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## Environmental risk assessment: long- chain chlorinated paraffins

Science report

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- **Delivering information, advice, tools and techniques**, by making appropriate products available to our policy and operations staff.



**Steve Killeen**

Head of Science

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- British Lubricants Federation;
- British Rubber Manufacturers Association;
- British Adhesives and Sealants Association.

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# Executive summary

This Risk Assessment Report has been produced by the Environment Agency to complement the reviews of short-chain chlorinated paraffins and medium-chain chlorinated paraffins that have been carried out under Council Regulation (EEC) 793/3<sup>1</sup> on the evaluation and control of the risks of “existing” substances. The purpose of this risk assessment is to inform risk management decisions for the whole chlorinated paraffin group and to allow the United Kingdom to comment on OSPAR proposals to take priority action on long-chain chlorinated paraffins (LCCPs). Further information on hazards may be forthcoming from the International Council of Chemical Associations High Production Volume (ICCA HPV) initiative in the near future; findings from this work will need to be taken into account in any revision of this assessment.

The term long-chain chlorinated paraffin covers a large group of compounds which vary in terms of carbon chain length, uses, physico-chemical properties and ecotoxicological properties. In order to try to take some of these differences into account, and in order to carry out a more meaningful exposure assessment, the LCCPs were subdivided into three groups for which representative data could be derived. The subgroups chosen were:

- C<sub>18–20</sub> liquid products;
- C<sub>>20</sub> liquid products;
- C<sub>>20</sub> solid products.

These groups were chosen because significant differences were found between the uses (and hence their potential for release to the environment) and physico-chemical properties (and hence their environmental behaviour) of these products. The risk characterisation considers the risks from these three subgroups individually and the combined risk from the LCCP group as a whole.

The methodology used in this assessment follows that given in the EU Technical Guidance Document<sup>2</sup> for risk assessment of existing substances.

## **PBT Assessment**

An assessment of the PBT (persistent, bioaccumulative and toxic) status of LCCPs has been made using the available measured and calculated data. The available data suggest that these substances do not meet the screening criteria for PBT classification.

### Persistence

Based on the laboratory studies and other data available, LCCPs are unlikely to be readily or inherently biodegradable. Although there is some evidence that they may biodegrade in the environment, it is thought likely that this process will be sufficiently slow that LCCPs meet the P or vP (very persistent) criteria.

### Bioaccumulation

Although the bioconcentration of LCCPs has been investigated in laboratory studies,

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<sup>1</sup> O.J. No L084, 05/04/1993, p. 0001 - 0075

<sup>2</sup> Technical Guidance Document, Part i-V, ISBN 92-827-801[1234]

none of the available data are considered sufficiently robust to allow a reliable bioconcentration factor (BCF) to be determined. Based on estimates of BCF – and taking the known accumulation properties of structurally similar substances into account – the BCF for LCCPs is considered to be <2,000 l/kg. Thus it is concluded that LCCPs are unlikely to meet the B or vB (very bioaccumulative) criteria.

### Toxicity

The available data indicate that the chronic NOEC for LCCPs is 0.029 mg/l. This value was obtained from tests with *Daphnia magna* with a C<sub>18-20</sub> liquid chlorinated paraffin. Other data suggest that the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins are not toxic to aquatic organisms. Therefore, based on these data, LCCPs do not meet the toxicity criterion from the marine risk assessment guidance.

### **“Quantitative” risk assessment: comparison of exposure with effects**

The risks from the normal use of LCCPs to water, sediments, soil and predators have been assessed by the application of standard models to the information available. The dataset is reasonably complete for this purpose, but there are some areas of uncertainty where further information could be valuable. This assessment therefore makes recommendations about the significance of the data gaps/data uncertainties, and suggests where further research should be focused.

The research involved searching publicly-available sources, and also extensive consultation with producers and users of LCCPs. The main uses of these substances are as additives in PVC, rubber, sealants and adhesives, paints and coatings, metal cutting/working fluids, leather fat liquors and textile treatments. Finished products containing LCCPs (e.g. PVC products and rubber products etc.) can act as sources of emission of LCCPs over the products' lifetime.

The potential emissions to the environment for the key life-cycle stages were estimated based on information from industry research, Emission Scenario Documents or, in the absence of any other information, worst case default assumptions. Using the available information, risk characterisation ratios (also known as PEC/PNEC ratios) greater than 1 (indicating an unacceptable risk for the environment) were identified for some uses (see below).

It should be noted that the available toxicity data for aquatic organisms are difficult to interpret and the choice of a suitable PNEC for protection of surface water and marine water is problematic. A conservative approach has been taken in the assessment to determine whether further research is needed in this area. The suitability of the equilibrium partitioning method for determining the PNEC for sediment (and also soil) is also unclear.

Some information provided by industry has been treated as confidential and is not included in the report, although the data have been used to inform the development of appropriate emission scenarios. These data are included in a confidential annex supporting the assessment, which is available via the Project Manager where appropriate.

The overall conclusions of the risk assessment are:

#### **1. There are risks associated with certain life-cycle stages, as indicated below.**

These risks are identified using the best information available. There are many data gaps, and where these occur, estimates have been made, which inevitably increase the uncertainty in any risk identified and conclusion drawn. It is recognised

that further information on both the intrinsic properties of LCCPs, their pattern of use and their emissions may help reduce this level of uncertainty.

<b>Life-cycle stage</b>	<b>Compartment at possible risk</b>
Use in emulsifiable metal cutting/ working fluids – intermittent release	Freshwater sediment Terrestrial predators Marine water Marine sediment
Use in textiles	Terrestrial predators Marine sediment

**2. Further information would be useful to revise the PECs for these scenarios**

The uncertainty about these findings above could be reduced with:

- clarification of whether LCCPs are used in emulsion metal cutting/working fluids;
- clarification of the current disposal practices of emulsion metal cutting/working fluids containing LCCPs.
- information on the emissions to the environment from textile processes using LCCPs.

**3. There are uncertainties associated with the PNEC for sediment.**

Some PEC/PNEC ratios are >1 for sediment. Toxicity testing with sediment dwelling organisms could be considered to reduce the uncertainties in the PNEC for sediment.

**4. There are some uncertainties with the PNEC and PEC for secondary poisoning.**

Some PEC/PNEC ratios are >1 for secondary poisoning for terrestrial predators (earthworm food chain). An earthworm bioaccumulation test with a C<sub>18-20</sub> liquid chlorinated paraffin could be considered to reduce the uncertainties in the PEC for secondary poisoning. However, the need for such testing is considered a low priority at present.

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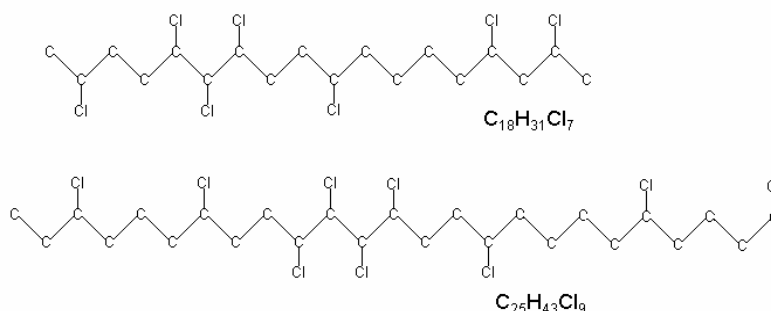
# 1. General substance information

## 1.1 Identification of the substance

This assessment covers chlorinated paraffins with carbon chain lengths  $\geq C_{18}$ . These are known as long-chain chlorinated paraffins (LCCPs). The IUCLID database contains information under the following two CAS numbers that is relevant to this assessment:

CAS No:	85422-92-0	63449-39-8
EINECS No:	287-196-3	264-150-0
EINECS Name:	Paraffin oils, chloro	Paraffin waxes and hydrocarbon waxes, chloro
Molecular formula:	$C_nH_{2n+2-y}Cl_y$ , where $n \geq 18$	$C_nH_{2n+2-y}Cl_y$ , where $n=18-32$ and $y=4-30$

Example structural formulae:



Molecular weight: see Section 1.2.1

Synonyms (see also below) Chlorinated paraffin wax; chloroparaffin; chlorinated paraffin waxes and hydrocarbon waxes; hydrocarbon waxes, chlorinated; chlorparaffin; paraffin oils and hydrocarbon oils, chloro; long-chain chlorinated paraffins; LCCPs.

The commercially supplied products can be considered as complex mixtures as they contain components with 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 atom. The complex nature of the products reflects the nature of the starting materials and production process and does not arise as a result of the deliberate mixing together of different chlorinated paraffin products. In this report the substances will be identified by carbon chain length range and degree of chlorination wherever possible.

Two other groups of chlorinated paraffins are made commercially. These are known as short-chain (typically  $C_{10-13}$ , also known as SCCPs) and medium-chain (typically  $C_{14-17}$ , also known as MCCPs) chlorinated paraffins. Information on these other types of chlorinated paraffins is only included in this report when it is considered to be relevant to the assessment of the long-chain chlorinated paraffins.

There are many different CAS numbers that can apply to chlorinated paraffins (Back *et al.*, 1994; IARC, 1990). Some of these CAS numbers would also potentially be applicable to, or may also cover, long-chain chlorinated paraffins, although the main CAS numbers used in the IUCLID database are those reported above. These alternate CAS numbers are shown in Table 1.1 below.

**Table 1.1 Alternative CAS numbers for LCCPs**

CAS Number	Identity	EINECS Number
61788-76-9	Alkanes, chloro	263-00-4
68920-70-7	Alkanes, C <sub>6-18</sub> , chloro	272-924-4
84082-38-2	Alkanes, C <sub>10-21</sub> , chloro	281-985-6
84776-06-7	Alkanes, C <sub>10-32</sub> , chloro	283-930-1
84776-07-8	Alkanes, C <sub>16-27</sub> , chloro	283-931-7
85049-26-9	Alkanes, C <sub>16-35</sub> , chloro	285-195-2
85535-86-0	Alkanes, C <sub>18-28</sub> , chloro	287-478-6
97659-46-6	Alkanes, C <sub>10-26</sub> , chloro	307-451-5
97553-43-0	Paraffins (petroleum), normal C <sub>&gt;10</sub> , chloro	307-202-0
106232-85-3	Alkanes, C <sub>18-20</sub> , chloro	not on EINECS
106232-86-4	Alkanes, C <sub>22-40</sub> , chloro	not on EINECS
108171-27-3	Alkanes, C <sub>22-26</sub> , chloro	not on EINECS

In the literature, similar LCCPs may often be referred to in different ways with regard to the carbon chain length, for example C<sub>>20</sub> and C<sub>22-26</sub> are frequently used. The fact that these different terms are used does not necessarily mean that they are referring to different substances. The actual chain length composition of most LCCPs appears to fall into two categories, those centring on a carbon chain length of around C<sub>18</sub> or C<sub>19</sub>, (usually termed C<sub>18-20</sub> products) and those centring on a carbon chain length of around C<sub>24</sub> or C<sub>25</sub> (usually termed C<sub>>20</sub> products). The composition of these products is discussed further in the following sections.

It is possible that related substances called chloroalkenes have been available in the recent past or are still in production. These are considered further in Appendix H.

## 1.2 Purity/impurity, additives

### 1.2.1 Purity/impurities

Table 1.2 shows the theoretical percentage by weight chlorine contents (% wt. Cl) of several compounds that can be considered as LCCPs.

The amount of chlorine present in the commercial products is usually expressed as an average percentage by weight. The commercial products contain many components with different carbon chain lengths and different numbers of chlorine atoms. Standard analytical methods do not permit separation and identification of these individual components and so it is not possible to identify exactly which compounds are present within the product, although Table 1.2 can be used as a guide to indicate the possible components present.

Work by Könnecke and Hahn (1962) provides a basis for estimation of the distribution of chlorine contents present in a given product. This work gives a prediction of approximately 80 per cent of the isomers present lying within  $\pm 10$  per cent of the stated average chlorine content and 90 per cent within  $\pm 15$  per cent. Thus in a long-chain 50% wt. Cl product, there is likely to be only around 5 per cent of mono- and dichlorinated isomers present, with a correspondingly low amount of highly chlorinated isomers present. The work was carried out with  $C_{26}$  chlorinated paraffins, but it is thought that a similar distribution will apply to chlorinated paraffins of other carbon chain lengths.

**Table 1.2 Theoretical chlorine contents of some long-chain chlorinated paraffins**

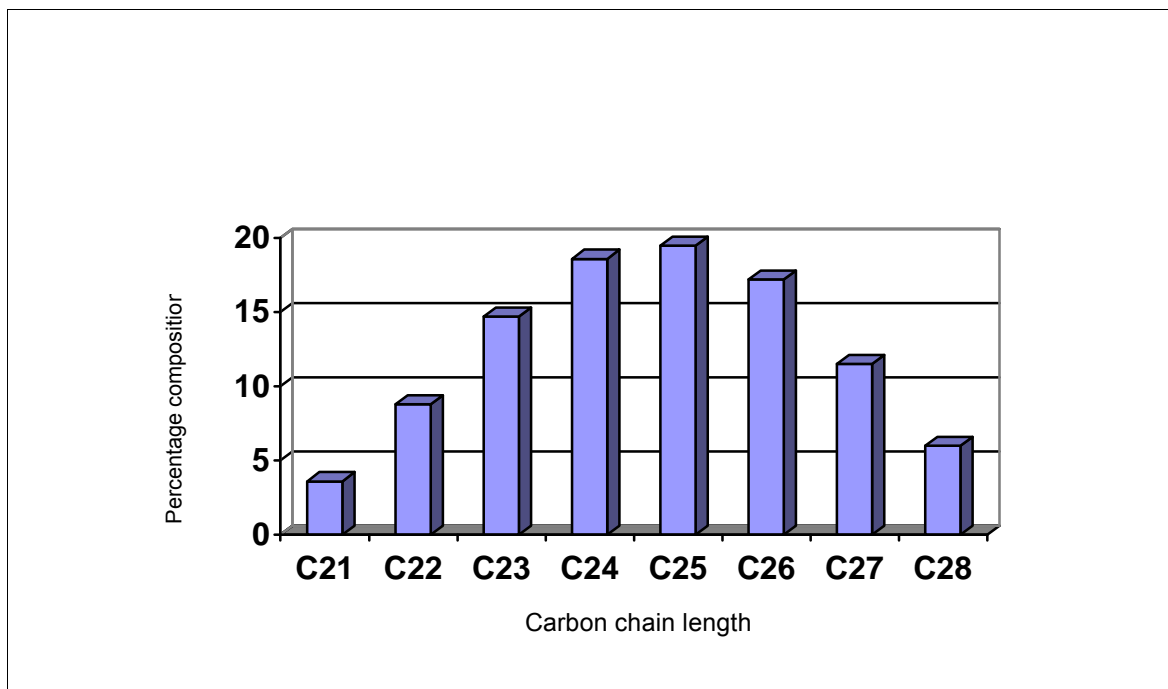
Formula	Molecular weight	% Cl by weight	Formula	Molecular weight	% Cl by weight
$C_{18}H_{36}Cl_2$	323	22.0%	$C_{24}H_{40}Cl_{10}$	683	52.0%
$C_{18}H_{33}Cl_5$	427	41.6%	$C_{24}H_{29}Cl_{21}$	1,063	70.2%
$C_{18}H_{30}Cl_8$	530	53.6%			
$C_{18}H_{22}Cl_{16}$	806	70.5%	$C_{25}H_{49}Cl_3$	456	23.4%
			$C_{25}H_{45}Cl_7$	594	41.9%
$C_{19}H_{38}Cl_2$	337	21.1%	$C_{25}H_{41}Cl_{11}$	732	53.4%
$C_{19}H_{35}Cl_5$	441	40.3%	$C_{25}H_{30}Cl_{22}$	1,111	70.3%
$C_{19}H_{32}Cl_8$	544	52.2%			
$C_{19}H_{23}Cl_{17}$	855	70.6%	$C_{26}H_{51}Cl_3$	470	22.7%
			$C_{26}H_{46}Cl_8$	642	44.2%
$C_{20}H_{40}Cl_2$	351	20.2%	$C_{26}H_{43}Cl_{11}$	746	52.4%
$C_{20}H_{36}Cl_6$	489	43.6%	$C_{26}H_{30}Cl_{24}$	1,194	71.4%
$C_{20}H_{33}Cl_9$	593	53.9%			
$C_{20}H_{24}Cl_{18}$	903	70.8%	$C_{27}H_{53}Cl_3$	484	22.0%
			$C_{27}H_{48}Cl_8$	656	43.3%
$C_{21}H_{41}Cl_3$	400	26.7%	$C_{27}H_{24}Cl_{12}$	794	53.7%
$C_{21}H_{38}Cl_6$	503	42.3%	$C_{27}H_{31}Cl_{25}$	1,243	71.4%
$C_{21}H_{35}Cl_9$	607	52.7%			
$C_{21}H_{25}Cl_{19}$	952	70.9%	$C_{28}H_{55}Cl_3$	498	21.4%
			$C_{28}H_{50}Cl_8$	670	42.4%
$C_{22}H_{43}Cl_3$	414	25.8%	$C_{28}H_{46}Cl_{12}$	808	52.7%
$C_{22}H_{39}Cl_7$	552	45.1%	$C_{28}H_{33}Cl_{25}$	1,257	70.6%
$C_{22}H_{36}Cl_{10}$	655	54.2%			
$C_{22}H_{26}Cl_{20}$	1,000	71.0%	$C_{29}H_{56}Cl_4$	546	26.0%
			$C_{29}H_{51}Cl_9$	719	44.5%
$C_{23}H_{45}Cl_3$	428	24.9%	$C_{29}H_{47}Cl_{13}$	857	53.9%
$C_{23}H_{41}Cl_7$	566	43.9%	$C_{29}H_{33}Cl_{27}$	1,340	71.6%
$C_{23}H_{38}Cl_{10}$	669	53.1%			
$C_{23}H_{27}Cl_{21}$	1,049	71.1%	$C_{30}H_{59}Cl_3$	526	20.3%
			$C_{30}H_{53}Cl_9$	733	43.6%
$C_{24}H_{47}Cl_3$	442	24.1%	$C_{30}H_{49}Cl_{13}$	871	53.0%
$C_{24}H_{43}Cl_7$	580	42.9%	$C_{30}H_{35}Cl_{27}$	1,354	70.8%

