than 100 µg/l if possible. This has made it difficult in some tests to separate out effects caused by the chlorinated paraffins from that caused by acetone e.g. increased growth of some invertebrates may be attributed to the presence of acetone.

Despite the inherent difficulties in testing these substances of low water solubility, it is clear that a number of effects are occurring at low chlorinated paraffin concentrations and that the tests available are of as good a quality as would be expected for a difficult substance of this type.

With regard to the acute tests, especially the fish ones, no effects were seen at concentrations way in excess of the compounds solubility. This does not necessarily invalidate the tests, it just makes it difficult to assess the concentration the organisms were actually exposed to. The results from these test are useful, in that they show that effects on fish are not likely to occur from short-term exposure. It would not be possible to carry out a short-term fish test (e.g. 96 hour) that showed effects at concentrations less than the water solubility since the substance is not toxic to fish at those concentrations over a short time period. These short-term results are consistent with the onset of effects seen in the long-term studies.

Fish tests

Lindén E, Bengtsson B-E, Svanberg O and Sundström G. The acute toxicity of 78 chemicals and pesticide formulations against two brackish water organisms, the Bleak (*Alburnus alburnus*) and the Harpacticoid (*Nitocra spinipes*). Chemosphere, 1979, 11/12, 843-851.

Test method

These tests were carried out by the Brackish Water Toxicology Laboratory (Swedish Environment Protection Board) using a method that has been developed and tested by the laboratory (may have taken part in an ISO ring test - not clear). No information on GLP.

Procedure

10 Fish exposed at each concentration under static conditions for 96 hours. No aeration was carried out during test. No analytical monitoring for test substance. Substance added as solution in acetone. Concentration of acetone never exceeded 0.5 ml/l.

Comments

The LC_{50} values were all greater than the water solubility of the substance. The test appears to be reliable.

Hoechst AG (1976 and 1977). Unpublished tests with Golden Orfe.

Test method

No details were given. The results were presented as a summary only. No information on GLP.

Procedure

No details given. The chlorinated paraffins appear to have been added directly to the test solution rather than via a stock solution (presumably to test as high a concentration as possible). Possibly a 48-hour test.

Comments

Due to few experimental details the results should be considered to be less reliable. However, the LC_{50}s reported were all greater than the water solubility and so are consistent with all the other short term fish tests.

Howard P H, Santodonato J and Saxena J. Investigation of selected potential environmental contaminants: Chlorinated paraffins. United States Environmental Protection Agency Report EPA 560/2-75-007

Test method

No details given. The results are quoted from a personal communication from W W Johnson of the Fish-Pesticide Research Lab. Columbia, Missouri . This same data was reported in "Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. W W Johnson and M T Finley. United States Department of the Interior Fish and Wildlife Service, Resource Publication 137, Washington D.C., 1980". Most probably an EPA method was used. No information on GLP.

Procedure

No details given. Both short (static) and long-term (flow-through) tests reported.

Comments

Due to few experimental details the results should be considered less reliable. However, the short term LC_{50}s reported were all greater than the water solubility and so are consistent with all the other short term fish tests.

Madeley J R and Maddock B G (1983). Toxicity of a chlorinated paraffin to rainbow trout over 60 days. ICI Report BL/B/2203.

Test method

This was initially a toxicity/bioaccumulation screening study to see if any effects occurred. It was later extended (further concentrations tested) in order to obtain a LC_{50}. The study was carried out to GLP.

Procedure

Groups of 30 fish (no replicates) exposed initially to three concentrations of chlorinated paraffin (measured as 0.1, 0.32 and 1.07 mg/l) plus control plus acetone control (acetone concentration 500 µl/l) for 60 days. Later, two additional concentrations tested (0.033 mg/l and 3.05 mg/l). A flow-through system was used. As well as mortality, effects on the fish behaviour were assessed.

Comments

The highest concentration tested was thought to be present as a suspension. It was found that fish died in small numbers over an extended time period in most test solutions. No concentration caused 100% mortality but there were only three survivors after 60 days at the highest exposure concentration. The fish developed a series of visible sub-lethal effects before death occurred. Death may have occurred due to starvation as a result of reduced feeding activity caused by exposure to the chlorinated

paraffin. Smaller fish were generally found to die earlier than larger fish, and this may explain to some extent the apparently erratic dose-response seen in the test, i.e. mortality was found to be higher at 0.033 mg/l than 0.1 mg/l but more small fish were present in the lower concentration group. The actual LC_{50} values are therefore likely to be relatively imprecise, however the test is useful in that it shows that important sub-lethal effects do occur at relatively low concentrations (starting at around 0.033 mg/l). The test, overall, is probably less reliable (in terms of determining LC_{50}) but does provide useful information.

Hill R W and Maddock B G (1983). Effect of a chlorinated paraffin on embryos and larvae of the sheepshead minnow (*Cyprinodon variegatus*) - study 1. ICI Report BL/B/2326.

Test method

28-day embryo larval test with sheepshead minnow. No protocol number given. but may be an EPA method. Carried out to GLP.

Procedure

40 Embryos (<36 hour) exposed to 5 concentrations (2.4, 4.1, 6.4, 22.1 and 54.8 µg/l; measured values) plus control plus acetone control (acetone concentrations 500 µl/l) using a flow-through system. Replicate tanks were used. Total exposure was 28 days.

Comments

No effects on hatchability and survival of larvae were seen. Length and larval weight were determined at 28 days. There were significant differences in the lengths of the control animals when compared with the acetone control animals. This was not seen in the weights. The animals exposed to chlorinated paraffins were all significantly longer and heavier than the acetone control. Thus no biologically important effects were seen in this test. The test is probably reliable (small problem with control versus solvent control animals).

Hill R W and Maddock B G (1983). Effect of a chlorinated paraffin on embryos and larvae of the sheepshead minnow (*Cyprinodon variegatus*) - study 2. ICI Report BL/B/2327.

Test method

32-day embryo larval test with sheepshead minnow. No protocol number given. but may be an EPA method. Carried out to GLP.

Procedure

The procedure was the same as study 1 above except that higher concentrations were tested (measured as 36.2, 71.0, 161.8, 279,7 and 620.5 µg/l) and the test was carried out for 32 days (i.e. the larvae, once hatched, were exposed for a full 28 days).

Comments

No effects were seen on hatchability or survival of larvae. Again, the length and weight of control larvae were significantly different (larger) than the acetone control animals. The chlorinated paraffin treated larvae were significantly larger than the acetone control at 36.2 and 71.0 µg/l but were significantly reduced at 620.5 µg/l. Thus the NOEC is 279.7 µg/l. The study is probably reliable, but again problems were seen in the acetone controls.

Invertebrate tests

Hüls AG (1984)

Test method

Used method DIN 38412 Teil 11. This is given as one of the standard procedures in the references to OECD 202 and so is probably equivalent. No information on GLP.