Zitko and Arsenault (1977) analysed the distribution of paraffin chain lengths after dechlorination of a  $C_{>20}$ , 42% wt. Cl product. These are shown in Figure 1.1. As can be seen the chain length distribution centres on around  $C_{24-25}$  for this type of product.

The purity of the chlorinated paraffin is related to the purity of the n-paraffin used as feedstock. In Western Europe, chlorinated paraffins are made from purified n-paraffin

feedstocks containing no more than 1–2 per cent isoparaffins and <100 mg aromatics/kg (the aromatics are removed by treatment of the n-paraffin with sulphuric acid). For some high stability applications, n-paraffins with <1 per cent isoparaffins and <10–100 mg aromatics/kg are used (BUA, 1992).

Information has been provided by industry on the levels of chlorinated paraffins, other than long-chain, that might be present in the commercial products. The data are based on the known impurities present in the two main paraffin feedstocks used to make the various products. These are shown in Table 1.3.



**Figure 1.1 Carbon chain length distribution for C<sub>>20</sub> products**

**Table 1.3 Chlorinated paraffin impurities present in the long-chain chlorinated paraffins**

Feedstock	Impurities
C <sub>18-20</sub>	<1% C <sub>16</sub> typically 17% C <sub>17</sub> (possible range 10–20%)
C <sub>&gt;20</sub>	0% C <sub>19</sub> <0.2% C <sub>20</sub>

As can be seen from Table 1.3, the C<sub>18-20</sub> chlorinated paraffin products are likely to contain a significant amount of C<sub>16-17</sub> chlorinated paraffin, which is also a constituent of medium-chain chlorinated paraffin products. The C<sub>>20</sub> chlorinated paraffin products are virtually free from other chlorinated paraffin impurities. The presence of C<sub>16-17</sub> chlorinated paraffins in the C<sub>18-20</sub> product is considered in Appendix G and the risk characterisation.

It is also possible that chlorinated paraffins with carbon chain lengths of C<sub>18</sub> and above may be present in other types of chlorinated paraffins, such as the medium-chain chlorinated paraffins. The purity of a typical 52% wt. Cl medium-chain chlorinated

paraffin was reported to be with 0.16 per cent C<sub>18</sub> chlorinated paraffins and <0.1 per cent C<sub>19</sub> chlorinated paraffins (Thompson *et al.*, 2001). Thus the amounts of C<sub>>18</sub> chlorinated paraffins present in short- and medium-chain chlorinated paraffins can be considered to be negligibly small.

### 1.2.2 Additives

It is known that additives/stabilisers such as long-chain epoxidised soya oil or glycidyl ether are added to some chlorinated paraffins to inhibit the release of hydrogen chloride at elevated temperatures (BUA, 1992). These are used at concentrations <0.05 per cent by weight (Campbell and McConnell, 1980). For some high thermal stability formulations other additives, such as organophosphorus compounds, have been reported to be used in conjunction with these at <1 per cent by weight (BUA, 1992).

## 1.3 Physico-chemical properties

The physico-chemical properties of LCCPs are discussed below and the available experimental data are summarised in Table 1.4.

The substances under consideration in this assessment contain components covering a wide range of carbon chain lengths (from C<sub>18</sub> to around C<sub>30</sub>) and chlorine contents. This variety means that a range of values for each physico-chemical property is to be expected, reflecting the complex nature of the products. The assessment methods outlined in the Technical Guidance Document (TGD) generally assume that a single value for certain key properties (e.g. water solubility, vapour pressure, Henry's Law constant and the log Kow value) will be available. For LCCPs, this assumption may oversimplify the environmental modelling and hence the assessment. Therefore, as well as outlining the available measured data, the following sections also consider estimated data and trends, and indicate the value or values that will be used in the assessment for these important properties.

In order to carry out the environmental risk assessment for this group of substances, a balance has to be struck between:

- the level of detail required to describe representatively the various products supplied in terms of their uses, environmental exposure, fate, behaviour and effects;
- overcomplicating the assessment so that no conclusion can be drawn from the available data.

To this end, the assessment will assume that the entire group of LCCPs can be broken down into essentially three subgroups (see Section 1.4). These subgroups reflect:

- the differences in the starting materials used (which determine the carbon chain length distribution in the final product);
- the physico-chemical properties (for example, some products are liquids and some are solids);
- the different uses between the main types of LCCPs supplied.

The properties appropriate to these three subgroups are discussed in the following sections and are summarised in Section 1.4.9. It should be remembered that these three subgroups still contain components with widely varying physico-chemical properties and so the approach taken is still an approximation. For this reason the physico-chemical properties for these subgroups have been selected with a view to carrying out a "realistic worst case" risk assessment, as outlined in the TGD.

**Table 1.4 Measured physico-chemical properties of LCCPs**

Property	Substance	Value	Reference	Remarks
Melting point	C <sub>18-20</sub> , 20% wt. Cl	-26°C	Ineos Chlor, 2005	The commercial products do not have a distinct melting point. The values quoted refer to the pour point or softening point.
	C <sub>18-20</sub> , 40% wt. Cl	-15°C	Ineos Chlor, 2005	
	C <sub>18-20</sub> , 44% wt. Cl	-25°C	IUCLID, 2000a	
	C <sub>18-20</sub> , 47% wt. Cl	-9°C	Ineos Chlor, 2005	
	C <sub>18-20</sub> , 50% wt. Cl	2°C	Ineos Chlor, 2005	
	C <sub>18-20</sub> , 52% wt. Cl	0°C	IUCLID, 2000a	
	C <sub>&gt;20</sub> , 42% wt. Cl	-30°C	IUCLID, 2000a	
		-15°C	Ineos Chlor, 2005	
	C <sub>&gt;20</sub> , 46% wt. Cl	4°C	Ineos Chlor, 2005	
	C <sub>&gt;20</sub> , 48% wt. Cl	-15°C	IUCLID, 2000a	
		10°C	Ineos Chlor, 2005	
	C <sub>&gt;20</sub> , 70% wt. Cl	95–105°C; 100°C	IULICD, 2000a	
Boiling point (at ntp)		>200°C	IUCLID, 2000a	Decomposition occurs with liberation of HCl at temperatures below their boiling point.

Table 1.4 continued overleaf

Table 1.4 continued

Property	Substance	Value	Reference	Remarks
Density (at 20–25°C)	C <sub>18–20</sub> , 20% wt. Cl	0.92 g/cm <sup>3</sup>	Ineos Chlor, 2005	The density decreases with increasing temperature.
	C <sub>18–20</sub> , 35% wt. Cl	1.1 g/cm <sup>3</sup>	IUCLID, 2000a	
	C <sub>18–20</sub> , 40% wt. Cl	1.13 g/cm <sup>3</sup>	Ineos Chlor, 2005	
	C <sub>18–20</sub> , 47% wt. Cl	1.21 g/cm <sup>3</sup>	Houghton, 1993	
			Ineos Chlor, 2005	
	C <sub>18–20</sub> , 50% wt. Cl	1.27 g/cm <sup>3</sup>	Houghton, 1993	
			Ineos Chlor, 2005	
	C <sub>18–20</sub> , 52% wt. Cl	1.3 g/cm <sup>3</sup>	IUCLID, 2000a	
	C <sub>&gt;20</sub> , 42% wt. Cl	1.16 g/cm <sup>3</sup>	Houghton, 1993	
			Ineos Chlor, 2005	
	C <sub>&gt;20</sub> , 46% wt. Cl	1.22 g/cm <sup>3</sup>	Ineos Chlor, 2005	
	C <sub>&gt;20</sub> , 48% wt. Cl	1.26 g/cm <sup>3</sup>	Houghton, 1993	
		1.24 g/cm <sup>3</sup>	Ineos Chlor, 2005	
	C <sub>&gt;20</sub> , 70% wt. Cl	1.63 g/cm <sup>3</sup>	IUCLID, 2000a	
Vapour pressure	C <sub>23</sub> , 42% wt. Cl	2.67×10 <sup>-3</sup> Pa at 65°C	Howard <i>et al.</i> , 1975	Few details are available on how the values were determined.
	C <sub>&gt;20</sub> , 42% wt. Cl	2.67×10 <sup>-4</sup> Pa at 80°C	IUCLID, 2000a; BUA, 1992	
	C <sub>23</sub> , 48% wt. Cl	2.67×10 <sup>-3</sup> Pa at 65°C	Howard <i>et al.</i> , 1975	
	C <sub>23</sub> , 54% wt. Cl	2.67×10 <sup>-3</sup> Pa at 65°C	Howard <i>et al.</i> , 1975	
Water solubility	C <sub>25</sub> , 42% wt. Cl	0.003 mg/l at 16–20°C	Campbell and McConnell, 1980	Seawater, radiochemical measurement Radiochemical measurement Radiochemical measurement.
	C <sub>25</sub> , 43% wt. Cl	0.0066 mg/l at 25°C	Madeley and Gillings, 1983	
	C <sub>25</sub> , 70% wt. Cl	0.0059 mg/l at 25°C	Madeley and Gillings, 1983	
Log octanol-water partition coefficient	C <sub>21.5</sub> , 42% wt. Cl	7.63–12.83	Renberg <i>et al.</i> , 1980	Determined by a high performance thin layer chromatography method.
	C <sub>22–26</sub> , 42% wt. Cl	9.29–>12.83		
	C <sub>18–26</sub> , 44% wt. Cl	7.46–11.48		
	C <sub>22–26</sub> , 49% wt. Cl	8.69–12.83		
Flash point	C <sub>≥18</sub> , >42% wt. Cl	>210°C	IUCLID, 2000a	
Autoflammability		not stated	IUCLID, 2000a	
Explosivity		not applicable	IUCLID, 2000a	
Oxidising properties		no oxidising properties	IUCLID, 2000a	

Appendix E considers the effects of the uncertainty in some of these key physico-chemical properties on the outcome of the risk assessment.

## 1.4 Physical state (at n.t.p.)

The actual physical form of the chlorinated paraffins can vary from free-flowing mobile liquids to highly viscous, glassy liquids, to waxy solids and powders (BUA, 1992; Houghton, 1993).

The commercial products supplied can be broadly divided into the subgroups outlined in Table 1.5 based on their carbon chain length distributions, chlorine contents, uses and physical state.

**Table 1.5 Subgroups of commercial LCCPs**

<b>Carbon chain</b>	<b>Chlorine contents</b>	<b>Physical state</b>
C <sub>18-20</sub>	ca. 30–35% wt. Cl ca. 44% wt. Cl ca. 48–52% wt. Cl	LIQUIDS
C <sub>&gt;20</sub>	ca. 40–43% wt. Cl ca. 48–54% wt. Cl ca. 70–72% wt. Cl	LIQUIDS  SOLID

These three subgroups will be considered in the assessment. This approach allows the differences in the physico-chemical properties and uses, and hence environmental releases and exposures of these three subgroups, to be taken into account.

It is also possible that some other LCCPs could be supplied with chlorine contents outside these ranges, for example a C<sub>>20</sub>, 12% wt. Cl solid product was reported in BUA (1992), but these are likely to be produced for specialist applications and will account for only a very small proportion of the total use of LCCPs. The above subgroups are believed to cover the major long-chain chlorinated paraffin products currently used in the EU.

### 1.4.1 Melting point

As the commercially supplied products contain many components, they do not have a distinct melting point. Pour points or softening points for several LCCPs are reported in IUCLID (2000a). These give values in the range -30 to -10°C for products with chlorine contents of 42–48% by weight, values around 0°C for products with chlorine contents around 50–52% by weight and around 100°C for products with chlorine contents around 70 per cent by weight. Similar values are also reported in BUA (1992) and Ineos Chlor (2005).

For this assessment, the melting point will be assumed to be around -30°C for LCCP products with chlorine contents in the 40–50% wt. Cl range, 0°C for products with chlorine contents in the 50–60% wt. Cl range and 100°C for products with chlorine contents around 70% wt. Cl. In terms of the procedures used in the TGD, the actual



value for the melting point is not important, but it is necessary to distinguish between solids and liquids at room temperature.

### 1.4.2 Boiling point

It is not possible to determine the actual boiling point of the various commercial products as they generally decompose with evolution of hydrogen chloride at temperatures of >210°C.

The Syracuse Research Corporation MPBPWIN (version 1.28) computer program has been used to estimate the boiling points of several LCCPs from some example chemical structures. The values which were obtained are given in Table 1.6.

**Table 1.6 LCCP boiling point values calculated using the Syracuse Research Corporation MPBPWIN (version 1.28) computer program**

Formula	% wt. Cl	Boiling point
C <sub>18</sub> H <sub>33</sub> Cl <sub>5</sub>	41.6	~413°C
C <sub>18</sub> H <sub>30</sub> Cl <sub>8</sub>	53.6	~467°C
C <sub>20</sub> H <sub>36</sub> Cl <sub>6</sub>	43.6	~454°C
C <sub>20</sub> H <sub>33</sub> Cl <sub>9</sub>	53.9	~508°C
C <sub>25</sub> H <sub>45</sub> Cl <sub>7</sub>	41.9	~530°C
C <sub>25</sub> H <sub>42</sub> Cl <sub>10</sub>	50.9	~583°C
C <sub>25</sub> H <sub>29</sub> Cl <sub>23</sub>	71.3	~827°C
C <sub>30</sub> H <sub>53</sub> Cl <sub>9</sub>	43.6	~623°C
C <sub>30</sub> H <sub>49</sub> Cl <sub>13</sub>	53.0	~695°C
C <sub>30</sub> H <sub>35</sub> Cl <sub>27</sub>	70.8	~956°C

These values are very uncertain, as the same program consistently overestimated the melting points of these substances (this may relate to the fact that the estimates are for pure substances rather than complex products). The predictions indicate that the boiling points of LCCPs are likely to increase with increasing carbon chain length and increasing degree of chlorination.