Test procedure

Static 24 hour tests using either acetone cosolvent (no concentration given) or an emulsifier. Generally 5-8 test concentrations used. A reference substance $K_2Cr_2O_7$ was used in each test (LC_{50} was always between 0.9 and 1.9 mg/l). Very few other details were given. No information on whether measured or nominal concentrations were used.

Comments

It is unclear if controls and solvent controls were used as well as the reference substance. In some tests with acetone as cosolvent there appears to have been problems maintaining the test concentration at typically 1 mg/l and above. The experiments with emulsifier did not seem to suffer from this problem. The LC_{50} values appear to have been calculated by linear regression, assuming a linear dose-response curve. Given the problems in some tests in maintaining the high test concentrations, the LOEC/NOEC can be considered reliable and the actual value of the LC_{50} can be less reliable.

Hüls AG (1986)

Test method

Reported in IUCLID as being to Directive 84/449/EEC, C.2. No information on GLP.

Test procedure

21-day Study. No other data

Comments

Results only have been provided. At present the results should be considered as less reliable based on a lack of detail.

EG and G Bionomics. The acute and chronic toxicity of a chlorinated paraffin to midges (*Chironomus tentans*). EG and G Bionomics, Aquatic Toxicology Laboratory, Wareham, Massachusetts, June 1983.

Test method

EG and G Bionomics test protocols were use. No information on GLP. The long-term test exposed eggs through to larvae through to adults.

Procedure

A 48-hour static test and a 49 day flow-through test were used. In the acute test, twenty 11-day old larvae were exposed to 5 chlorinated paraffin concentrations (4 replicates at each concentration (5 larvae per replicate) plus control plus solvent control). Stock chlorinated paraffin solution made up in acetone and maximum concentration of acetone of 0.5 ml/l was used in solvent control. No aeration was carried out during the test. Results based on measured concentrations.

The long-term test was carried out using static and a flow-through system at a replacement rate of 8 aquarium volumes/day. The flow-through test vessels contained sediment to a depth of 0.6 cm. Five exposure concentrations were used, along with control and solvent control (maximum acetone concentration of 0.041 ml/l). Each exposure concentration was conducted in quadruplicate. The midges used for the test were received as eggs. The eggs (approximately 447-720) were placed in 40 ml of each chlorinated paraffin solution and the % hatch of these eggs was determined after 3 days. 100 larvae of each treatment were then transferred to the flow-through vessel of the same treatment (25 per replicate), which was operated under static conditions for the first 48 hours exposure to allow the midges to settle and construct dwelling tubes, and then the experiment was run under flow-through conditions. The solutions were inspected daily for emergence of adults. All adults from each treatment were transferred to beakers containing 50 ml of the chlorinated paraffin solution (static conditions). The first 5 egg masses then obtained from each treatment were counted, incubated in 50 ml of test solution and the % hatch was determined. Again measured concentrations were obtained.

Comments

The short term test appears to be reliable.

In the long term test, there were problems in maintaining the highest concentration of chlorinated paraffin tested (chlorinated paraffin was seen floating on top of the test solution). This may have resulted in some contamination of the lower concentrations. This problem was rectified by day 19 of the test and the results are based on measured concentrations over the whole test period. There also appear to have been some

problems with dissolved oxygen at the higher chlorinated paraffin concentrations. This was thought to have been due to the presence of increasing amounts of acetone. The highest concentration had a dissolved oxygen concentration of 4.8 mg/l (54% of saturation) which was claimed to be in excess of the oxygen requirements of the organism. The test is probably reliable.

Thompson R S and Madeley J R (1983). The acute and chronic toxicity of a chlorinated paraffin to Daphnia magna. ICI Report BL/B/235.

Test method

Not test method was identified in the report. The study incorporates a static 48-hour acute test (similar to OECD 202), a 14-day semi-static test (used as a rangefinding study for the 21-day test) and a 21-day flow-through test (similar to OECD 202). The tests were carried out to GLP.

Procedure

The tests appear to follow closely the OECD protocols. The concentrations of chlorinated paraffins were verified by measurement. Stock solutions were made up in acetone and controls and solvent controls were carried out.

Comments

The lowest NOEC from the 21-day study was used in the risk assessment to define the PNEC.

The acute study is reliable.

Several end-points were monitored during the 21-day study and there may have been an effect on one of these endpoints (total offspring/parent) in one control (effects not seen in a duplicate control). Significant effects were seen in the test solutions on other endpoints (e.g. no of dead offspring) from concentrations of 8.9 µg/l and above (no effects seen in any of the controls) and so a clear LOEC of 8.9 µg/l and NOEC of 5 µg/l were determined. This test appears to be reliable.

Madeley J R and Thompson R S (1983). Toxicity of a chlorinated paraffin to mussels (*Mytilus edulis*) over 60 days. ICI Report BL/B/2291.

Test method

This was initially a toxicity/bioaccumulation screening study to see if any effects occurred. It was later extended (further concentrations tested) in order to obtain a LC_{50}. The study was carried out to GLP.

Procedure

Groups of 50 mussels initially exposed to measured concentrations of 0.13 and 0.93 mg/l plus control plus acetone control (acetone concentration 500 µl/l) using a flow-through system. No replicates were carried out. At a later date, three other concentrations (0.013, 0.044 and 0.071 mg/l; measured) were also tested. A qualitative determination of sub-lethal effects on filter feeding activity was also undertaken.

Comments

The highest concentration tested was thought to be a suspension rather than a true solution. Significant mortality was seen at 0.071, 0.13 and 0.93 mg/l and these were used to determine a LC_{50}. Filtering activity was seen to be reduced at the lower two exposure groups but this effect was minimal at 0.013 mg/l. Like the 60-day trout screening study above, this study is probably less reliable but does provide useful information.

Thompson R S and Madeley J R (1983). The acute and chronic toxicity of a chlorinated paraffin to the mysid shrimp (*Mysidopsis bahia*). ICI Report BL/B/2373.

Test method

No protocol numbers were given but the tests seem to be relatively standard 96-hour and 28-day flow through tests. Test carried out to GLP.

Procedure

In the acute test, 20 mysid (<24 hour old in the first series; <72 hour old in the second series) were exposed to chlorinated paraffins in two series; measured concentrations of 14.9, 24.0, 43.9 and 84.4 µg/l and 5.0, 7.1, 13.7 and 23.8 µg/l. In addition controls and solvent controls (150 µl/l acetone) were carried out.

In the 28-day tests, duplicate vessels, each containing 20 mysids/concentration were exposed to measured chlorinated paraffin concentrations of 0.6, 1.2, 2.4, 3.8 and 7.3 µg/l. Control and solvent control (125 µl/l acetone) were also carried out.

Comments

The acute LC_{50} obtained from the two different series were similar (15.5 and 14.1 µg/l). The control throughout series 1 and for the first two days of series 2 were thought to be contaminated with a small amount of chlorinated paraffin. However, no effects were seen in these control and so the tests are probably reliable.

In the chronic tests, rather high levels of parent mortality were seen in controls (20%) and solvent control (27%). No significant differences were seen between mortalities at any test concentration and solvent control but two mortality at 1.2 and 2.4 µg/l were significantly different from control. It was concluded that these deaths were not treatment related but may be due to the acetone co-solvent which appeared to stimulate microbial growth. No significant effects on number of offspring/adult (again there may

have been a problem with the acetone control) or body length was seen. This test, given the problems with the control, is probably less reliable.

Algal tests

Thompson R S and Madeley J R (1983). Toxicity of a chlorinated paraffin to the green alga Selenastrum capricornutum. ICI Report BL/B/2321.

Test method.

No protocol number given. Approximates to OECD 201 but duration was up to 14 days, but could be terminated after 10 days. May have been an EPA method. Test carried out to GLP.

Procedure

Six replicate cultures for control and triplicates of solvent control (100 µl/l acetone) and 5 test concentrations (measured concentrations of 0.11, 0.22, 0.39, 0.57, 0.90 and 1.2 mg/l), 2 control blanks and one blank for solvent control and each concentration were run. Initial algal cell density was 10^4 cells/ml. Cell density was monitored by particle counting.

Comments

There was evidence that some chlorinated paraffin was lost from solution by adsorption/absorption by algae. There were some differences between the cell densities in controls and solvent controls on day 7 and 10. Cell densities in test solutions were significantly lower than solvent control on day 3 onwards (1.2 mg/l) and from day 4 onwards (0.57 and 0.90 mg/l). Growth rates were also significantly lower than solvent control on days 3 to 4 (0.57 mg/l) and days 2 to 3 (1.2 mg/l). NOEC was determined as 0.39 mg/l. EC_{50} s were also determined, but since the maximum reduction in cell biomass seen at the end of the test was 45%, they are all greater than the highest concentration tested. The results are probably reliable.

Thompson R S and Madeley J R (1983). Toxicity of a chlorinated paraffin to the marine alga *Skeletonema costatum*. ICI Report BL/B/2328.

Test method

No protocol number given. Approximates to OECD 201 but duration was up to 14 days, but could be terminated after 10 days. Test carried out to GLP.

Procedure

Six replicate cultures for control and triplicates of solvent control (100 µl/l acetone) and 5 test concentrations (initial measured concentrations of 4.5, 6.7, 12.1, 19.6, 43.1 and 69.8 µg/l), 2 control blanks and one blank for solvent control and each

concentration were run. Initial algal cell density was $0.8 \cdot 10^4$ cells/ml. Cell density was monitored by particle counting and absorbance measurement.

Comments

There was evidence that some chlorinated paraffin was lost from solution by adsorption/absorption by algae. Since effects were seen only over the first few days, the initial measured concentrations were used for calculation. The test substance affected growth during the early stages of the test but by day 10, all cultures had similar cell densities to controls. Again, there was some difference between controls and solvent controls (only significant at the p=0.2 level). After 4 days, the cell densities in the 43.1 and 69.8 µg/l groups were significantly (p=0.01) lower than solvent control. Growth rates were significantly lower than solvent controls in first two days at 19.6, 43.1 and 69.8 µg/l, but recovered after day 3. Thus the NOEC was 12.1 µg/l. The results were consistent with the test substance having increased the duration of the initial lag phase prior to exponential growth, but the recovery of growth rate might have been due to loss of test substance from solution with time. Since the effects were seen over the first 2-3 days, this is probably a reliable 72-96 hour study. As a 10 day study, it is less reliable as it is not clear if the lack of effects seen at the end of the test is real or due to loss of test substance.

Appendix B EUSES Modelling

In the main report, several local emission scenarios were developed for production of short chain length chlorinated paraffins. In order to incorporate all of these in the model, Use Pattern 1 refers only to the production process, with the two different release estimates appearing under the headings production and formulation. In the EUSES printout the uses are identified as shown below.

EUSES printout	Scenario from main report
Use Pattern 1	Production of short chain length chlorinated paraffins
[Production]	Release estimated by TGD defaults
[Formulation]	Release estimated using other data
Use Pattern 2	Formulation and use of metal cutting/working fluids
[Formulation]	Release during formulation of fluids
[Processing]	Release during use of fluids (using lower release estimate)
Use Pattern 3	Use in rubber as a flame retardant
[Processing]	Release during processing step
Use Pattern 4	Formulation and use in leather finishing
[Formulation]	Release during production/formulation of sulphated products (Scenario A)
[Processing]	Release during use in leather finishing (Scenario B)

The PEC_{local} for metal cutting fluids using the higher release estimates and formulation of leather finishing products for Scenario B have been estimated from the PECs for the other scenarios, using the appropriate scaling.

In the regional and continental model, the sum of the highest release figures estimated for each use has been used as input as a worst case approach.

Appendix C Results of Koc determination for short chain length chlorinated paraffins

As a results of the draft risk assessment for the short chain length chlorinated paraffins (SCCPs), industry volunteered to carry out a K_{oc} determination. The reason for this was that they felt that the method used in the Technical Guidance document for determination of K_{oc} might substantially underestimate the adsorption of the substance onto soil and sediment. If this was the case, then the risks to the soil and sediment compartment could be lower than determined in the risk assessment.

K_{oc} value currently used in the risk assessment

The K_{oc} value currently used in the risk assessment is 91,200 l/kg. This is estimated from the equation below (from the Technical Guidance Document), using a log K_{ow} value of 6.

$$\log K_{oc} = 0.81 \cdot \log K_{ow} + 0.10 \qquad \text{- equation 1}$$

$$\log K_{oc} = 4.96 \qquad K_{oc} = 91{,}200 \text{ l/kg}$$

Short chain length chlorinated paraffins are mixtures of compounds with different carbon chain lengths and degrees of chlorination. The log K_{ow} (and hence K_{oc}) value is likely to vary between the components, and would be expected to increase with increasing chlorination and carbon chain length. Measured values for the log K_{ow} indicate that this is indeed found, and values between 4.4 and 8.7 have been measured for various formulations. A value of log K_{ow} of 6 was chosen as it is around the mid point of the range measured, and may represent the log K_{ow} of some of the more common commercial products used (e.g. those containing around 50-55% chlorine contents).

In the risk assessment, the K_{oc} value is important for determining the concentrations in sediment and for determining the PNECs for both soil and sediment.