In terms of the risk assessment, the actual value for the boiling point is not important. The available data clearly indicate that all products will be either liquids or solids at room temperature.

### 1.4.3 Density

Houghton (1993), IUCLID (2000a) and Ineos Chlor (2005) give the densities of various LCCPs at 20–25°C (Table 1.7).

**Table 1.7 LCCP densities**

Carbon chain length	Chlorine content	Density
C <sub>18–20</sub>	20% wt. Cl	0.92 g/cm <sup>3</sup>
	35% wt. Cl	1.1 g/cm <sup>3</sup>
	40% wt. Cl	1.13 g/cm <sup>3</sup>
	47% wt. Cl	1.21 g/cm <sup>3</sup>

Carbon chain length	Chlorine content	Density
	50% wt. Cl	1.27–1.28 g/cm <sup>3</sup>
	52% wt. Cl	1.3 g/cm <sup>3</sup>
C <sub>&gt;20</sub>	42% wt. Cl	1.16 g/cm <sup>3</sup>
	48% wt. Cl	1.22 g/cm <sup>3</sup>
	70% wt. Cl	1.24–1.26 g/cm <sup>3</sup>
		1.63 g/cm <sup>3</sup>

As can be seen from the available data, the density of the product increases with increasing chlorine content.

#### 1.4.4 Vapour pressure

Howard *et al.* (1975) reported that the vapour pressures of C<sub>23</sub> chlorinated paraffins containing 42%, 48% or 54% wt. Cl were all around  $2 \times 10^{-5}$  mmHg ( $2.67 \times 10^{-3}$  Pa) at 65°C. Few details of how these were measured appear to be available.

Several values for the vapour pressure have been reported in IUCLID (2000a). These include a value of 2.66 at 80°C for a C<sub>>20</sub>, 42% wt. Cl product (no units for the vapour pressure are given, but the value was apparently calculated from an effusiometric technique) and a value of  $2.67 \times 10^{-6}$  hPa ( $2.67 \times 10^{-4}$  Pa) at 80°C, again for a C<sub>>20</sub>, 42% wt. Cl product (no details of method).

Ineos Chlor (2005) gives the vapour pressure of a C<sub>>20</sub>, 42% wt. Cl product as  $<2.0 \times 10^{-6}$  mmHg ( $<2.67 \times 10^{-3}$  Pa) at 80°C, determined using an effusiometric technique. This value is undoubtedly the same value as referred to above.

As the measurements have been carried out on commercial products that contain many components, it is likely that the vapour pressures measured represent those of the most volatile components of the product.

Drouillard *et al.* (1998a) determined the sub-cooled liquid vapour pressures of a series of short-chain (C<sub>10–13</sub>) chlorinated paraffins at 25°C using a vapour pressure gas-liquid chromatography technique. They found that vapour pressures of the short-chain chlorinated paraffins decreased with both increasing carbon chain length and degree of chlorination. They derived the following equation relating vapour pressure (in Pa at 25°C) to the number of carbon and chlorine atoms present in a molecule:

$$\log(\text{vapour pressure}) = -(0.353 \times \text{no. of C atoms}) - (0.645 \times \text{no. of Cl atoms}) + 4.462$$

Using this equation, vapour pressures for an LCCP can be estimated. Estimates are shown in Appendix B for all possible combinations of carbon and chlorine numbers. It should be noted that the reliability of this equation for the LCCPs is unknown. The highest predicted vapour pressure for an LCCP is  $2.9 \times 10^{-3}$  Pa at 25°C for C<sub>18</sub>H<sub>37</sub>Cl<sub>1</sub> (12.3% wt. Cl) and the lowest estimated vapour pressure is  $3.3 \times 10^{-26}$  Pa at 25°C for C<sub>30</sub>H<sub>32</sub>Cl<sub>30</sub> (73.1% wt. Cl). Vapour pressures clearly cover an exceptionally wide range.

A further estimate of vapour pressure for LCCPs has been obtained using the Syracuse Research Corporation MPBPWIN (version 1.28) program. This program estimates the vapour pressure at 25°C from chemical structure. The values obtained for some example LCCPs are shown in Table 1.8 (in the calculations the melting point was set to -25°C for the 42–44% wt. Cl substances, 0°C for the 51–54% substances and 100°C for the 71% wt. Cl substances).

**Table 1.8 Vapour pressures for example LCCPs calculated using the Syracuse Research Corporation MPBPWIN (version 1.28) computer program**

Formula	Chlorine content (% wt. Cl)	Vapour pressure
C <sub>18</sub> H <sub>33</sub> Cl <sub>5</sub>	41.6	5.3×10 <sup>-4</sup> Pa (3.9×10 <sup>-6</sup> mmHg)
C <sub>18</sub> H <sub>30</sub> Cl <sub>8</sub>	53.6	2.5×10 <sup>-5</sup> Pa (1.9×10 <sup>-7</sup> mmHg)
C <sub>20</sub> H <sub>36</sub> Cl <sub>6</sub>	43.6	5.1×10 <sup>-5</sup> Pa (3.9×10 <sup>-7</sup> mmHg)
C <sub>20</sub> H <sub>33</sub> Cl <sub>9</sub>	53.9	2.3×10 <sup>-6</sup> Pa (1.8×10 <sup>-8</sup> mmHg)
C <sub>25</sub> H <sub>45</sub> Cl <sub>7</sub>	41.9	6.3×10 <sup>-7</sup> Pa (4.8×10 <sup>-9</sup> mmHg)
C <sub>25</sub> H <sub>42</sub> Cl <sub>10</sub>	50.9	2.7×10 <sup>-8</sup> Pa (2×10 <sup>-10</sup> mmHg)
C <sub>25</sub> H <sub>29</sub> Cl <sub>23</sub>	71.3	1.4×10 <sup>-15</sup> Pa (1.1×10 <sup>-17</sup> mmHg)
C <sub>30</sub> H <sub>53</sub> Cl <sub>9</sub>	43.6	2.4×10 <sup>-9</sup> Pa (1.8×10 <sup>-11</sup> mmHg)
C <sub>30</sub> H <sub>49</sub> Cl <sub>13</sub>	53.0	3.1×10 <sup>-11</sup> Pa (2.3×10 <sup>-13</sup> mmHg)
C <sub>30</sub> H <sub>35</sub> Cl <sub>27</sub>	70.8	6.1×10 <sup>-19</sup> Pa (4.6×10 <sup>-21</sup> mmHg)

The vapour pressure is an important physico-chemical property for the TGD risk assessment methodology. It is used, along with water solubility, to define the Henry's Law constant, which is necessary to estimate the transport of the substance to air in the environment. The vapour pressure also plays a part in the estimation of releases. The available measured vapour pressure data for LCCPs are limited in their coverage of the products available (and in themselves are not consistent) and so the estimated data have to be considered. These estimates show a very wide range of values which makes it extremely difficult to select values to represent the three subgroups considered in this assessment. Based on the estimated data reported above and in Appendix B, the following values at 25°C will be used in the assessment where appropriate (Table 1.9).

**Table 1.9 Representative vapour pressure values for LCCP subgroups, as used in this assessment**

Subgroup	Best representmtative value	Approximate range
C <sub>18-20</sub> liquids (typically 40–52% wt Cl)	2.5×10 <sup>-4</sup> Pa	5×10 <sup>-4</sup> – 2×10 <sup>-8</sup> Pa

Subgroup	Best representative value	Approximate range
C <sub>&gt;20</sub> liquids (typically 40–54% wt. Cl)	2.5×10 <sup>-5</sup> Pa	5×10 <sup>-5</sup> – 3×10 <sup>-15</sup> Pa
C <sub>&gt;20</sub> solids (typically 70% wt. Cl)	1.5×10 <sup>-14</sup> Pa	3×10 <sup>-14</sup> – 1×10 <sup>-23</sup> Pa

For comparison, a vapour pressure of 1.3 – 2.7×10<sup>-4</sup> Pa at 20°C was determined for a medium-chain chlorinated paraffin (C<sub>14–17</sub>, 52% wt. Cl) product (Campbell and McConnell, 1980), and the values selected here are reasonably consistent with this measurement, and also with the information reported below on the relative volatility of these compounds.

For the environmental assessment, the key property derived from the vapour pressure is the Henry's Law constant (H), which is discussed in Section 1.4.8. Here, since the value of H depends on both vapour pressure and water solubility (and both these appear to vary in roughly the same way with carbon chain length and chlorine content), the variation in H for each component of the various commercial products is much less than is predicted for the vapour pressure (and water solubility) alone, and so representative values of H can be defined more easily than representative values for the vapour pressures.

In addition to the vapour pressure estimates, information is available on the volatility of various LCCPs (Houghton, 1993; BUA, 1992; Ineos Chlor, 2005). The standard method for determining the volatility of these products is to measure the weight loss on heating at 180°C for four hours under a flow of nitrogen of 12 litres per hour (Ineos Chlor, 2005), but data are also available for heating at 90°C for 24 hours. These data are shown below in Table 1.10. Data on a medium-chain chlorinated paraffin (C<sub>14–17</sub>, 52% wt. Cl) are also included for comparison. This method only provides an indirect indication of the actual volatility of the chlorinated paraffin as they are known to release chlorine on heating. The thermal stability (in terms of loss of hydrogen chloride) for some of these products has also been determined over four hours, at a slightly lower temperature of 175°C, and these data are also shown in Table 1.10 for comparison.

**Table 1.10 Weight loss on heating chlorinated paraffins**

Substance	Weight loss on heating at 90°C for 24 hour (% w/w)	Weight loss on heating at 180°C for four hours (% /w) <sup>a, b, c</sup>	Weight loss of HCl on heating at 175°C for four hours (% w/w) <sup>b</sup>
[C <sub>14-17</sub> , 52% wt. Cl] <sup>d</sup>	[ca. 0.5] <sup>d</sup>	[ca. 1.4] <sup>d</sup>	[0.2] <sup>d</sup>
C <sub>18-20</sub> , 20% wt. Cl		8.3	
C <sub>18-20</sub> , 35% wt. Cl	0.7	-	-
C <sub>18-20</sub> , 40% wt. Cl		3.3	
C <sub>18-20</sub> , 44% wt. Cl	0.2	-	-
C <sub>18-20</sub> , 47-48% wt. Cl	0.2	0.8-1.6	0.2
C <sub>18-20</sub> , 50-52% wt. Cl	0.2	0.7-1.3	0.2
C <sub>18-27</sub> , 42% wt. Cl	0.3 <sup>c</sup>	-	-
C <sub>&gt;20</sub> , 42% wt. Cl	-	0.4-0.50	0.2
C <sub>&gt;20</sub> , 46% wt. Cl		0.4	
C <sub>&gt;20</sub> , 48% wt. Cl	-	0.3-0.4	0.2
C <sub>&gt;20</sub> , 70% wt. Cl	no detectable loss	-	0.2

Notes: <sup>a</sup> Data from BUA (1992).

<sup>b</sup> Data from Houghton (1993).

<sup>c</sup> Value refers to weight loss on heating at 130°C for two hours.

<sup>d</sup> Information on medium-chain chlorinated paraffin included for comparative purposes only.

Howard *et al.* (1975) reports the evaporation rate at 100°C of various LCCPs. These data are shown in Table 1.11. Again, these data indicate a similar relative volatility as shown in Table 1.10.

**Table 1.11 Evaporation rates of various LCCPs (Howard *et al.*, 1975)**

Substance (average carbon chain length)	Evaporation rate at 100°C
C <sub>20</sub> , 37-38% wt. Cl	80×10 <sup>-6</sup> g/cm <sup>2</sup> /hour
C <sub>22</sub> , 42% wt. Cl	2.5×10 <sup>-6</sup> g/cm <sup>2</sup> /hour
C <sub>24</sub> , 43% wt. Cl	60×10 <sup>-6</sup> g/cm <sup>2</sup> /hour
C <sub>&gt;20</sub> , 48-54% wt. Cl	40×10 <sup>-6</sup> g/cm <sup>2</sup> /hour
C <sub>22</sub> , 50-52% wt. Cl	2.5×10 <sup>-6</sup> g/cm <sup>2</sup> /hour
C <sub>20</sub> , 69-72% wt. Cl	1.5×10 <sup>-6</sup> g/cm <sup>2</sup> /hour

### 1.4.5 Water solubility

A detailed investigation of the water solubility of two radiolabelled LCCPs has been carried out by Madeley and Gillings (1983). The substances tested were an n-pentacosane-13-<sup>14</sup>C that was chlorinated to either 43% wt. Cl or 70% wt. Cl. The radiochemical purity of the n-pentacosane was 98 per cent and the chemical purity was around 90 per cent (the major impurity was n-tetracosane). This radiolabelled n-paraffin was diluted with a non-radiolabelled n-paraffin feedstock (CWX40) before chlorination. The tests were carried out by weighing 50 mg of the test substance onto a glass slide and placing the glass slide substance-side up into the test vessel containing five litres of

water. The vessel was then stirred gently (100 rpm) in the dark for 91 days at  $19 \pm 0.7^\circ\text{C}$ . After this period, the test system was maintained for a further 87 days with no stirring. Samples were taken at approximately seven-day intervals for analysis. Both  $^{14}\text{C}$  and parent compound analyses (by a relatively crude TLC procedure) were carried out.

During the stirring phase of the experiment, the measured concentrations were not consistent, possibly owing to the presence of chlorinated paraffin droplets/suspensions. The non-stirring phase of the experiment allowed for settlement of any droplets/suspensions and for equilibrium to become established. By the end of this phase, the  $^{14}\text{C}$  measurements indicated that the concentration had reached steady state (the measured concentration remained constant for at least 7–24 days).

The mean concentrations determined at steady state were  $6.4 \mu\text{g/l}$  in the experiments with the  $\text{C}_{25}$ , 43% wt. Cl substance and  $5.9 \mu\text{g/l}$  with the  $\text{C}_{25}$ , 70% wt. Cl substance. The mean concentration determined by parent compound analysis was  $<5 \mu\text{g/l}$  (i.e. below the detection limit of the method used). In experiments with  $\text{C}_{11}$  and  $\text{C}_{15}$  chlorinated paraffins under similar conditions, there was evidence for chemical change during the test or preferential dissolution of  $^{14}\text{C}$ -labelled impurities (the solubility by parent compound analysis was lower than that obtained by  $^{14}\text{C}$  measurements). For the LCCPs, the detection limit for the parent compound analysis is very close to the solubility values obtained by  $^{14}\text{C}$  measurements and so it is not clear if this was a complicating factor in these tests.

Campbell and McConnell (1980) gave the water solubility of a  $\text{C}_{25}$ , 42% wt. Cl chlorinated paraffin as  $3 \mu\text{g/l}$  at a temperature of  $16\text{--}20^\circ\text{C}$  in seawater. The value is reportedly based on radioactive tracer measurements but few other details of the study are available.