Measured K_{oc} value (Thompson et al. (1998)

The K_{oc} values of two straight chain chlorinated alkanes were determined:

55% wt Cl n-decane (approx. formula $C_{10}H_{17.2}Cl_{4.8}$)
and 55% wt Cl n-tridecane (approx. formula $C_{13}H_{21.8}Cl_{6.2;}$ ^{14}C-labelled)

The method used was based on OECD 106 but was modified to use a larger water: solid ratio. The experiment was carried out in 3 parts: a study to look at the kinetics of the process, a study where a single application of the chlorinated paraffin was made to the aqueous phase and finally, one where multiple applications to the aqueous phase were made (this was to allow a higher amount of the chlorinated paraffin to be added to the system without exceeding the water solubility of the substance). The concentrations of the substance in the solid and water phase were determined by both ^{14}C measurements and parent compound analysis where possible. However, only in the case of experiments with multiple application of the test substance was the concentration in the water phase above the detection limit of the parent compound analysis. Here, the results obtained by ^{14}C and parent compound measurements were in good agreement.

In the kinetic study, two soils [a loamy sand (0.85% organic carbon) and a loam (14.5% organic carbon)], along with a sediment [mean particle diameter 51 µm (5.8% organic carbon)] were used. In the two other studies to determine the K_{oc}, the same sediment was used, but the soil used was a clay loam (3.4% organic carbon).

The kinetic studies, using 0.4 g dry weight of soil or sediment in 20 ml of aqueous phase (sediment/soil to water ratio 1:50), indicated that equilibrium was reached within 16 hours.

In the single spiking studies, 0.5, 1.0 and 2.0 g dry weight of sediment were used in a total aqueous volume of 250 ml (sediment to water ratio 1:500; 1:250 and 1:125). The chlorinated decane or tridecane (39 µg) was added as a solution in acetone to give an initial chlorinated paraffin concentration of 0.15 mg/l (acetone concentration in test solution 0.1 ml/l).The sediment/water mixtures were then mixed for 17 hours and then the phases were analysed for chlorinated paraffin. In this experiment, although both parent compound and ^{14}C-measurements were used to analyse the water and sediment phases, only the ^{14}C-measurements were sensitive enough to determine the concentration present in the aqueous phase. The mean log K_{oc} value found was 5.42 for the chlorinated tridecane. No significant difference was seen in the K_{oc} determined in experiments using the three different sediment concentrations.

Multiple spiking studies were carried out using 0.5 g dry weight of sediment or soil in 250 ml of test water (sediment/soil to water ratio 1:500). Initially 30 µg of the chlorinated paraffin (as an acetone solution) was added (initial aqueous chlorinated paraffin concentration = 0.12 mg/l). This was shaken for 2 hours and then the spiking and mixing procedure was repeated a further 4 times such that the total addition of chlorinated paraffin was 150 µg (final acetone concentration was 0.05 ml/l). This was then mixed for a further 16 hours. In this case, all parent compound analyses of the aqueous phase were above the limit of detection. For the chlorinated tridecane, good agreement between the concentrations measured in the sediment and water was obtained by both the direct (parent compound) and ^{14}C-measurements. The log K_{oc} values obtained were 5.26 for the sediment and 5.38 for the soil. The geometric mean of all determinations was 5.32. For the chlorinated decane, only parent compound analysis was possible. Here the log K_{oc} values obtained were 5.21 for sediment and 5.36 for soil. The geometric mean was 5.31.

The paper concluded that overall, a log K_{oc} of 5.3 (K_{oc} = 199,526 l/kg) was appropriate for a short chain length chlorinated paraffin with around 55% Cl by weight.

Significance of measured K_{oc} in terms of the risk assessment

The measured K_{oc} value of 199,526 l/kg is higher than the estimated value currently used in the risk assessment of 91,200 l/kg. However, the measured value does indicate that the estimation method used in the Technical Guidance Document is appropriate for this type of substance, since a log K_{ow} value of 6.42 would give a K_{oc} value similar to the measured value (this log K_{ow} value was thought, based on the available measurements, to be a reasonable value for the type of substance used in the K_{oc} determination (Thompson *et al.*, 1998)). Thus, the measured data indicate that a K_{oc} value of 91,200 l/kg is appropriate for a SCCP with log K_{ow} of 6.

Therefore, the key question for the risk assessment is which value of log K_{ow} to use to represent the products currently used. As mentioned above, the value of 6 was chosen as this

appeared to fit in with the measured data available for the most common short chain length chlorinated paraffin products.

In order to consider this further, the PECs and PNECs for several scenarios for the sediment and the terrestrial compartment used in the assessment have been recalculated (using EUSES) using the measured K_{oc} of 199,526 l/kg. The results of this are summarised in the **Table A**.

As can be seen from **Table A**, the PEC/PNEC ratios for the terrestrial compartment have reduced by around a factor of 2 in the local scenarios. A reduction in the PEC/PNEC ratios was also seen for the sediment compartment. However, the PEC/PNEC ratios would still lead to the same conclusions as included in the original risk assessment.

References

Thompson R. S., Gillings E. and Cumming R. I. (1998). Short-chain chlorinated paraffin (55% chlorinated): Determination of organic carbon partition coefficient. Zeneca Confidential Report BL6426/B.

Table A PECs, PNECs and PEC/PNECs for sediment and the terrestrial compartment

Scenario	PEC		PNEC		PEC/PNEC[c]	
	K_{oc} = 91,200 l/kg	K_{oc} = 199,526 l/kg	K_{oc} = 91,200 l/kg	K_{oc} = 199,526 l/kg	K_{oc} = 91,200 l/kg	K_{oc} = 199,526 l/kg
Sediment						
Production (2 sites)	<0.71 and <0.84 mg/kg	<1.48 <1.74	0.88 mg/kg	1.92 mg/kg[a]	<8.1 <9.5	<7.7 <9.1
Metal working (formulation)	8.5 mg/kg	16.6	0.88 mg/kg	1.92 mg/kg[a]	97	86
Metal working (use)	2.8 mg/kg	5.23	0.88 mg/kg	1.92 mg/kg[a]	32	27
Rubber formulations	<0.67 mg/kg	<1.42	0.88 mg/kg	1.92 mg/kg[a]	<7.6	<7.4
Paints and sealing compounds	negligible	negligible	0.88 mg/kg	1.92 mg/kg[a]	negligible	negligible
Leather formulation	153 mg/kg	292 mg/kg	0.88 mg/kg	1.92 mg/kg[a]	1,740	1,521
Leather use	153 mg/kg	292 mg/kg	0.88 mg/kg	1.92 mg/kg[a]	1,740	1,521
Textile applications	negligible	negligible	0.88 mg/kg	1.92 mg/kg[a]	negligible	negligible
Regional	1.16 mg/kg	2.43 mg/kg	0.88 mg/kg	1.92 mg/kg[a]	13	13
Terrestrial compartment (agricultural soil)						
Production (2 sites)	negligible	negligible	0.80 mg/kg	1.76 mg/kg[b]	negligible	negligible
Metal working (formulation)	20.1 mg/kg	21.2	0.80 mg/kg	1.76 mg/kg[b]	251	120
Metal working (use)	5.1 (or 23.2) mg/kg	5.4	0.80 mg/kg	1.76 mg/kg[b]	64 or 290	31
Rubber formulations	<0.073 mg/kg	0.086	0.80 mg/kg	1.76 mg/kg[b]	<0.92	<0.49
Paints and sealing compounds	negligible	negligible	0.80 mg/kg	1.76 mg/kg[b]	negligible	negligible
Leather formulation	385 mg/kg	406 mg/kg	0.80 mg/kg	1.76 mg/kg[b]	4,813	2,307
Leather use	385 mg/kg	406 mg/kg	0.80 mg/kg	1.76 mg/kg[b]	4,813	2,307
Textile applications	negligible	negligible	0.80 mg/kg	1.76 mg/kg[b]	negligible	negligible
Regional	10.8 mg/kg	20.7 mg/kg	0.80 mg/kg	1.76 mg/kg[b]	135	117

[a] $PNEC_{sediment} = K_{susp\text{-}water} \cdot PNEC_{water} \cdot 1000 / RHO_{sed}$ where $K_{susp\text{-}water}$ = 4,988 m^3/m^3

RHO_{sed} = 1,300 kg/m^3

(strictly speaking RHOsusp should be used instead of RHOsed, but this is not yet implemented in EUSES. However, since RHOsusp is 1,150 kg/m^3, if this was used the PNEC would be higher by a factor of 1.13. The resulting PEC/PNECs would be lower by a similar factor)

[b] $PNEC_{soil} = K_{soil\text{-}water} \cdot PNEC_{water} \cdot 1000 / RHO_{soil}$ where $K_{soil\text{-}water}$ = 5,987 m^3/m^3

RHO_{soil} = 1,700 kg/m^3

$PNEC_{water}$ = 0.5 µg/l

[c] PEC/PNEC increased by factor of 10 to take into account the possibility of direct ingestion.

Appendix D Effect of proposed risk reduction measures on the conclusions of the environmental risk assessment

Introduction

Risk reduction measures have been proposed for short-chain chlorinated paraffins for the formulation and use of metal working fluids and formulation and use of leather finishing products, based on the risk assessment for the aquatic compartment. The proposed risk reduction measures take the form of marketing and use restrictions of short-chain chlorinated paraffins in these areas.

In the environmental risk assessment report, a conclusion (**i**) (i.e. further information and/or testing required) was obtained for the soil and sediment compartment for production of chlorinated paraffins (sediment only), formulation and use of metal working fluids and leather finishing products, use in rubber formulations (sediment only) and also at a regional level. This appendix addresses these endpoints further in light of the proposed risk reduction measures and also new information received since the conclusions in the main report were agreed.

Effect of risk reduction measures proposed for short-chain chlorinated paraffins on regional concentrations

Marketing and use restrictions have been proposed for short-chain chlorinated paraffins for the formulation and use of metal working fluids and formulation and use of leather finishing products. Such restrictions will lead to a reduction in emissions to waste water from these applications to essentially zero. This in turn will lead to negligible levels in sediment and soil for these uses (the main route to soil was predicted to be from application of sewage sludge from waste water treatment plants).

For the other two areas where a conclusion (**i**) exists (short-chain chlorinated paraffin production sites and sites manufacturing rubber containing short-chain chlorinated paraffins), the risk reduction measures proposed for leather finishing and metal working applications will have an indirect effect on the PECs by reducing the background (regional) concentration. **Table B** outlines the releases estimated from the various applications in the risk assessment report, along with the possible future releases taking into account the proposed marketing and use restrictions.

In addition to the proposed marketing and use restrictions, further information on regional releases has become available since the original assessment was agreed. Firstly, the Scientific Committee for Toxicity, Ecotoxicity and the Environment (CSTEE) provided unpublished information on the release of short-chain chlorinated paraffins from painted surfaces. They indicated that the total EU release from this source was around 9 tonnes/year, but could be higher due to the presence of surfaces painted in previous years. Assuming a similar contribution from surfaces painted over the previous 10 years, the worst case release estimates from this source would be around 90 tonnes/year in the EU. Thus, the regional release would be 10% of this figure (i.e. 9 tonnes/year) and the continental release would be 81 tonnes/year. These releases are shown in Table 1 and would be to the air compartment.

Secondly, information has been obtained on the possible release from polymeric products (e.g. rubber products) over their working lifetime (UCD, 1998). A release factor of 0.05% of the annual consumption has been recommended for general polymeric products based on data derived for a plasticiser such as diethylhexyl phthalate (DEHP). This figure is based on the estimated amounts volatilised from the major applications, related to the annual consumption of the substance. Thus, although the actual amount of substance present in articles at any one time will be higher than the annual consumption (the lifetime of many products is >1 year), this is accounted for in the way the factor has been derived.

The vapour pressure of DEHP is around $2.2 \cdot 10^{-5}$ Pa at 20°C. The short-chain chlorinated paraffins used in rubber applications typically have high chlorine contents (e.g. 63-71% wt Cl). Recently, Drouillard et al (1997) measured the vapour pressures of several short-chain chlorinated paraffins of known carbon chain length and chlorine content at 25°C and found that the vapour pressure decreased with increasing carbon chain length and degree of chlorination. From the data generated the following equation was derived which allows the vapour pressure to be estimated for any specific short-chain chlorinated paraffin:

$$\log (vp) = -0.353 \cdot (C\ No) - 0.645 \cdot (Cl\ No) + 4.462$$

where vp = vapour pressure (Pa)
C No = number of carbon atoms
Cl No = number of chlorine atoms

This equation has been used to calculate the vapour pressure for every possible combination of carbon chain length and number of chlorine atoms for short-chain chlorinated paraffins, and the results are shown in the Annex at the end of this Appendix. From these results, it can be seen that the vapour pressure for the short-chain chlorinated paraffins with chlorine contents in the range 63-71% is generally between $2.6 \cdot 10^{-4}$ Pa and $1.4 \cdot 10^{-8}$ Pa, with an average vapour pressure of around $3 \cdot 10^{-5}$ Pa at 25°C. Thus, it might be expected that the volatility of the short-chain chlorinated paraffins used in rubber may be similar to that found for DEHP.

As a worst case, the factor of 0.05% will be applied to the annual consumption of short-chain chlorinated paraffins used in rubber (1,310 tonnes/year) to give a total EU release of 655 kg/year from rubber products. Thus the regional release is 65.5 kg/year and the continental release is 589.5 kg/year. These figures are summarised in **Table B**.