An estimate of water solubility can be obtained from log Kow. The Syracuse Research Corporation WSKOW (version 1.30) program has been used to estimate the water solubility for a  $\text{C}_{18}\text{H}_{33}\text{Cl}_5$ , 41.6% wt. Cl chlorinated paraffin, a  $\text{C}_{25}\text{H}_{45}\text{Cl}_7$ , 41.9% wt. Cl chlorinated paraffin and a  $\text{C}_{25}\text{H}_{29}\text{Cl}_{23}$ , 71.3% wt. Cl chlorinated paraffin. The estimates were carried out twice, once using the log Kow value predicted by the program from chemical structure (log Kow of 10.16, 13.96 and 16.92 respectively) and once using a log Kow value of around 7.5, 7.6 and 14 (the lower limit of the measured data; see Section 1.4.6) for the three chlorinated paraffins respectively. The water solubility estimates obtained were:

- $\text{C}_{18}\text{H}_{33}\text{Cl}_5$        $0.017 - 6.1 \mu\text{g/l}$
- $\text{C}_{25}\text{H}_{45}\text{Cl}_7$        $1.6 \times 10^{-6} - 2.0 \mu\text{g/l}$
- $\text{C}_{25}\text{H}_{29}\text{Cl}_{23}$      $1.6 \times 10^{-11} - 1.0 \times 10^{-8} \mu\text{g/l}$

The upper limits of the estimates for both the  $\text{C}_{18}\text{H}_{33}\text{Cl}_5$  and  $\text{C}_{25}\text{H}_{45}\text{Cl}_7$  chlorinated paraffins are reasonably consistent with the available measured data for LCCPs.

For the risk assessment, the water solubility will be taken to be around  $5 \mu\text{g/l}$  for all LCCPs, based on the experiments of Madeley and Gillings. Theoretical calculations indicate that the water solubility would be expected to be similar to this value for  $\text{C}_{18\text{--}20}$  products and to decrease with both increasing carbon chain length and chlorine contents. However, the available experimental data gave similar values for two LCCPs of differing chlorine contents. In addition, Drouillard *et al.* (1998b) found a trend of increasing water solubility for several short chain chlorinated paraffins with increasing chlorine content, up to five chlorine atoms per molecule.

The water solubility is used in the TGD methodology mainly to determine the Henry's Law constant. Suitable values for this constant are discussed in Section 1.4.8 and so the actual value for the water solubility chosen here is not expected to have a large influence on the overall assessment<sup>3</sup>. However, it is important to consider the water solubility when interpreting the aquatic toxicity data.

The limited available data indicate that the solubility in salt water is similar to, but slightly lower than, in freshwater.

#### 1.4.6 n-Octanol-water partition coefficient

Renberg *et al.* (1980) determined the octanol-water partition coefficients for various commercial LCCPs using a high performance thin layer chromatography (HPTLC) method. The partition coefficients determined (log values) were 7.46–11.84 for a C<sub>18–26</sub>, 44% wt. Cl product, 7.63–12.83 for a C<sub>21.5</sub>, 42% wt. Cl product, 9.29–12.83 for a C<sub>22–26</sub>, 42% wt. Cl product and 8.69–12.83 for a C<sub>22–26</sub>, 49% wt. Cl product. The range quoted reflects the different HPTLC retention times, and hence octanol-water partition coefficients, of the various components of the commercial products.

The Syracuse Research Corporation Log Kow (version 1.6) estimation program has been used to estimate log Kow values for several example LCCPs from chemical structure using a fragment constant method. The values obtained are shown in Table 1.12.

**Table 1.12 Estimated log Kow values for several example LCCPs from chemical structure, using the Syracuse Research Corporation Log Kow (version 1.6) estimation program**

Formula	Chlorine content (% wt. Cl)	Log Kow
C <sub>18</sub> H <sub>33</sub> Cl <sub>5</sub>	41.6	10.2
C <sub>18</sub> H <sub>30</sub> Cl <sub>8</sub>	53.6	10.7
C <sub>20</sub> H <sub>36</sub> Cl <sub>6</sub>	43.6	11.3
C <sub>20</sub> H <sub>33</sub> Cl <sub>9</sub>	53.9	11.9
C <sub>25</sub> H <sub>45</sub> Cl <sub>7</sub>	41.9	14.0
C <sub>25</sub> H <sub>42</sub> Cl <sub>10</sub>	50.9	14.5
C <sub>25</sub> H <sub>29</sub> Cl <sub>23</sub>	71.3	16.9
C <sub>30</sub> H <sub>53</sub> Cl <sub>9</sub>	43.6	16.8
C <sub>30</sub> H <sub>49</sub> Cl <sub>13</sub>	53.0	17.5
C <sub>30</sub> H <sub>35</sub> Cl <sub>27</sub>	70.8	20.1

BUA (1992) reported log Kow values for several LCCPs estimated using the CLOGP 3.4 computer program. The values calculated were 9.1 for C<sub>18</sub>H<sub>34</sub>Cl<sub>4</sub>, 36.2% wt. Cl.; 7.9 for C<sub>18</sub>H<sub>30</sub>Cl<sub>8</sub>, 53.6% wt. Cl.; 10.1 for C<sub>20</sub>H<sub>38</sub>Cl<sub>4</sub>, 33.7% wt. Cl.; 8.7 for C<sub>20</sub>H<sub>33</sub>Cl<sub>9</sub>, 53.9 % wt. Cl.; and 11.6 for C<sub>26</sub>H<sub>44</sub>Cl<sub>10</sub>, 49.9% wt. Cl. It is interesting to note from these values that

<sup>3</sup> It is probably incorrect to assume that all LCCPs have the same water solubility. Although it would be useful to have reliable data on the water solubilities of the various groups of LCCPs, such determinations would be extremely difficult to carry out practically, and the analysis carried out in Appendix E indicates that the importance of the actual water solubilities to the overall conclusions of the risk assessment is minimal. Therefore more reliable determination of the water solubilities is not considered to be a priority at present.

the log Kow value appears to decrease with increasing chlorine content, which is the opposite trend to that found in the above estimates (Table 1.12). It is possible that the values reported in BUA (1992) have been transposed – if this is the case then the two sets of estimated values are comparable.

Overall, it is clear that LCCPs have very high log Kow values. The agreement between the measured and predicted data is reasonable, given the inherent problems in determining log Kow values for this type of substance. The range of values measured for a given commercial product reflects the fact that they contain many components, with different components having different log Kow values. The following log Kow values will be taken to be appropriate for use in this assessment (based on the Renberg *et al.* (1980) measurements and estimated data).

**Table 1.13 Representative log Kow values for LCCP subgroups, as used in this assessment**

Subgroup	Approx. mid-range log Kow value	Approximate range
C <sub>18-20</sub> liquids (typically 40–52% wt Cl)	9.7	7.5–11.8
C <sub>&gt;20</sub> liquids (typically 40–54% wt. Cl)	10.3	7.6–13
C <sub>&gt;20</sub> solids (typically 70% wt. Cl)	17	14–20

In terms of the risk assessment, the log Kow value is important for determining the partitioning behaviour of the substance (i.e. it is used to estimate partition coefficients for adsorption onto solids, bioconcentration etc.). For LCCPs, other data are available that allow appropriate estimates for most of these to be made. These are discussed in Section 3.2.6 and 3.2.9.

## 1.4.7 Hazardous physico-chemical properties

### 1.4.7.1 Flash point

A flash point of >210°C is reported in IUCLID (2000a) for LCCPs with chlorine contents >42% wt. Cl.

### 1.4.7.2 Autoignition

Decomposition starts to occur at temperatures of 200°C and above, with liberation of hydrogen chloride. This decomposition forms the basis of the gas-phase flame retardant activity of some LCCPs.

### 1.4.7.3 Explosivity

The substance is not expected to be explosive.



#### 1.4.7.4 Oxidising properties

The substance is not expected to have oxidising properties.

### 1.4.8 Other relevant physico-chemical properties

#### 1.4.8.1 Granulometry

No information is available.

#### 1.4.8.2 Surface tension

No information is available.

#### 1.4.8.3 Henry's Law constant

No measured values for the Henry's Law constant (H) are available. Henry's Law constants can be determined from the ratio of the vapour pressure to water solubility. For LCCPs, water solubilities of 6.6 µg/l and 5.9 µg/l have been measured for a C<sub>25</sub> chlorinated paraffin with chlorine contents of 43% wt. and 70% wt. respectively. The only measured vapour pressure data available have been determined at elevated temperatures, and so it is not possible to calculate a Henry's Law constant at temperatures relevant for the environment.

Estimates are available for the vapour pressures at 25°C for these substances (see Section 1.4.4) and the values obtained are around 6.3×10<sup>-7</sup> Pa (using the MPBPWIN program) or 1.3×10<sup>-9</sup> Pa (Appendix B) for a C<sub>25</sub>, 41.9% wt. Cl substance and around 1.4×10<sup>-15</sup> Pa (using the MPBPWIN program) or 6.3×10<sup>-20</sup> Pa (Appendix B) for a C<sub>25</sub>, 71.3% wt. Cl substance. Using these values, the Henry's Law constant can be estimated as 1.3×10<sup>-4</sup>–0.062 Pa m<sup>3</sup>/mol for a C<sub>25</sub>, ~42–43% wt. Cl substance and 1.2×10<sup>-14</sup>–2.7×10<sup>-10</sup> Pa m<sup>3</sup>/mol for a C<sub>25</sub>, ~70–72% wt. Cl substance. It should be noted that these values depend on the water solubility (the actual solubility could be lower than assumed here) and an estimated vapour pressure, and so are inherently uncertain.

Estimates of Henry's Law constant have also been obtained using the Syracuse Research Corporation Henry (version 3.00) program. This estimates the Henry's Law constant at 25°C from chemical structure using a bond contribution method, a group contribution method, and an "Experimental Value Adjusted" (EVA) method. The program indicates that the bond contribution method is able to estimate values for many different types of structures, but the group contribution method estimates are generally preferred for substances when all the fragment values are available. The EVA method is based on the bond contribution method, but takes into account the known Henry's Law constant for a substance with a similar structure and so should provide a more reliable estimate.

In this case Henry's Law constants have been determined for the following specific short-chain chlorinated paraffins (Drouillard *et al.*, 1998a) and these have been used in the EVA estimates:

- 1,10-dichlorodecane -  $H = 499 \text{ Pa m}^3/\text{mole}$ ;
- 1,2,9,10-tetrachlorodecane -  $H = 17.7 \text{ Pa m}^3/\text{mole}$ ;
- 1,2,10,11-tetrachloroundecane -  $H = 6.32 \text{ Pa m}^3/\text{mole}$ ;
- 1,12-dichlorododecane -  $H = 648 \text{ Pa m}^3/\text{mole}$ .

The results of these estimates for several example structures are shown in Table 1.14.

The Drouillard *et al.* (1998a) paper also gives values for H for a pentachlorodecane, a pentachloroundecane and a mixture of penta- and hexachlorododecane, all of unknown structure. These data are also reported in Table 1.14 along with the values estimated using the above methods for comparison purposes. These show that the bond contribution method appears to consistently overestimate the value for H, whereas the group contribution method generally appears to underestimate the value for H, particularly for the substances with higher chlorine contents (of around 48% wt. and above). The EVA method, however, does appear to provide reasonably reliable estimates for H. In particular, the lower end of the range of values estimated agree very well with the known values of H.

Table 1.14 Estimated Henry's Law constants for LCCPs

Formula	Chlorine content (% wt. Cl)	Estimated Henry's Law constant (Pa m <sup>3</sup> /mole)			Measured value (Pa m <sup>3</sup> /mole) <sup>c</sup>
		Bond contribution method	Group contribution method	EVA method (four estimates)	
<b>Substances used to generate the EVA estimates</b>					
C <sub>10</sub> H <sub>20</sub> Cl <sub>2</sub> (1,10-dichlorodecane) <sup>a</sup>	33.5	11,855	312	Not applicable	648
C <sub>10</sub> H <sub>18</sub> Cl <sub>4</sub> (1,2,9,10-tetrachlorodecane) <sup>a</sup>	50.7	1,469	0.19	Not applicable	17.7
C <sub>11</sub> H <sub>20</sub> Cl <sub>4</sub> (1,2,10,11-tetrachloroundecane) <sup>a</sup>	48.3	1,956	0.27	Not applicable	6.32
C <sub>12</sub> H <sub>24</sub> Cl <sub>2</sub> (1,12-dichlorodecane) <sup>a</sup>	29.7	20,873	622	Not applicable	499
<b>Estimates for LCCPs</b>					
C <sub>18</sub> H <sub>33</sub> Cl <sub>5</sub>	41.6	5,005	0.084	210, 60, 16 and 155 mean = 110±88	Not available
C <sub>18</sub> H <sub>30</sub> Cl <sub>8</sub>	53.6	219	1.2×10 <sup>-6</sup>	9.2, 2.6, 0.7 and 6.7 mean = 4.8±3.9	Not available
C <sub>20</sub> H <sub>36</sub> Cl <sub>6</sub>	43.6	3,101	0.004	131, 37, 10 and 96 mean = 69±55	Not available
C <sub>20</sub> H <sub>33</sub> Cl <sub>9</sub>	53.9	136	6.1×10 <sup>-8</sup>	5.7, 1.6, 0.4 and 4.2 mean = 3.0±2.4	Not available
C <sub>25</sub> H <sub>45</sub> Cl <sub>7</sub>	41.9	4,509	5.7×10 <sup>-4</sup>	189, 54, 15 and 140 mean = 100±79	Not available
C <sub>25</sub> H <sub>42</sub> Cl <sub>10</sub>	50.9	198	8.4×10 <sup>-9</sup>	8.3, 2.4, 0.6 and 6.1 mean = 4.4±3.5	Not available
C <sub>25</sub> H <sub>29</sub> Cl <sub>13</sub>	71.3	2.5×10 <sup>-4</sup>	8.6×10 <sup>-30</sup>	1.06×10 <sup>-5</sup> , 3.0×10 <sup>-6</sup> , 8.2×10 <sup>-7</sup> and 7.9×10 <sup>-6</sup> mean = 5.6×10 <sup>-6</sup> ±4.5×10 <sup>-6</sup>	Not available
C <sub>30</sub> H <sub>53</sub> Cl <sub>9</sub>	43.6	2,310	1.9×10 <sup>-6</sup>	97, 28, 7.5, and 72 mean = 51±41	Not available

Table 1.14 continued overleaf.

**Table 1.14: continued**

	Chlorine content (% wt. Cl)	Estimated Henry's Law constant (Pa m <sup>3</sup> /mole)			Measured value (Pa m <sup>3</sup> /mole) <sup>c</sup>
		Bond contribution method	Group contribution method	EVA method (four estimates)	
C <sub>30</sub> H <sub>49</sub> Cl <sub>13</sub>	53.0	35.6	7.0×10 <sup>-13</sup>	1.5, 0.4, 0.1, and 1.1 mean = 0.8±0.6	Not available
C <sub>30</sub> H <sub>35</sub> Cl <sub>27</sub>	70.8	1.6×10 <sup>-5</sup>	1.8×10 <sup>-35</sup>	6.8×10 <sup>-7</sup> , 1.9×10 <sup>-7</sup> , 5.2×10 <sup>-8</sup> , and 5.0×10 <sup>-7</sup> mean = 3.6×10 <sup>-7</sup> ±2.9×10 <sup>-7</sup>	Not available
<b>Estimates for other chlorinated paraffins with known Henry's Law constants</b>					
C <sub>10</sub> H <sub>17</sub> Cl <sub>5</sub> <sup>a</sup>	56.4	390	3.7×10 <sup>-3</sup>	22, 6.2, 1.7, and 16 mean = 11.5±9.2	2.68–4.92
C <sub>11</sub> H <sub>19</sub> Cl <sub>5</sub> <sup>a</sup>	54.0	518	5.3×10 <sup>-3</sup>	29, 8.3, 2.2 and 21 mean = 15.1±12.1	0.68–1.46
C <sub>12</sub> H <sub>21</sub> Cl <sub>5</sub> /	Penta – 51.8	Penta – 932	Penta – 0.011	Penta – 38, 11, 3.0 and 28 mean = 20±16	1.37
C <sub>12</sub> H <sub>20</sub> Cl <sub>6</sub> <sup>a, b</sup>	Hexa – 56.5	Hexa – 322	Hexa – 2.6×10 <sup>-4</sup>	Hexa – 14, 3.9, 1.0 and 10 mean = 7.2±5.9	

Notes: <sup>a</sup> Estimates provided for comparative purposes only.

<sup>b</sup> The substance was reported to be a mixture of penta- and hexachlorododecane - separate estimates are provided for each of these components.

<sup>c</sup> Values taken from Drouillard *et al.* (1998a).

For the risk assessment, the EVA estimates will be considered as the best available data because they are estimated from data on other chlorinated paraffins, and the method appears to work reasonably well for those chlorinated paraffins for which the Henry's Law constant is known. The best estimates appear to be at the lower end of the range of values obtained for each compound using this method. However, it should still be born in mind that the extrapolation from the short-chain chlorinated paraffin data to the estimated data for LCCPs is uncertain.

The values that will be considered to be representative in the assessment are outlined in Table 1.15.

**Table 1.15 Representative values of Henry's Law constant (H) for LCCP subgroups, as used in this assessment**

Subgroup	Best representative estimate for Henry's Law constant (H)	Approximate range
C <sub>18-20</sub> liquids (typically 40–52% wt Cl)	16 Pa m <sup>3</sup> /mole	10–210 Pa m <sup>3</sup> /mole
C <sub>&gt;20</sub> liquids (typically 40–54% wt. Cl)	15 Pa m <sup>3</sup> /mole	1–190 Pa m <sup>3</sup> /mole
C <sub>&gt;20</sub> solids (typically 70% wt. Cl)	1×10 <sup>-6</sup> Pa m <sup>3</sup> /mole	5×10 <sup>-8</sup> –1×10 <sup>-5</sup> Pa m <sup>3</sup> /mole

#### 1.4.9 Summary of physico-chemical properties used in the risk assessment

The physico-chemical properties selected for use in the risk assessment for the three groups of LCCPs considered are summarised in Table 1.16.

**Table 1.16 Summary of selected physico-chemical properties**

Physico-chemical property	C <sub>18-20</sub> liquids	C <sub>&gt;20</sub> liquids	C <sub>&gt;20</sub> solids
Melting point (°C)	-30 <sup>a</sup> 0 <sup>b</sup>	-30 <sup>a</sup> 0 <sup>b</sup>	100 <sup>c</sup>
Boiling point (°C)	>210 (decomp)	>210 (decomp)	>210 (decomp)
Density (g/cm <sup>3</sup> at 20–25°C)	0.92–1.3	1.16–1.26	1.63
Vapour pressure (Pa at 25°C)	2.5×10 <sup>-4</sup>	2.5×10 <sup>-5</sup>	1.5×10 <sup>-14</sup>
Water solubility (µg/l at ca. 20°C)	5	5	5
n-Octanol-water partition coefficient (log Kow)	9.7	10.3	17
Henry's Law constant (Pa m <sup>3</sup> /mol at 25°C)	16	15	1×10 <sup>-6</sup>

Notes: <sup>a</sup> For products with chlorine contents of 42–48% by wt.  
<sup>b</sup> For products with chlorine contents of 50–52% by wt.  
<sup>c</sup> For products with chlorine contents of around 70% by wt.

## 2. General information on exposure

### 2.1 Production

Chlorinated paraffins are produced by the direct chlorination of n-paraffin feedstocks. The n-paraffin fractions used as feedstocks are C<sub>18-20</sub> and C<sub>>20</sub> (for example C<sub>24-30</sub> feedstock), although the precise composition may vary depending on the petroleum oil source (Houghton, 1993). The C<sub>18-20</sub> feedstock is not thought to be currently used by producers in the United States (CPIA, 2001).

The reaction is carried out by passing chlorine gas through the liquid paraffin – or a solution of the paraffin if the product is highly viscous (Howard *et al.*, 1975) – at a temperature of around 80–100°C. The reaction is exothermic and so cooling is required to maintain the correct temperature. Ultra-violet light may be used as a catalyst in some production processes. The reaction is terminated once the desired degree of chlorination has been obtained, by stopping the flow of chlorine into the reaction vessel. The degree of chlorination is monitored during the reaction by density, viscosity or refractive index measurements. The excess chlorine and hydrogen chloride gas (formed as a by-product in the reaction) is then removed by purging with air or nitrogen; stabilisers (typically epoxidised vegetable oil) may also be added (Houghton, 1993).

No contact with water is reported to occur during the production process (Howard *et al.*, 1975).

The global production of total chlorinated paraffins was estimated to be above 300,000 tonnes/year in the late 1980s (Omori *et al.*, 1987). Production of total chlorinated paraffins in Western Europe was estimated to be about 140,000 tonnes/year in 1993 by BUA (1992). The European consumption of total chlorinated paraffins for 1993 was estimated as 100,000–120,000 tonnes/year, and it was estimated that around 15 per cent of this was LCCPs (Willis *et al.*, 1994).

### 2.2 Uses

About 5,000–10,000 tonnes of LCCPs were used in the EU each year for the years 1998–2004. The main current areas of use are as a secondary plasticiser in PVC, as a flame retardant in rubber, as a plasticiser/flame retardant in sealants/adhesives and paints, as an extreme pressure additive to metal cutting/working fluids, as a component of leather fat liquoring treatments and for waterproofing textiles. The actual usage figures are considered as confidential information (Euro Chlor, 2000 and 2005), but the relative use in each application for 2004 is shown in Figure 2.1. The actual raw data are summarised in a confidential Annex.

In very general terms, the chlorinated paraffins with chlorine contents in the range 40–50% wt. Cl are used in plasticising applications, whereas the chlorinated paraffins with very high chlorine contents (e.g. 70% wt. Cl) are used mainly as flame retardants (Zitko and Arsenault, 1974).

For use in PVC it is possible that pellets (masterbatch) containing LCCPs could be manufactured outside the EU and then imported into the EU for further processing to give the final product. Similarly, such pellets could be manufactured within the EU and exported for subsequent processing. A similar situation may also exist for finished PVC products, or other products such as sealants, paints etc., which contain LCCPs. The actual amounts of LCCPs imported into and exported from the EU in this way are very difficult, if not impossible, to estimate. For the purposes of this assessment it will be assumed that the net import into the EU of these products will be small compared with the amount assumed to be used in the EU.

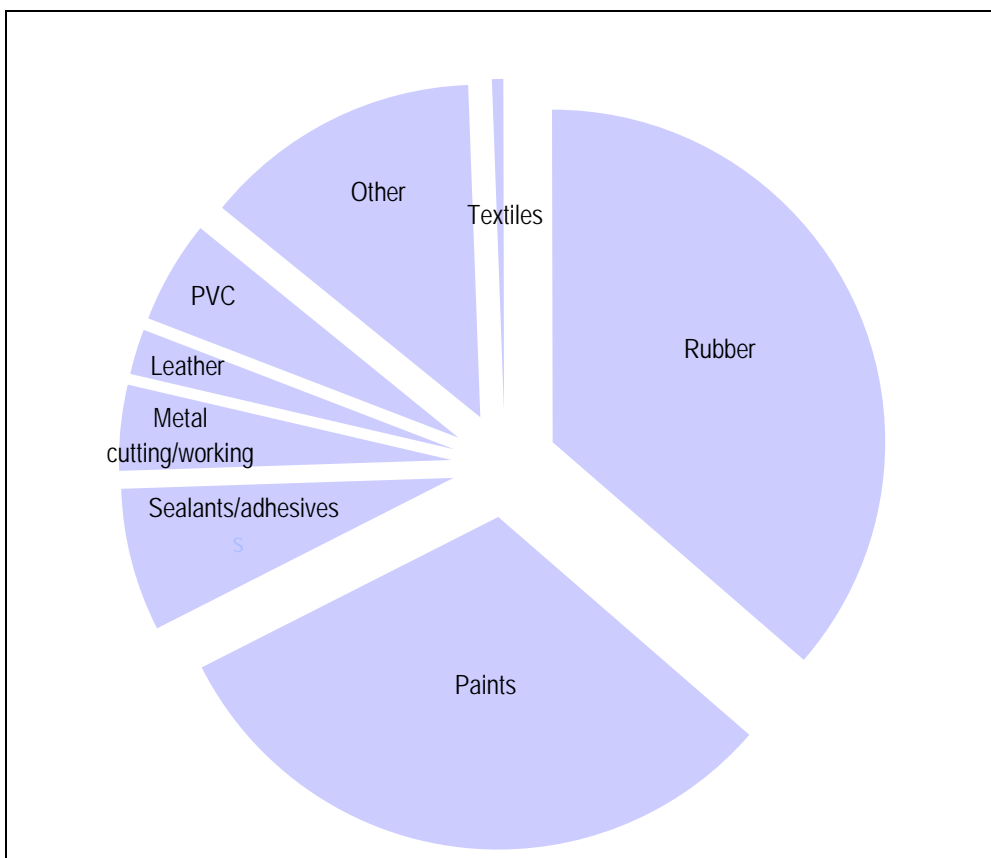
It is also possible that LCCPs themselves may be imported into the EU, however, the amounts involved, although unknown, are thought to be relatively small.

Similar to the case with medium-chain chlorinated paraffins (ECB, 2005a), it is possible that some of the leather fat liquor formulations containing LCCPs produced in the EU are exported for use outside the EU, thus the actual quantity of LCCPs applied to leather in the EU may be lower than indicated by the Euro Chlor figures.

The "other" category in Figure 2.1 represents sales to distributors etc., who most likely then supply the substance for use in the same areas outlined above, although it cannot be excluded that other, as yet unidentified, uses of LCCPs may exist. In this assessment, this "other" tonnage will be taken into account by assuming that it is redistributed amongst the other known uses.

The actual amounts of chlorinated paraffins used in the various applications, based on the known sales from Western European producers, are considered as confidential and so do not appear in this report (they are summarised in a confidential Annex). However, the assessment has been based on these known figures. The assessment considers the main types of LCCPs used in each application. It is possible that other types of LCCPs may be used in some applications but these will only be very minor uses.





**Figure 2.1 Uses of long-chain chlorinated paraffins in the EU**

### 2.2.1 Use in PVC

LCCPs are used in PVC. The main types currently thought to be used in this area are the  $C_{18-20}$  liquid chlorinated paraffins, although small amounts of the  $C_{>20}$  liquid chlorinated paraffins may have been used in the past. Examples of applications include high temperature cables, and plastisol applications such as flooring and PVC leather cloth.

The chlorinated paraffins are used mainly as secondary plasticisers. The primary plasticisers are generally phthalates or phosphate esters (Houghton, 1993). The phosphate esters are generally only used when flame retardant benefits are needed. Primary plasticisers in PVC are used to increase the elongation properties and softness of the polymer. Secondary plasticisers, when used in combination with primary plasticisers, cause an enhancement of the plasticising effect, and so are also known as extenders.

There are two main types of PVC produced: suspension and paste forming (emulsion) PVC. The methods for incorporation of the plasticisers into the two types are different. World-wide, approximately 70 per cent of the total PVC resin is suspension PVC, 20 per cent is emulsion PVC and the remaining 10 per cent consists of bulk PVC (9 per cent of total resin production; produces irregular particles with little or no impurities) and solution PVC (1 per cent of total resin production; used to make specialised resins for metal coatings, record manufacture, powder coatings and surface coatings) (Rubin, 1990).

Polymers of suspension PVC (also known as pearl, bead or granular) are produced by suspending vinyl chloride monomer in water and carrying out the polymerisation using

a monomer-soluble initiator. This technique forms PVC particles with a relatively large particle size (e.g. 100–150 µm). These particles are highly porous and so can absorb large amounts of plasticiser.

The PVC particles are typically processed using a dry-blend cycle. In this cycle, all the polymer formulation ingredients, including plasticisers, are heated to around 70–110°C and mixed to form a dry powder product. This can be either stored or further processed immediately. Processing of the dry powder can take the form of extrusion, injection moulding or calendering (a process for producing sheets or films). The powder can also be extruded and chipped to form pellets of PVC compound which can subsequently be further processed to give the final product. Many producers of PVC products purchase PVC compound as it is easy to store and similarly many companies exist that produce PVC compound (Kirk-Othmer, 1996).

Paste-forming (plastisol) PVC polymers are produced as a paste or plastisol rather than a dry powder. A plastisol is a suspension of a solid in a liquid in which it does not dissolve, but does form an homogenous mixture at elevated temperatures; the term organosol is used for a plastisol that contains more than 10 parts of a solvent per 100 parts of resin (Rubin, 1990).

Microsuspension polymerisation or emulsion polymerisation is usually used to form the PVC for these paste-forming applications. Both these processes result in the formation of much smaller PVC particles compared with those produced by suspension polymerisation processes. The small particle size means that the initial product has low porosity and so formulation with additives (e.g. plasticisers) is not possible using a dry-blending cycle, and instead a paste is formed. This paste or plastisol can then be spread, coated, rotationally cast or sprayed onto the desired item, or may be semi-gelled for storage (i.e. heat is applied to convert it into a semi-solid form). A wide range of plasticisers are used in these applications as the choice affects the viscosity of the plastisol, which is important in the further processing steps, and it is common for two or three different plasticisers to be used in a single formulation to achieve the desired final properties (Kirk-Othmer, 1996).

During the formation of finished products, the PVC formulation may be exposed to temperatures of 180°C for up to several minutes. In some processes, for example sheet and film production by calendering or spread coating, there is the potential for volatilisation of the plasticiser as the hot plastic is exposed to the surrounding air. Processes involving injection moulding and extrusion are carried out in closed equipment and little exposure of the hot product to air occurs; the potential for volatilisation of the plasticiser is reduced.

In some facilities filtering or incineration of the exhaust gas is used to reduce the air emissions from the process. It has been reported that concentrations of primary plasticiser (e.g. di-(2-ethylhexyl) phthalate (DEHP)) are typically 500 mg/m<sup>3</sup> in air extracted from spread coating ovens, which can be reduced to <20 mg/m<sup>3</sup> by the use of filtration equipment, with exhaust air incineration reducing the emission to practically zero. The use of filters and/or incinerators in calendering and spread coating plants has been steadily increasing in recent years (Kirk-Othmer, 1996). Figures for 1990 are shown in Table 2.1. The figures refer to the percentage of the total phthalate plasticiser processed in each application. Of the processes listed in Table 2.1, LCCPs are used mainly in spread coating (e.g. PVC leather cloth) and calendered flooring.

**Table 2.1 Exhaust air treatment in Western Europe by process in 1990 (Kirk-Othmer, 1996)**

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

As the figures in Table 2.1 refer to the percentage of phthalate use, it is not possible to determine the percentage of processing sites using LCCPs that have exhaust air treatment. If it is assumed that the distribution is the same as for phthalates, then it appears that at least 50 per cent of sites using LCCPs will have exhaust air treatment.

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

### 2.2.2 Use in rubber

Chlorinated paraffins with high chlorine contents (e.g. 70% wt. Cl) can be used as flame retardants in natural and synthetic rubbers (Zitko and Arsenault, 1974). Chlorinated paraffins with lower chlorine contents may also be used in rubber. Here they have a plasticising and flame retarding function. An important use for flame retarded rubber appears to be in conveyor belts for mining applications, but the rubber is also used in other applications.

The amount of chlorinated paraffin added is generally in the range 1–4 per cent by weight (Zitko and Arsenault, 1974), but can be up to 15 per cent by weight for some applications (BUA, 1992).