Table B Effects of proposed risk reduction measures on release estimates

Source	Release estimates before marketing and use restrictions			Release estimates after marketing and use restrictions		
	Amount released/site (local model)	**Regional release**	**Continental release[d]**	**Amount release/site (local model)**	**Regional release**	**Continental release[d]**
Production (default)		1,000 or 30,000 kg/year to water	500 or 15,000 tonnes/year to water			
Production (site specific)	<0.089 kg/day to water	<26.7 kg/year to water	<9.9 kg/year to water	<0.089 kg/day to water	<26.7kg/year to water	<9.9 kg/year to water
Metal working - formulation	1.3 kg/day to water	2,345 kg/year to water	21,105 kg/year to water	negligible	negligible	negligible
Metal working - use	0.33 or 1.5 kg/day to water	169,000kg/year to water	1,519,000 kg/year to water	negligible	negligible	negligible
Paints and sealing compounds	negligible	negligible	negligible	negligible	negligible	negligible
Rubber (production)	<0.004 kg/day to air/water[a]	<1.2 kg/year to air/water[a]	<10.8 kg/year to air/water[a]	<0.004 kg/day to air/water[a]	<1.2 kg/year to air/water[a]	<10.8 kg/year to air/water[a]
Leather formulation (Scenario A)	0.01-0.12 kg/day to air 20-25 kg/day to water	0.39 kg/year to air 780 kg/year to water	3.51 kg/year to air 7,020 kg/year to water	negligible	negligible	negligible
Leather use	0.5 kg/day to air 25 kg/day to water	39 kg/year to air 1,950 kg/year to water	351 kg/year to air 17,550 kg/year to water	negligible	negligible	negligible
Textile applications	negligible	negligible	negligible	negligible	negligible	negligible
Release from painted surfaces over 10 years		not included	not included		9,000 kg/year to air	81,000 kg/year to air
Release from rubber products over lifetime		not included	not included		65.5 kg/year to air	589.5 kg/year to air
Totals (for EUSES model)		39.39 kg/year to air 204,076 kg/year to water[b,c]	354.5 kg/year to air 1,579,696 kg/year to water[b,c]		9,065 kg/year to air <27.9 kg/year to water[c]	81,589 kg/year to air 20.7 kg/year to water[c]

[a]Release is assumed to be to water for the purposes of the PEC estimation
[b]Includes the default release estimate from production
[c]In the EUSES model, 70% of this is released via a waste water treatment plant and 30% is released directly to surface water
[d]Continental release = total EU release – regional release

The $PEC_{regional}$ obtained using the release estimates taking into account the proposed marketing and use restrictions, and the new exposure data from paints and rubber products, are shown in **Table C**. The values have been estimated using the EUSES model, with the same physico-chemical properties as used in the main risk assessment report. The original $PEC_{regional}$ from the risk assessment report are included for comparison.

Table C Effects of proposed marketing and use restrictions on $PEC_{regional}$

PEC	Value estimated before marketing and use restrictions (from main report)		Value estimated after marketing and use restrictions	
	Value	PEC/PNEC	Value	PEC/PNEC
$PEC_{regional}$ (surface water – dissolved)	0.33 µg/l	0.66	$1.39 \cdot 10^{-4}$ µg/l	$2.8 \cdot 10^{-4}$
$PEC_{regional}$ (sediment)	1.16 mg/kg wet wt	13	$4.85 \cdot 10^{-4}$ mg/kg wet wt	$5.5 \cdot 10^{-3}$
$PEC_{regional}$ (agricultural soil)	10.8 mg/kg wet wt	135	$2.08 \cdot 10^{-3}$ mg/kg wet wt	0.026
$PEC_{regional}$ (natural soil)	0.0115 mg/kg wet wt	0.14	$6.55 \cdot 10^{-4}$ mg/kg wet wt	$8.2 \cdot 10^{-3}$

$PNEC_{surface\ water}$ = 0.5 µg/l
$PNEC_{sediment}$ = 0.88 mg/kg wet wt (equilibrium partitioning method: PEC/PNEC ratio increased by a factor of 10 to take into account possible ingestion of sediment-bound substance)
$PNEC_{soil}$ = 0.80 mg/kg wet wt (equilibrium partitioning method: PEC/PNEC ratio increased by a factor of 10 to take into account possible ingestion of sediment-bound substance)

K_{oc} data relevant to the risk assessment

In the main risk assessment the K_{oc}, and subsequent partition coefficients, are estimated from a log K_{ow} of 6, which represents approximately the mid-point of the values determined for short-chain chlorinated paraffins. The values for these partition coefficients are shown in **Table D**.

Measured data indicate that the K_{oc} for a 55% wt Cl substance is around 199,500 l/kg, which is slightly higher than that used in the main risk assessment (see Appendix C). The partition coefficients for sediment and soil derived from this K_{oc} value are also shown in **Table D**.

Table D Partition coefficients for short-chain chlorinated paraffin

Partition coeffcient	Estimated from log K_{ow} = 6	Based on measured K_{oc} value
K_{oc}	91,200 l/kg	199,500 l/kg
$Kp_{(soil)}$	1,824 l/kg	3,990 l/kg
$Kp_{(sed)}$	4,560 l/kg	9,975 l/kg
$Kp_{(susp)}$	9,120 l/kg	19,950 l/kg
$K_{soil\text{-}water}$	2,736 m^3/m^3	5,985 m^3/m^3
$K_{sed\text{-}water}$	2,281 m^3/m^3	4,988 m^3/m^3
$K_{susp\text{-}water}$	2,281 m^3/m^3	4,988 m^3/m^3

As well as affecting the PECs for sediment and soil, the value of the partition coefficient used in the risk assessment also affects the PNECs for sediment and soil when they are calculated by the equilibrium partitioning method. The PECs and PNECs obtained using the set of partition coefficients based on the measured K_{oc} are summarised in **Table E** (the values based on the log K_{ow} of 6 are shown in **Table C**).

Table E Effects of measured Koc value on $PEC_{regional}$

PEC	K_{oc} value estimated before marketing and use restrictions (from main report: Appendix C)		K_{oc} value estimated after marketing and use restrictions	
	Value	PEC/PNEC	Value	PEC/PNEC
$PEC_{regional}$ (sediment)	2.43 mg/kg wet wt	13	$1.02 \cdot 10^{-3}$ mg/kg wet wt	$5.3 \cdot 10^{-3}$
$PEC_{regional}$ (agricultural soil)	20.7 mg/kg wet wt	117	$3.99 \cdot 10^{-3}$ mg/kg wet wt	0.023

$PNEC_{surface\ water}$ = 0.5 µg/l
$PNEC_{sediment}$ = 1.92 mg/kg wet wt (equilibrium partitioning method: PEC/PNEC ratio increased by a factor of 10 to take into account possible ingestion of sediment-bound substance)
$PNEC_{soil}$ = 1.76 mg/kg wet wt (equilibrium partitioning method: PEC/PNEC ratio increased by a factor of 10 to take into account possible ingestion of sediment-bound substance)

Effects on local PEC/PNEC ratios

PEC_{local} *(production)*

In the risk assessment report, the PEC_{local} for production is estimated using site-specific release and dilution data. The PEC_{local} for production sites will change as a result of the proposed marketing and use restrictions due to a reduction in the $PEC_{regional}$.