A survey of the use of chlorinated paraffins amongst members of the British Rubber Manufacturers' Association Ltd. has been carried out (BRMA, 2001). The survey included three main sectors within the rubber industry: the new tyre sector; the general rubber goods sector; and the polyurethane foam sector. In all, responses were received from 25 companies (around 30 per cent of the membership). Of these, 15 companies reported using chlorinated paraffins of one type or another. The main area

of use of chlorinated paraffins in general was in the general rubber goods sector. The results of the survey are summarised in Table 2.2.

**Table 2.2 Results of survey of chlorinated paraffin use in rubber in the United Kingdom**

Chlorinated paraffin type	Application	Amount of chlorinated paraffin present in rubber	Amount of chlorinated paraffin used at a site
Short-chain (C <sub>10-13</sub> )	Conveyor belting	10.1–16.8%	48–51 tonnes/year
	Medium-chain (C <sub>14-17</sub> )	Cable cover	25 tonnes/year
Medium-chain (C <sub>14-17</sub> )	Rubber hose	6.2%	1 tonne/year
	Pipe seals	4%	35 tonnes/year
	Industrial roller coverings	up to 20%	2 tonnes/year
	Flame retardant items for railway use	7.2%	4.2 tonnes/year
	Long-chain (C <sub>&gt;20</sub> )	Various fire resistant rubber products	10%
Long-chain (C <sub>&gt;20</sub> )	Manufacture of flexible ducting	7%	1.5 tonnes/year
	Rubber belting	4.6%	0.1 tonnes/year
Unidentified (probably short-chain (C <sub>10-13</sub> ))	Shoe soles	6.5%	6 tonnes/year
	Industrial sheeting	13%	1.2 tonnes/year

For the LCCPs, the survey indicated that both C<sub>>20</sub> liquid and C<sub>>20</sub> solid products are used in rubber (and this is confirmed based on the confidential EU consumption figures for LCCPs provided by Euro Chlor (2005)). No use of chlorinated paraffins in car tyres was found in the survey.

The survey results show that the amount of chlorinated paraffin present in rubber products is generally in the range of 4–17 per cent, with a maximum of 20 per cent. These figures agree well with those reported in the literature. The LCCPs appear to be used at loadings of around 5–10 per cent.

### 2.2.3 Use in textiles

Fire proofing of cellulosic textiles was reported to have been one of the major applications for chlorinated paraffins in this area in the past. The chlorinated paraffin could be added to the fibres prior to spinning, or used to treat the finished fabric (Zitko and Arsenault, 1974).

Information on the current uses of LCCPs in this area is sparse. The amounts used are very small and the main current use appears to be for waterproofing of textiles rather than as a flame retardant for cellulosic textiles.

### 2.2.4 Use in paints

Information from the literature on the LCCP contents of paints and varnishes are shown in Table 2.3.

**Table 2.3 Example long-chain chlorinated paraffin contents of paints and varnishes**

Paint type <sup>c</sup>	Chlorinated paraffin	Content of paint	Reference
Marine paint	C <sub>&gt;20</sub> , 70% wt. Cl <sup>a, b</sup>	5%	Back <i>et al.</i> , 1994
Marine paint – high build primer	C <sub>&gt;20</sub> , 42% wt. Cl	4%	Bowerman, 1971
Varnish (outdoor)	C <sub>&gt;20</sub> , 70% wt. Cl	7%	
	C <sub>&gt;20</sub> , 70% wt. Cl <sup>a</sup>	11.7%	von Eckhardt and Grimm, 1967
Alkyd resin varnish (outdoor)	C <sub>&gt;20</sub> , 70% wt. Cl <sup>a</sup>	8.9%	von Eckhardt and Grimm, 1967
Alkyd resin varnish (low flammability)	C <sub>&gt;20</sub> , 70% wt. Cl <sup>a</sup>	10.0%	von Eckhardt and Grimm, 1967
Chemical and water proof paint	C <sub>18–20</sub> , 45–47% wt. Cl	1.7%	von Eckhardt and Grimm, 1967
		15.6%	
Paint for concrete	C <sub>&gt;20</sub> , 70% wt. Cl		
	C <sub>18–20</sub> , 45–47% wt. Cl	5%	von Eckhardt and Grimm, 1967
		9%	
	C <sub>&gt;20</sub> , 70% wt. Cl		
Weather resistant paint for iron and concrete	C <sub>18–20</sub> , 45–47% wt. Cl	6.8%	von Eckhardt and Grimm, 1967
		5.5	
	C <sub>&gt;20</sub> , 70% wt. Cl		
Weather resistant paint for iron, concrete and asbestos cement	C <sub>&gt;20</sub> , 70% wt. Cl	10%	von Eckhardt and Grimm, 1967
Weather resistant paint for concrete and facades	C <sub>18–20</sub> , 45–47% wt. Cl	5.5%	von Eckhardt and Grimm, 1967
		1.5%	
	C <sub>&gt;20</sub> , 70% wt. Cl		
Road markings	C <sub>18–20</sub> , 45–47% wt. Cl	5%	von Eckhardt and Grimm, 1967
		8%	
	C <sub>&gt;20</sub> , 70% wt. Cl		

Notes: <sup>a</sup> The references frequently refer to a solid 70% wt. Cl chlorinated paraffin without specifically giving the carbon chain length. This is taken here to be a C<sub>>20</sub>, 70% wt. Cl product.

<sup>b</sup> The paint may also contain short- or medium-chain chlorinated paraffins.

<sup>c</sup> Paint assumed to be solvent-based unless otherwise stated.

Chlorinated paraffins in general are used as plasticisers, binders and flame retardants in paints. The concentrations used are usually in the range 5–15 per cent by weight. They are reported to be used in marine paints based on chlorinated rubber. Such paints may contain chlorinated paraffins with 70% wt. Cl as binder and chlorinated paraffins with around 40% wt. Cl as plasticiser (Zitko and Arsenault, 1974).

Previously, a survey of the use of chlorinated paraffins in paints and coatings in the United Kingdom was carried out by the British Coatings Federation (BCF, 1999). The survey principally covered medium-chain chlorinated paraffins, but the responses also included some information on LCCPs. A total of 141 companies were contacted and initial responses were obtained from 106 of these. Of the companies responding, 22 (~21 per cent) indicated that they used medium-chain chlorinated paraffins or other chlorinated paraffins. More detailed information on the use of chlorinated paraffins was obtained from 12 (~55 per cent) of the 22 companies. The chlorine content of the

chlorinated paraffins used range from around 40% wt. Cl to 70% wt. The types of paint/coating and the typical chlorinated paraffin contents are shown in Table 2.4.

**Table 2.4 Chlorinated paraffin content of paints and coatings (BCF, 1999)**

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

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

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

In addition, another survey has recently been undertaken (BCF, 2001), this time focusing on the use of LCCPs in coatings in the United Kingdom. The results from this survey indicated that only small quantities of these substances are used in coatings, and the quantities involved appear to be falling, primarily due to a move away from chlorinated rubber-based products to lower VOC coatings. The survey revealed an LCCP usage of around 10 tonnes/year in paints, with the typical content in paint being <1–6 per cent. It was not possible to determine the total usage in paints from this survey. The main types and applications of paints containing LCCPs were identified as:

- chlorinated rubber-based chemical/moisture resistant steel protection coatings;
- chlorinated rubber-based floor paints;

- chlorinated rubber-based line marking coatings;
- chlorinated rubber-based finishes for metal substrates;
- vinyl primers and finishes for metal substrates;
- acrylic clear coatings for masonry.

The number of sites of use for these types of paints and coatings in the United Kingdom was estimated to be more than 200.

Several paint companies in the United Kingdom have also been contacted independently. One company has indicated that they use  $C_{>20}$  liquid chlorinated paraffins mainly in chlorinated rubber and modified vinyl paints, whereas the  $C_{>20}$  solid chlorinated paraffin is used in intumescent paints. Another company indicated that both  $C_{>20}$  liquid and  $C_{>20}$  solid chlorinated paraffins are used in professional marine products and protective coatings (e.g. for land-based and offshore structures such as oil refineries and oil rigs), with the  $C_{>20}$  liquid chlorinated paraffins also being used in speciality DIY paints. The typical chlorinated paraffin content of the paint is 2–6 per cent in marine products, 3–10 per cent in protective coatings and 1–5 per cent in speciality DIY paints.

Another survey of the use of LCCPs in paints and coatings in the United Kingdom was undertaken in 2007 (BCF, 2007). This identified seven companies that were using LCCPs in the manufacture of paints and coatings, but it was thought that around 10 companies actually used LCCPs in these products. The amount used at each company was generally around five tonnes per year but could be up to eight tonnes per year. The long-chain chlorinated paraffin content in the paints and coatings ranged between one per cent and 15 per cent but was generally in the range 4–10 per cent. The main uses identified were in marine coatings, protective coatings, single pack anti-corrosion coatings, masonry/swimming pool coatings, intumescent coatings and marking paints for roads. The survey reported that the use of LCCPs in intumescent paints is a growing area of use, and that the use in chlorinated rubber-based paints was decreasing mainly as a result of a general decline in the use of this type of paint resulting from legislation on VOCs. The main types of LCCPs used were the  $C_{>20}$  liquid and  $C_{>20}$  solid products, with the  $C_{>20}$  solid products being used mainly in intumescent coatings. No use of the  $C_{18-20}$  liquid products was identified in this survey.

Other information from industry indicates that acrylic and acrylic copolymer masonry paints are now the paint types most likely to contain LCCPs.

Although no use of the  $C_{18-20}$  liquid chlorinated paraffins in paints and coatings was identified in the United Kingdom in the BCF (2007) survey, information provided by Euro Chlor (2007) indicate that there is use of this type of LCCP in paints and coatings within the EU.

Overall, although some of the available data concerns use of chlorinated paraffins in general, it is clear that  $C_{18-20}$  liquid,  $C_{>20}$  liquid and  $C_{>20}$  solid LCCPs are used in various types of paints, mainly in the professional area. The available information indicates that the use of LCCPs in formulation of paints in the UK is relatively small, but in terms of the EU as a whole, use of LCCPs in paints appears to be the second largest application of LCCPs in general (see Figure 2.1 earlier).

### 2.2.5 Use in sealants

Chlorinated paraffins, including the long-chain ones, are used as plasticisers/flame retardants in adhesives and sealants. Examples include polysulphide, polyurethane, acrylic and butyl sealants used in building and construction, and in sealants for double and triple glazed windows. The chlorinated paraffins are typically added at amounts of 10–15 per cent by weight of the final sealant, but could be added at amounts up to 20 per cent by weight in exceptional cases (BUA, 1992).

The difference between an adhesive and sealant can be difficult to define as some sealants are used as adhesives and *vice versa*. Generally, sealants are considered to be materials that are installed into a gap or joint to prevent water, wind, dirt or other contaminants from passing through the joint or crack. Adhesives, on the other hand, are used to transfer loads and are typically designed with much higher tensile and shear strength than sealants (Palmer and Klosowski, 1997).

Of the LCCPs, it is thought that mainly the C<sub>18–20</sub> and C<sub>>20</sub> liquid chlorinated paraffins are used in this area, mainly in sealants. Emissions from adhesives over their lifecycle are likely to be similar to those for sealants.

A small use of LCCPs has been identified in the United Kingdom in specialist primers and adhesives, where flame retardancy is important. The quantities involved in this application appear to be very small.

### 2.2.6 Use in metalworking/cutting fluids

Generally, only the liquid chlorinated paraffins are used in lubricants (Howard *et al.*, 1975). Information provided by the EU suppliers of LCCPs indicates that the major types of chlorinated paraffin used in this application are the C<sub>>20</sub> liquid products, with only a very minor usage of the C<sub>18–20</sub> chlorinated paraffins.

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

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

The market for metal forming fluids in the United Kingdom is around 500 tonnes per year. These contain up to 70% by weight of chlorinated paraffin, but the average content is around 50 per cent by weight. (Euro Chlor, 1998). The main type of chlorinated paraffin used in these applications used to be short-chain (C<sub>10–13</sub>), but suitable alternatives are now available.

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



An analytical method for determining the presence of chlorinated paraffins in cutting fluids and lubricants is available (Randegger-Vollrath, 1998). Among the 37 cutting fluids analysed, eight were found to contain short-chain length chlorinated paraffins in the concentration range 1–70 per cent, 11 were found to contain medium-chain chlorinated paraffins and two were found to contain LCCPs. The cutting fluids analysed were obtained from Swiss manufacturers or importers. The type of long-chain chlorinated paraffin present could not be identified with the method used.

A survey of the use of LCCPs by the formulators of metalworking lubricants and cutting fluids in the United Kingdom has been carried out (BLF, 2001). The response from the survey was low, possibly indicating that the substances are not in widespread use in this area. The amounts reported to be used by individual companies ranged between one and 20 tonnes per year, and it was estimated that the total usage in the United Kingdom would be less than 100 tonnes per year. The main area of application was thought to be in die lubricants in the more difficult deep drawing operations. There is, however, some uncertainty in this information due to the low response rate in the survey.

A further survey was carried out in 2007 among members of the United Kingdom Lubricants Association that were formulators of metalworking lubricants and cutting fluids (UKLA, 2007). No use of LCCPs was identified from the replies received in this survey.

For the present assessment it will be assumed that LCCPs are, or could be, used in both oil-based and water-based fluids. Recent information from industry has indicated that LCCPs are not used in emulsifiable metalworking fluids (Euro Chlor, 2008) however, the coverage of the survey is unclear (it is based on the customers of members of Euro Chlor but the percentage of customers responding is unclear).

## **2.2.7 Use in leather fat liquors**

Chlorinated paraffins are used in fat liquors for leather. They are used in conjunction with sulphated or sulphonated oils (Houghton, 1993), chlorosulphonated paraffins, natural fats and oils (Euro Chlor, 1998). Typically, chlorinated paraffins with a relatively low chlorine content (e.g.  $\leq 40\%$  wt. Cl) are used in these applications.

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

- high light-fastness;
- strong binding to the leather compared to other additives (low migration);
- dry feel surface finish with excellent suppleness.

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

The fat liquor is applied to the leather as a diluted solution. The fat liquoring step is the last stage of leather preparation. The amount of fat liquor used in this step is around 7–12 per cent, based on the shaved weight of the leather to be treated (i.e. around 70–120 g of fat liquor/kg of leather). Since the fat liquor typically contains around 10 per cent (range 5–15 per cent) chlorinated paraffin, the amount of chlorinated paraffin used

in this step is around 7–12 g chlorinated paraffin/kg leather (range 3.5–18 g chlorinated paraffin/kg leather). The process itself takes place in enclosed rotating drums at temperatures in the region of 40–60°C, with each batch taking around 1–4 hours depending on the end-product being produced. The pH of the reaction is carefully controlled throughout the process by the addition of formic acid to the emulsion (pH is changed from around 5.5 at the start to 3.6 at the end of the process). The pH is used to affect the nature of the leather surface, the rate of absorption of the fat liquor and the stability of the emulsion. The high binding efficiency of the leather for the chlorinated paraffin means that the relative composition of the additives in the fat liquor solution changes with time during the process. It is believed that not more than two per cent of the original amount of chlorinated paraffin is present in the spent fat liquor solution at the end of the process (industry estimate based on experience of the process (Euro Chlor, 1998)).

Of the LCCPs, both C<sub>18–20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins are thought to be used in leather fat liquors.

## 2.2.8 Other uses

There are several other uses of chlorinated paraffins mentioned in the literature. In most of these reports the types of chlorinated paraffins used are not clear, and many may refer to historic uses. Some of these are outlined below. If LCCPs are currently used in any of these applications then the amounts are likely to be very small.

### 2.2.8.1 *Plastics other than PVC*

It has been reported that other plastics, such as polyolefins (for example polyethylene and polypropylene) may be flame retarded with chlorinated paraffins containing around 70% wt. Cl. They are used at a concentration of around 3–8 per cent by weight, together with antimony trioxide as synergist or in combination with other flame retardants (Zitko and Arsenault, 1974; Howard *et al.*, 1975).

Chlorinated paraffin concentrations of around 4–35 per cent by weight have been reported as being suitable for flame retarding plastics based on polystyrene (Zitko and Arsenault, 1974).

Other reported applications of chlorinated paraffins include flame retarding acrylics and modacrylics, polyesters, phenolic resins and polyurethane products (Zitko and Arsenault, 1974).

It has been confirmed that European chlorinated paraffin producers do not currently supply LCCPs for use in plastics other than PVC, but it is thought that historically, solid grades of LCCPs were made in the EU for flame retardant use in electrical equipment cases (Euro Chlor, 2001b).

Most of the available information on these uses refers to chlorinated paraffins in general, rather than specifically LCCPs. If there is any current use of LCCPs in these applications then they are most likely to be highly chlorinated 70% wt. Cl products that are imported into the EU, and the quantity used is likely to be small. The emissions are likely to be similar to those associated with PVC and rubber, and so the assessment of these uses should also be applicable to any other uses that may occur in polymers.

### 2.2.8.2 Printing inks

The European Confederation of Paint, Printing Ink and Artists' Colours Manufacturers' Associations (CEPE) operates a voluntary recommendation for the exclusion of certain raw materials from printing inks and related products. As part of this, they publish an Exclusion List, which has the full support of all its manufacturing members for printing inks. Chlorinated paraffin plasticisers are on this exclusion list and so it is very unlikely that LCCPs are currently used in this application in the EU.

## 2.3 Trends

About 5,000–10,000 tonnes of LCCPs are used in the EU each year for the years 1998–2004. A small upward trend in EU consumption is evident over this time period but it is possible that at least some of this increase in EU consumption in more recent years is related to the expansion of the EU to 25 countries. The main current areas of use are as:

- a secondary plasticiser in PVC;
- a flame retardant in rubber;
- a plasticiser/flame retardant in sealants/adhesives and paints;
- an extreme pressure additive to metal cutting/working fluids;
- a component of leather fat liquoring treatments;
- a waterproofing agent for textiles.

Of these areas, there appears to have been a marked increase in the use of LCCPs in rubber, in particular between the years 1999 and 2004 (although a high level of use in this area was also evident in 1998); the use of LCCPs in sealants, textiles and leather fat liquors has markedly decreased over the same time period. The use of LCCPs in the other areas have either increased slightly (plasticiser in PVC) or decreased slightly (paints, metalworking lubricants) between 1999 and 2004.

It is possible that the use of LCCPs in some areas could increase in the future as they replace other types of chlorinated paraffins (notably medium-chain chlorinated paraffins) for which controls on use are being considered (Entec, 2004). The extent of any replacement of medium-chain chlorinated paraffins with LCCPs will depend upon the final form of the risk reduction measures taken forward for medium-chain chlorinated paraffins, and also any changes to the classification and labelling of medium-chain chlorinated paraffin (a proposal for the classification and labelling of medium-chain chlorinated paraffins as R64 – may cause harm to breastfed babies – is currently being considered (ECB, 2005b)).

LCCPs have been identified as *potential* alternatives for medium-chain chlorinated paraffins in the following applications:

- Paints:
  - anti-corrosion primers/topcoats for metals based on PVC-related copolymer;
  - Outdoor wall paints, acrylics.

- Rubber and polymers other than PVC:
  - conveyor belts and tubes for compressed air in the mining industry;
  - bellows for buses, metro and trains;
  - profiles for fire-proof doors.
- Leather fat liquors.

In many cases other (non-chlorinated paraffin) alternatives also exist.

It should be stressed that at this stage the final form of any risk reduction measures needed for medium-chain chlorinated paraffins is still to be decided.

Industry has also indicated that it is theoretically possible that LCCPs could be used to substitute other types of chlorinated paraffins in some applications. However, there are technical problems relating to the acceptability of the physical properties. For example, for a given chlorine content the viscosities and densities of the LCCPs are higher than those of short- and medium-chain length chlorinated paraffins. This difference can be overcome in some applications, such as paints, by adding solvent, but this difference cannot be easily overcome for most of the applications. In addition, there are economic issues relating to substitution as the paraffinic feedstock for LCCPs is more expensive than that for other types of chlorinated paraffins.

For paints and coatings, there is a general move away from chlorinated paraffin-containing products to higher solids/lower VOC alternative coatings such as epoxy resins as a result of increased controls on VOC emissions. There is no move within the industry to use LCCPs to replace other types of chlorinated paraffins in paints and coatings (BCF, 2001).

For metalworking and cutting fluids, there is a general trend away from the use of chlorinated paraffins in general in this area and it is unlikely that the amounts of LCCPs used will increase as a result of replacement of other types of chlorinated paraffin (BLF, 2001). Recent information from industry has indicated that LCCPs are not used in emulsifiable metalworking fluids (Euro Chlor, 2008), however, the coverage of the survey is unclear (it is based on the customers of members of Euro Chlor but the percentage of customers responding is unclear).

In summary, the available information indicates that LCCPs are not generally being seen as possible replacements for other types of chlorinated paraffins. It is possible that an increased use of LCCPs could occur in some areas in the future once the actual form of the risk reduction measures that will be applied to medium-chain chlorinated paraffins are known, but at this stage it is very difficult to estimate what potential increase (or otherwise) in the consumption of LCCPs could arise as a result of such measures.

The emission estimation, PEC calculations and risk characterisation in this assessment are based on the use pattern of LCCPs in 2004, but assume a consumption of around 10,000 tonnes/year. This approach allows for a potential future increase in the consumption of LCCPs.

Very recently, confidential information has become available on the use pattern of LCCPs in the EU in 2006 (Euro Chlor, 2007). This information arrived too late to be taken into account in the emission estimates used in this risk assessment, however the trends in these new data are discussed below.

The data show that the total consumption of LCCPs in 2006 has decreased slightly compared with 2004. There have been marked decreases in the consumption on LCCPs in rubber and PVC plasticisers, and a smaller decrease in the use in metalworking lubricants in 2006 compared with 2004. There has been an increase in their consumption in water proofing textiles, paints, sealants and adhesives, and leather fat liquors in 2006 compared with 2004.

In terms of the different types of LCCPs, there has been a marked increase in the consumption of the C<sub>18-20</sub> liquid chlorinated paraffins in 2006 compared with 2004. The increase in consumption is in metalworking lubricants, water proofing textiles, paints, sealants and adhesives and leather fat liquors. However, there was a marked reduction in the use of C<sub>18-20</sub> liquid chlorinated paraffins in PVC plasticisers compared with 2004.

For the C<sub>>20</sub> liquid chlorinated paraffins, the consumption for all uses except for paints has decreased since the situation in 2004, with the largest decrease occurring in rubber. The amount of C<sub>>20</sub> liquid chlorinated paraffins used in paints and coatings was similar in 2006 to that in 2004.

For the C<sub>>20</sub> solid chlorinated paraffins, there has been a marked decrease in the amounts used in both rubber and paints in 2006 compared with 2004.

## 2.4 Legislative controls

There do not currently appear to be any regulations relating specifically to the release of LCCPs in the environment. However, as chlorinated hydrocarbons, LCCPs will be covered indirectly by discharge consents etc. that are determined in terms of total organic carbon (TOC) or total adsorbable chlorine (AOX) content. For example, many lubricant blending facilities in the United Kingdom use oil-separation systems to achieve levels of oil of <5 mg/l in their discharges, and many leather formulators work to AOX levels of <0.5–1 ppm in their discharges.

In Germany, certain halogen-containing wastes, for example metalworking fluids with >2 g halogen/kg and halogen-containing plasticisers, are classified as potentially hazardous waste and are incinerated (BUA, 1992).

In addition to this, the current manufacturers of chlorinated paraffins recommend management processes (Euro Chlor, 2001b) for chlorinated paraffins. These are shown in Table 2.5. The recovery treatments are strongly recommended by the current manufacturers.

**Table 2.5 Treatment methods currently recommended by Euro Chlor**

Type of waste	Preparation for disposal/recovery	Treatment methods
Liquid wastes e.g.: oily waste from metalworking; plasticiser condensates; water based mixtures and emulsions	Water separation e.g.: thermal splitting; ultrafiltration; chemical splitting.	Recovery e.g.: incineration with energy recovery (limiting chlorine content to 1 per cent); clean-up and re-use.  Disposal e.g.: incineration without energy recovery; absorb onto solids and then landfill.
Solid wastes e.g.: plastics; rubber and resins; dried sludges from user processes.		Recovery e.g.: incineration with energy recovery; re-process thermoplastics; grind/chip rubber.  Disposal e.g.: incineration without energy recovery; landfill

A number of uses of chlorinated paraffins in general are covered by the Integrated Pollution Prevention and Control (IPPC) Directive 1996/61/EC. Depending on the quantities involved (Entec, 2004), companies falling under this legislation include:

- producers of LCCPs;
- metalworking sites (only large companies in the ferrous and non-ferrous metals sectors);
- some PVC compounding/conversion sites;
- leather processors (larger sites).

These sites are covered by the IPPC Directive based on the nature and size of the installation rather than on the specific use of chlorinated paraffins. The IPPC Directive does, however, place specific requirements on Member States to produce emission limit values for organohalogen compounds in general, which would include LCCPs. In addition, the “local authority pollution prevention and control regime” in the United Kingdom places requirements on the emissions to air from coating processes which include spread coating (relevant to the production of PVC wall coatings), as well as various other coating processes. These requirements are likely to encompass many companies involved in the formulation and application of paints.

# 3. Environmental exposure

## 3.1 Environmental releases

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

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

Some of the information obtained for this assessment, particularly regarding the total amounts of LCCPs used in the EU for various applications, is considered as confidential. As a result, the raw data do not appear in this report (they are summarised in a confidential Annex), but the raw industrial data have been used to derive some of the figures used.

The emission estimates derived in the following sections are based on a total EU consumption of LCCPs of 10,000 tonnes/year using the 2004 use pattern data. The actual EU consumption in 2004 reported by Euro Chlor is well below this level but there are a number of factors that need to be taken into account here. For instance, the available information indicates that the actual EU consumption of LCCPs is increasing, and the consumption figures available do not take into account any imports of LCCPs, neither as the substances themselves nor as components of semi-finished articles. In addition, it is also possible that future controls on some uses of other chlorinated paraffins (for example those being considered on medium-chain chlorinated paraffins; see Section 2.3) may result in increased use of LCCPs as a replacement. The actual extent of any possible increase in use of LCCPs in the future as a result of these controls is very difficult to predict (particularly as the precise control measures that will be applied to medium-chain chlorinated paraffins are unknown at this stage). The use of an annual EU consumption value of 10,000 tonnes/year for LCCPs as a basis for this assessment allows for an approximately 25 per cent increase in their use in the future compared with the known consumption in 2004.

### 3.1.1 Releases from production

There is no production of LCCPs in the United Kingdom. Information on European production sites is given in the confidential annex.

### 3.1.1.1 *Default release estimate*

Default release estimates for production can be obtained using the emission factors contained in Appendix 1 of the TGD. These are carried out for a typical production site, assuming a production of around 5,000 tonnes/year as an example.

The default emission factors (Table A1.1 of Appendix 1 of the TGD; Main Category 1c; vapour pressure <1 Pa) are 0 to air and 0.003 (0.3 per cent) to waste water for all types of LCCPs. The number of days of release can be estimated as 300 (Table B1.1 of Appendix 1 of the TGD).

Therefore, using these figures, the default release estimates for a 5,000 tonnes/year production site are:

0 kg/day to air  
100–200 kg/day to waste water (over 300 days).

### 3.1.1.2 *Industry-specific release information*

Mukherjee (1990) reported that chlorinated paraffin emissions from a production plant in Germany were around 0.1 g/kg of product, based on an air concentration of around 30 mg/Nm<sup>3</sup>, presumably in the exhaust gases. BUA (1992) gives an atmospheric emission of around 250 kg/year of chlorinated paraffin for Germany in the form of dust and vapour. It is not known which type of chlorinated paraffin these figures refer to.

Emissions to water at a German plant manufacturing solid chlorinated paraffins have been reported by BUA (1992). The effluent from the plant (prior to waste water treatment) was thought to contain around 1 kg/year of chlorinated paraffin.

More recent emission data have been provided for an LCCP production site in the EU. The data supplied are confidential but an emission factor to waste water of 1.3–19 g/tonne of product can be derived from this information (the data are summarised in a confidential Annex). This factor will be used to calculate the emissions from a generic site producing 1,000 tonnes/year of C<sub>18–20</sub> liquid chlorinated paraffins, 5,000 tonnes/year of C<sub>>20</sub> liquid chlorinated paraffins and 100 tonnes/year of C<sub>>20</sub> solid chlorinated paraffins, over 300 days/year.

C <sub>18–20</sub> liquid	Local release:	19 kg/year or 0.063 kg/day to waste water
C <sub>&gt;20</sub> liquid	Local release:	95 kg/year or 0.32 kg/day to waste water
C <sub>&gt;20</sub> solid	Local release:	1.9 kg/year or 0.0063 kg/day to waste water

### 3.1.1.3 *Transportation losses*

In theory, chemicals can be released to the environment during loading of transport containers at production sites and unloading of containers at the sites where the substance is used. These losses can take the form of spillages (to waste water) or volatilisation losses. LCCPs have very low vapour pressures at ambient temperatures and so any losses to the atmosphere should be negligible from loading or emptying containers. Losses to waste water could occur but these are considered as part of the



general losses from production sites and sites of use (e.g. formulation sites) and are already included in the release estimates reported and so are not considered separately here.

### 3.1.2 Release from use in PVC

LCCPs are used as (secondary) plasticisers in PVC. The main types currently used are the C<sub>18-20</sub> products, although small amounts of C<sub>>20</sub> liquid products may have also been used in the recent past.

Chlorinated paraffins are usually added at 10–15 parts per hundred resin (phr), although some of the more highly chlorinated substances (e.g. >52% wt. Cl) are more compatible with PVC and can be used at around 25 phr, for example in a cable compound. Taking into account the other additives present in the PVC such as primary plasticiser, filler, stabiliser, lubricant etc., these loadings on a resin basis equate to a chlorinated paraffin content of around 6–10 per cent by weight, based on the PVC compound for the typical 10–15 phr loading and 15 per cent by weight based on the 25 phr loading. The higher loadings are generally found in extrusion compounds with the lower loadings being used in PVC for coating processes.

Based on the above information, an LCCP content of 10–15 per cent by weight of the PVC compound/product is a reasonable worst case value, with a lower limit of around six per cent by weight of the PVC.

#### 3.1.2.1 Default release estimate

Appendix 1 of the TGD gives default release estimates for substances used in the polymers industry. The release factors for plasticisers (Use Category 47) during the polymer processing step for thermoplastics are 0.005 (0.5 per cent) to air (vapour pressure <1 Pa; estimated boiling point ≥400°C) and 0.001 (0.1 per cent) to waste water (Table A3.11 of Appendix 1 of the TGD). The same default emission factor would apply to all types of LCCPs.

Based on the available data, the amount of PVC produced (in the regional model) containing LCCPs is estimated at 350–520 tonnes/year for the C<sub>18-20</sub> liquid type, assuming that production of PVC is widespread throughout the EU. Using Table B3.9 of Appendix 1 of the TGD, the amount of PVC containing LCCPs produced on a site can be estimated at between 78 tonnes/year over 31 days and 88 tonnes/year over 35 days.