Confidential site-specific release information is available for the two current production sites. At one of these sites, an environmental improvement program has been completed since the main report was agreed and this is taken into account in the following PEC calculation. At neither site is sewage sludge applied to agricultural land and so the PEC_{local} (soil) will be similar to the regional background.

At the production sites, the maximum total concentration in the receiving water is 0.032 µg/l for Site 1 and 0.026 µg/l for Site 2. Adsorption onto suspended sediment needs to be taken into account in order to obtain the dissolved concentration ($C_{local(water)}$). These are shown below using the two values for $K_{susp\text{-}water}$ estimated above:

Site 1:	$C_{local(water)}$	= <0.028 µg/l	A
		or <0.025 µg/l	B
Site 2:	$C_{local(water)}$	= <0.023 µg/l	A
		or <0.020 µg/l	B

where $C_{local(water)}$ = total concentration in the receiving water/$(1+Kp_{susp} \cdot 15 \cdot 10^{-6})$
and Kp_{susp} = 9,120 l/kg, based on a log K_{ow} of 6 (A)
or 19,950 l/kg, based on a K_{oc} of 199,500 (B)

The revised $PEC_{regional}$ for surface water is $1.39 \cdot 10^{-4}$ µg/l (using the partition coefficients estimated from a log K_{ow} of 6) or $1.33 \cdot 10^{-4}$ µg/l (using the measured K_{oc} value of 199,500 l/kg) and so the following revised PEC_{local}s can be calculated:

Site 1:	PEC_{local} (surface water) =	$<0.028 + 1.39 \cdot 10^{-4} = <0.028$ µg/l	A
		or $<0.025 + 1.33 \cdot 10^{-4} = <0.025$ µg/l	B
	PEC_{local} (sediment) =	0.056 mg/kg wet wt	A
		or 0.108 mg/kg wet wt	B
Site 2:	PEC_{local} (surface water) =	$<0.023 + 1.39 \cdot 10^{-4} = <0.023$ µg/l	A
		or $<0.020 + 1.33 \cdot 10^{-5} = <0.020$ µg/l	B
	PEC_{local} (sediment) =	0.046 mg/kg wet wt	A
		or 0.087 mg/kg wet wt	B

where PEC_{local} (sediment) = $K_{susp\text{-}water} / P_{susp} \cdot PEC_{local}$ (surface water) $\cdot 1000$

$K_{susp\text{-}water}$ = 2,281 m^3/m^3, based on a log K_{ow} of 6 (A)
or 4,988 m^3/m^3, based on a K_{oc} of 199,500 l/kg (B)
P_{susp} = bulk density of suspended matter = 1,150 kg/m^3

The PNEC for sediment using the equilibrium partitioning method is 0.88 mg/kg wet wt (based on a log K_{ow} of 6) or 1.92 mg/kg wet wt (based on a K_{oc} of 199,500 l/kg). Thus the revised PEC/PNEC ratios for sediment (increased by a factor of 10 to account for direct ingestion of sediment-bound substance) for these two sites are:

Site 1:	PEC/PNEC (sediment)	= 0.64	A
		or 0.56	B
Site 2:	PEC/PNEC (sediment)	= 0.52	A
		or 0.45	B

PEC_{local} (rubber)

In the risk assessment report the PEC_{local} for use in rubber is estimated based on a release rate of 0.004 kg/day to waste water using the default size for waste water treatment plant and river dilution. This lead to a PEC_{local}(surface water) of 0.34 µg/l, a PEC_{local}(sediment) of 0.67 mg/kg wet wt and a PEC_{local}(soil) of 0.073 mg/kg wet wt. and gave a PEC/PNEC ratio >1 for sediment but <1 for agricultural soil and surface water.

The PEC_{local}(sediment) for rubber depends on both the regional surface water concentration and the partition coefficients used in a similar manner to that outlined above for the production sites.

The recalculated values, taking into account the measured K_{oc} value and the likely reduction in the $PEC_{regional}$(surface water), are shown below:

Release rate to water at site	= 0.004 kg/day
Size of waste water treatment plant	= 2,000 m^3/day
Influent concentration	= 2 µg/l
Removal during waste water treatment	= 93%
Effluent concentration	= 0.14 µg/l
Dilution in receiving water	= 10

Kp_{susp}	= 9,120 l/kg, based on a log K_{ow} of 6	(A)
	or 19,950 l/kg, based on a K_{oc} of 199,500	(B)
$C_{local(water)}$	= 0.012 µg/l	(A)
	or 0.011 µg/l	(B)

The revised $PEC_{regional}$ for surface water is $1.39 \cdot 10^{-4}$ µg/l (using the partition coefficients estimated from a log K_{ow} of 6) or $1.33 \cdot 10^{-4}$ µg/l (using the measured K_{oc} value of 199,500 l/kg) and so the following revised PEC_{locals} can be calculated:

PEC_{local}(surface water)	= $0.012 + 1.39 \cdot 10^{-4} = 0.012$ µg/l	A
	or $0.011 + 1.33 \cdot 10^{-3} = 0.011$ µg/l	B
PEC_{local}(sediment)	= 0.024 mg/kg wet wt	A
	or 0.048 mg/kg wet wt	B

where PEC_{local} (sediment) = $K_{susp\text{-}water} / P_{susp} \cdot PEC_{local}$ (surface water) $\cdot$ 1000

and	$K_{susp\text{-}water}$ = 2,281 m^3/m^3, based on a log K_{ow} of 6	(A)
	or 4,988 m^3/m^3, based on a K_{oc} of 199,500 l/kg	(B)
and	P_{susp} = bulk density of suspended matter = 1,150 kg/m^3	

The PNEC for sediment using the equilibrium partitioning method is 0.88 mg/kg wet wt (based on a log K_{ow} of 6) or 1.92 mg/kg wet wt (based on a K_{oc} of 199,500 l/kg). Thus the revised PEC/PNEC ratios for sediment (increased by a factor of 10 to account for direct ingestion of sediment-bound substance) are:

PEC/PNEC(sediment)	= 0.27	A
	or 0.25	B

Summary of changes to PEC/PNEC ratios and revised conclusions

Table F shows the revised PEC/PNEC ratios for sediment and soil for uses where conclusion (**i**) was indicated in the main report, taking into account the proposed risk reduction measures for metal working and leather finishing fluids (and other new information as indicated above).

The PEC/PNEC ratios are <1 for soil and sediment for all endpoints, and based on these calculations it can be predicted that:

- the risk to sediment and soil at the regional level will be low;

- the risk to sediment from production sites and use in rubber will be low at the local level; and

- the risk to sediment and soil from formulation and use of metal working fluids and formulation and use of leather finishing (leather fat liquoring) products will be low as a direct result of the risk reduction measures proposed for the water compartment.

Table F Summary of changes to PEC/PNEC ratios

Scenario	Original PEC/PNEC[a]	Revised PEC/PNEC[b]
Sediment compartment[c]		
PEC_{local} (production) – 2 sites	<8.1 and <9.5	<0.56-<0.64 and <0.45-<0.52
PEC_{local} Metal working (formulation)	97	<1
PEC_{local} Metal working (use)	32 or 113	<1
PEC_{local} Rubber formulations	<7.6	<0.25-<0.27
PEC_{local} Leather finishing (formulation)	1,740	<1
PEC_{local} Leather finishing (use)	1,740	<1
$PEC_{regional}$	13	5.3×10^{-3}
Soil compartment		
PEC_{local} Metal working (formulation)	251	<1
PEC_{local} Metal working (use)	64 or 290	<1
PEC_{local} Leather finishing (formulation)	4,813	<1
PEC_{local} Leather finishing (use)	4,813	<1
$PEC_{regional}$	135	0.023

[a]PEC/PNEC ratios from main risk assessment report

[b]PEC/PNEC ratios calculated taking into account proposed risk reduction measures for metal working and leather, and also new exposure data for regional release from painted surfaces and rubber products, and site-specific information for production

[c]Strictly speaking, when the equilibrium partitioning method is used for the $PNEC_{sediment}$, the density of suspended sediment (1,150 kg/m3) should be used instead of that of the bulk sediment (1,300 kg/m^3) to ensure that both the PEC and PNEC are determined on the same basis. This is not yet implemented in EUSES. If the correct density was used the PNEC would be higher by a factor of 1.13 and the resulting PEC/PNEC ratios would be lower by a similar factor. This would not change the conclusions drawn

Result

When the proposed risk reduction measures for formulation and use of metal working and leather finishing fluids are taken into account, the conclusion of the risk assessment of all environmental compartments for production and all other uses of short-chain chlorinated paraffins, and also at the regional level, is:

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

This finding may need to be reconsidered once the marketing and use restrictions have had time to take effect, since market conditions may change for the other uses.

References

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.

UCD (1998). Use Category Document – Plastics Additives. Revised Draft for Discussion with OECD, June 1998. Building Research Establishment, produced under contract to the Environment Agency.

ANNEX to Appendix D Vapour Pressure Estimates

The following Table gives the vapour pressures for short-chain chlorinated paraffins calculated using the following equation:

$$\log (vp) = -0.353 \cdot (C\ No) - 0.645 \cdot (Cl\ No) + 4.462$$

where vp = vapour pressure (Pa)
C No = number of carbon atoms
Cl No = number of chlorine atoms

Reference: 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.

No.carbon atoms	No. chlorine atoms	No. hydrogen atoms	Molecular weight	%Cl	Vapour pressure (Pa)
10	1	21	176.5	20.1	1.936E-00
10	2	20	211	33.6	4.385E-01
10	3	19	245.5	43.4	9.931E-02
10	4	18	280	50.7	2.249E-02
10	5	17	314.5	56.4	5.093E-03
10	6	16	349	61.0	1.153E-03
10	7	15	383.5	64.8	2.612E-04
10	8	14	418	67.9	5.916E-05
10	9	13	452.5	70.6	1.340E-05
10	10	12	487	72.9	3.034E-06
11	1	23	190.5	18.6	8.590E-01
11	2	22	225	31.6	1.945E-01
11	3	21	259.5	41.0	4.406E-02
11	4	20	294	48.3	9.977E-03
11	5	19	328.5	54.0	2.259E-03
11	6	18	363	58.7	5.117E-04
11	7	17	397.5	62.5	1.159E-04
11	8	16	432	65.7	2.624E-05
11	9	15	466.5	68.5	5.943E-06
11	10	14	501	70.9	1.346E-06
11	11	13	535.5	72.9	3.048E-07
12	1	25	204.5	17.4	3.811E-01
12	2	24	239	29.7	8.630E-02
12	3	23	273.5	38.9	1.954E-02
12	4	22	308	46.1	4.426E-03
12	5	21	342.5	51.8	1.002E-03
12	6	20	377	56.5	2.270E-04
12	7	19	411.5	60.4	5.140E-05
12	8	18	446	63.7	1.164E-05
12	9	17	480.5	66.5	2.636E-06
12	10	16	515	68.9	5.970E-07
12	11	15	549.5	71.1	1.352E-07
12	12	14	584	72.9	3.062E-08
13	1	27	218.5	16.2	1.690E-01
13	2	26	253	28.1	3.828E-02
13	3	25	287.5	37.0	8.670E-03
13	4	24	322	44.1	1.963E-03
13	5	23	356.5	49.8	4.446E-04
13	6	22	391	54.5	1.007E-04
13	7	21	425.5	58.4	2.280E-05
13	8	20	460	61.7	5.164E-06
13	9	19	494.5	64.6	1.169E-06
13	10	18	529	67.1	2.649E-07
13	11	17	563.5	69.3	5.998E-08
13	12	16	598	71.2	1.358E-08
13	13	15	632.5	73.0	3.076E-09

European Commission

EUR 190010 - European Union Risk Assessment Report
Alkanes, C_{10-13}, chloro-, Volume 4

Editors: B.G. Hansen, S.J. Munn, G. Schoening, M. Luotamo, A. van Haelst, C.J.A. Heidorn G. Pellegrini, R. Allanou, H. Loonen

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The report contains the comprehensive risk assessment of the substance alkanes, C_{10-13}, chloro-. 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 the assessment of risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation considers the emissions and the resulting exposure to the environment and the human population in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection target in the aquatic, terrestrial and soil compartment has been determined. For human health the scenarios for occupational exposure, consumer exposure and human exposed indirectly via the environment have been examinated and the possible risks have been identified.

The risk assessment concludes that there is a risk to aquatic organisms arising from the local emissions of chloro (C_{10-13}) alkanes from metal working applications and leather finishing and from formulation of products for these uses. This conclusion also applies to secondary poisoning for formulation and use in leather finishing and use in metal finishing.

A need for further information for the environment with special attention to soil and sediment has also been identified. A risk for human health could not be determined.
The conclusion of this report will lead to risk reduction measures to be decided by the risk management committee of the Commission.

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