Using the base figures given above, the following default release estimates can be calculated:

C <sub>18-20</sub> liquid	Local release:	39–66 kg/year or 1.3–1.9 kg/day to air 8–13 kg/year or 0.25–0.37 kg/day to waste water
	Regional release:	262 kg/year to air 52 kg/year to waste water
	Total EU release:	2,620 kg/year to air 520 kg/year to waste water

### 3.1.2.2 Industry-specific release information

The Emission Scenario Document (ESD) on plastics additives (OECD, 2004b) considers the possible release of additives from their use in PVC. Around 220,000 tonnes/year of flexible PVC is produced in the United Kingdom in closed, partially open and open systems, depending on the processing method used to produce the final product. Thus possible releases of LCCPs from many different processes have to be considered. According to the OECD (2004b), the worst case amounts of flexible PVC processed at a site are 744 tonnes/year for a site using open processing systems, 3,990 tonnes/year for a site using partially open processing systems and 341 tonnes/year for a site using closed processing systems. These are based on the known production volume of flexible PVC in the United Kingdom, along with information on the number and size distribution of production sites.

In the following calculations it will be assumed that all the flexible PVC produced at a site contains LCCP at either 10 per cent by weight (for coating processes) or 15 per cent by weight (for extrusion and other processes).

The amounts of LCCPs estimated to be used on a polymer processing site using the OECD (2004b) methodology are shown in Table 3.1.

**Table 3.1 Estimated amounts of LCCPs used at flexible PVC processing sites**

Type of processing	Amount of PVC processed	Estimated amount of LCCPs used per site	
		10% LCCP in resins (coating processes)	15% LCCP in resins (extrusion/other processes)
Open system	744 tonnes/year	74.4 tonnes/year	112 tonnes/year
Partially open system	3,990 tonnes/year	[399 tonnes/year] <sup>a</sup>	599 tonnes/year
Closed system	341 tonnes/year	[34.1 tonnes/year] <sup>a</sup>	51 tonnes/year

Note: <sup>a</sup> Coating processes are usually carried out in open systems as defined in OECD (2004b).

The estimates for the amount of LCCPs used at a worst case site given in Table 3.1 are much higher than those obtained using the Technical Guidance Default values. In particular, the amount estimated to be used at a site operating a partially open process is actually higher than the known total EU usage of LCCPs in PVC. This discrepancy probably arises because LCCPs are not the major chlorinated paraffin used in PVC (medium-chain chlorinated paraffins have a much higher usage) and so as a result, it is very unlikely that a large PVC production site will use only LCCPs in production of PVC (as is assumed in the calculations in Table 3.1) and most of the PVC produced at the site will contain medium-chain chlorinated paraffins.

In terms of the local risk assessment, the most relevant information is the daily amount of LCCP used at a worst case site. Table 3.2 gives a comparison of the values obtained by using the OECD (2004b) methodology (processing occurs over 300 days) and the default methodology given in the TGD. As can be seen, there is general agreement between the two methods when the estimates are expressed as a daily usage rate. Therefore, in this current assessment the daily usage rates obtained from the OECD (2004b) method will be used, along with the number of days obtained from the default Technical Guidance Method. This approach then takes into account the fact

that a large PVC site will only use LCCPs in a proportion of the PVC made at the site (i.e. although PVC will be produced every day at the site, LCCPs will only be used on a few occasions during the year), which is in line with the known relative amounts of medium- and long-chain chlorinated paraffins used in this application.

**Table 3.2 Comparison of estimates for the daily worst case amounts of LCCPs used on a PVC processing site**

Type of processing	Daily amount of C <sub>18-20</sub> liquid chlorinated paraffin used on a site (tonnes/day)		Estimated number of days (TGD method)
	OECD (2004b) estimate	TGD default estimate	
Open system	0.25 – coating processes 0.37 – extrusion/other processes	0.22–0.38	31–35 days mid point – 33 days
Partially open system	2.0 – extrusion/other processes	0.22–0.38	31–35 days mid point – 33 days
Closed system	0.17 – extrusion/other processes	0.22–0.38	31–35 days mid point – 33 days

The following sections estimate LCCP releases during the different steps of PVC processing.

**Raw materials handling (formulation – step 1)**

The LCCPs typically used in PVC in the EU are liquids of low vapour pressure. Losses to the atmosphere are likely to be negligible when the substance is handled at ambient temperature. The liquid plasticisers are usually transported and handled in bulk, using enclosed storage systems and so a minimal loss by spillage can occur. The worst case release figure for loss through spillage is estimated at 0.01 per cent (OECD, 2004b).

Using this release figure and the information discussed above, the release to the environment from sites using the various processing types can be estimated as follows:

C <sub>18-20</sub> liquid	Open processing:	coating	0.025 kg/day over 33 days (0.83 kg/year)
		extrusion/other	0.037 kg/day over 33 days (1.2 kg/year)
	Partially open processing:	extrusion/other	0.2 kg/day over 33 days (6.6 kg/year)
		Closed processing:	extrusion/other

Based on the total EU usage of LCCPs in this application, the total EU emission from this source can be estimated as 52 kg/year for the C<sub>18-20</sub> products. According to the TGD, the regional releases are 10 per cent of these figures, i.e. 5.2 kg/year, assuming the processing of PVC is widespread throughout the EU.

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

### **Compounding (formulation – step 2)**

There are two general methods used for compounding PVC: dry blending and plastisol blending (OECD, 2004b; see Section 2.2.1 for further details).

Dry blending is used to prepare blends for extrusion, injection moulding and sometimes calendaring (Banbury blending is also occasionally used to prepare blends for calendaring, but the emissions from this process are similar to those associated with dry blending (OECD, 2004b)).

Dry blending accounts for the compounding of around 65–70 per cent of all plasticisers used in PVC. Dry blending involves mixing the PVC powder/granules with the plasticiser using a high speed rotating agitator which heats the material by friction (the maximum temperature reached is 100–120°C). The plasticiser is completely absorbed by the PVC in the process, and the only source of release to air is from the hot material.

The loss to air of a plasticiser such as di-(2-ethylhexyl) phthalate (DEHP) from the process is estimated to be a maximum of 0.01 per cent. The vapour pressure of DEHP is around  $2.2 \times 10^{-5}$  Pa at 20°C and so DEHP can be considered to be of somewhat lower volatility than the C<sub>18–20</sub> liquid chlorinated paraffins (approximate estimated vapour pressure  $2.5 \times 10^{-4}$  Pa at 25°C) but of similar volatility to the C<sub>>20</sub> liquid chlorinated paraffins (approximate estimated vapour pressure  $2.5 \times 10^{-5}$  Pa at 25°C), taking into account the small difference in temperature between the DEHP data and the LCCP data. When considering these comparisons, it should be born in mind that there is considerable uncertainty over the actual vapour pressures of LCCPs (see Section 1.4.4).

Other information is available that allows a comparison to be made of the relative volatility of LCCPs to that of DEHP. These data refer to the weight loss on heating the plasticisers for four hours. The data for LCCPs are discussed in detail in Section 1.4.4 and are summarised below in Table 3.3, along with the data obtained for DEHP under similar conditions (Euro Chlor, 1999).

**Table 3.3 Weight loss on heating plasticisers and LCCPs for four hours at 180°C**

<b>Substance</b>	<b>Weight loss after heating for 4 hours at 180°C</b>
DEHP	1.9%
C <sub>18–20</sub> , 47–48% wt. Cl	0.8–1.6%
C <sub>18–20</sub> , 50–52% wt. Cl	0.7–1.3%
C <sub>&gt;20</sub> , 42% wt. Cl	0.4–0.5%
C <sub>&gt;20</sub> , 48% wt. Cl	0.3–0.4%

From these data it can be seen that at an elevated temperature the C<sub>18–20</sub> liquid products appear to be around 1.2–2.7 (typically around 2.5) times less volatile than DEHP and the C<sub>>20</sub> liquid products around 3.8–6.3 (typically around five) times less volatile than DEHP. It should also be born in mind that some of the weight loss seen with the chlorinated paraffins will be due to evolution of HCl from decomposition of the

chlorinated paraffin at the elevated temperature used (the weight loss from HCl formation was generally around 0.2 per cent under similar conditions; see Section 1.4.4) and so these values probably represent the upper limits of the relative volatilities.

Although these data are not directly comparable with the losses expected from the dry blending process, they do provide some experimental indication of the relative volatility of the LCCPs compared with DEHP. Given the uncertainties over the actual vapour pressure of LCCPs, these data are used here in preference to comparisons of relative volatility based on the vapour pressures of DEHP and LCCPs. In terms of the actual volatility from PVC, the relative volatility of the plasticisers will also depend to some extent on their compatibility (or solubility) in the PVC. As discussed in Section 2.2.1, the compatibility of the chlorinated paraffin with both PVC and the primary plasticiser varies with both the carbon chain length and degree of chlorination.

Based on the available experimental weight loss data, it appears that both the C<sub>18-20</sub> liquid products and the C<sub>>20</sub> liquid products are less volatile from PVC than DEHP (by a factor of 2.5 and 5, respectively). Therefore the DEHP emission factor of 0.01 per cent to air will be reduced to 0.004 per cent for the C<sub>18-20</sub> liquid products (the equivalent factor for the C<sub>>20</sub> liquid products would be 0.002 per cent but there is no current use of this type of chlorinated paraffin in PVC).

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

The estimated worst case emissions to air of LCCPs from the dry blending process are shown below.

C <sub>18-20</sub> liquid	Open processing:	extrusion/other	0.015 kg/day over 33 days (0.49 kg/year)
	Partially open processing:	extrusion/other	0.080 kg/day over 33 days (2.6 kg/year)
	Closed processing:	extrusion/other	0.0068 kg/day over 33 days (0.22 kg/year)

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

Using the above emission factors, and assuming that 70 per cent of the LCCPs are used in dry blending processes (i.e. the same as for PVC plasticisers in general), then the total EU release from this source can be estimated as 14.6 kg/year for the C<sub>18-20</sub> liquid products. The regional release will be taken to be 10 per cent of these figures (1.5 kg/year for the C<sub>18-20</sub> liquid products). These releases are initially to the air.

### **Conversion (processing)**

This section considers the releases from several processing methods. The release estimates assume that some fume reduction equipment is used. Such equipment is generally found at large sites (using >250 tonnes of plasticiser/year). The equipment is less common at smaller plants (using <250 tonnes of plasticiser/year) and the releases for some processes could be around 10 times higher at plants where fume reduction

equipment is not present. The 250 tonne plasticiser limit is considered to be a reasonable criterion to distinguish between larger and smaller plants (OECD, 2004b). This figure refers to the total plasticiser used in the flexible PVC (as discussed earlier, chlorinated paraffins are generally used as secondary plasticisers along with other plasticisers such as DEHP, and chlorinated paraffins other than long-chain are used for the bulk of this application).

According to the OECD (2004b), the typical total plasticiser level in flexible PVC is 30–50 per cent. Thus 250 tonnes/year plasticiser is equivalent to a production of around 500–830 tonnes/year of flexible PVC. As can be seen from the figures reported in Table 3.1, the sites with open and partially open system are generally large (and so use fume reduction equipment), whereas sites with closed systems fall into the size of site where fume reduction equipment may not always be used. The following sections describe the possible losses to the environment from the various processes. The resulting release estimates are summarised in Table 3.4.

### ***Calendering (open system)***

A reasonable worst case emission of plasticiser (e.g. DEHP) from a calendering process is around 0.05 per cent to air. From the above discussion, it is suggested that this emission factor is reduced by a factor of around 2.5 for C<sub>18–20</sub> liquid chlorinated paraffins (and by a factor of around 5 for C<sub>>20</sub> liquid chlorinated paraffins) to take account of their lower volatilities compared to DEHP. This adjustment gives an emission factor of 0.02 per cent for the C<sub>18–20</sub> chlorinated paraffins (the equivalent factor for the C<sub>>20</sub> liquid chlorinated paraffins would be 0.01 per cent). This figure assumes that emission reduction equipment is used (OECD, 2004b). For sites with no emission reduction equipment the emission factor could be expected to be around a factor of 10 higher than this figure.

### ***Extrusion (partially open or closed system)***

The major types of flexible PVC products produced by extrusion are wire, cable and hoses, and blow-moulded film. For wire, cable and hose production there is no emission/exposure from the extruder itself. The main source of release is likely when the hot material leaves the die. As the surface area and exposure time (of the hot plastic to air) is lower than for calendering processes, an emission factor of 0.01 per cent to air is estimated for a typical plasticiser (e.g. DEHP) (OECD, 2004b). Taking into account the lower volatility of LCCPs, the equivalent emission factor is 0.004 per cent for C<sub>18–20</sub> liquid products (and 0.002 per cent for C<sub>>20</sub> liquid products). This emission factor assumes that emission reduction equipment is used. For applications where this equipment is not generally used, the emission factors may be around 10 times higher than these values (i.e. 0.04 per cent for C<sub>18–20</sub> liquid products).

### ***Injection moulding (closed system)***

Injection moulding can be considered to be comparable to extrusion except that both the moulding and cooling phases of the process take place in closed systems. Therefore, emissions should be lower than for extrusion processes. However, as a worst case OECD (2004b) recommends an emission factor of 0.01 per cent to air for a general plasticiser such as DEHP. Again, for the less volatile LCCPs, this figure can be reduced by a factor of around 2.5 for a C<sub>18–20</sub> liquid chlorinated paraffin, giving an emission factor of 0.004 per cent (the equivalent emission factor for a C<sub>>20</sub> liquid chlorinated paraffin would be 0.002 per cent). For applications where this equipment is not generally used, the emission factors may be around 10 times higher than this value (i.e. 0.04 per cent for C<sub>18–20</sub> liquid products).

### ***Plastisol spread coating (open system)***

Spread coating products include articles such as cushioned flooring, wall coverings, tarpaulins etc. These products are gelled in tunnel ovens heated with hot air at about 180°C. The emission factor for a typical plasticiser such as DEHP from the process is around one per cent to air within the oven, based on both calculation and laboratory experiment (OECD, 2004b). This figure refers to the air leaving the equipment. Not all of this reaches the environment since condensation takes place in cooler pipes, ducts and stacks. Air treatment is thought to be relatively common within the industry (75 per cent of the activity in 1989 had air treatment and the figure was approaching 100 per cent in 1998 (OECD, 2004b)).

Two types of air treatment are used: air filtration which typically removes 95 per cent of the plasticiser in the air; and incineration. Thus the overall emission factors for a typical plasticiser such as DEHP are estimated at between 0 and 0.05 per cent to air for the vast majority of sites with air emission treatment and 0.5 per cent to air for a site with no air emission treatment (OECD, 2004b). For the less volatile C<sub>18-20</sub> chlorinated paraffins, these factors can be reduced by a factor of 2.5. This gives emission factors for C<sub>18-20</sub> liquid products of 0-0.02 per cent to air for sites with air emission treatment and 0.2 per cent to air for sites with no air emission treatment (the equivalent factors for the C<sub>>20</sub> liquid products would be 0-0.01 per cent to air and 0.1 per cent to air for sites with and without air emission treatment respectively).

### ***Other plastisol processes***

Other processing methods for plastisol PVC include car body coating and sealing, rotational coating, dipping and slush moulding. Of these, car underbody coating and sealing is the most important in terms of volume, but it is thought that chlorinated paraffins are not used in this application. In these processes, the coatings are dried in long air-heated tunnel ovens at temperatures of 130-160°C. The ovens in this industry have integrated air incinerators since the same process is used to simultaneously dry paint coats (OECD, 2004b). Therefore, the releases of LCCPs from this process, if they are used, should be near zero.

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

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

The estimated worst case releases of LCCPs to air from plastic processing obtained for various types of processes using the above information are shown in Table 3.4. As can be seen from the emission estimates, the actual releases from the various sites are very similar. Although the overall emission factors at large sites may be lower than at small sites owing to the use of emission controls on air releases, larger sites also process a larger quantity of plastics, so the overall emissions are roughly the same.

The actual breakdown of the use of LCCPs between the various processes is unknown. However, the OECD (2004b) gives the following breakdown of the production of flexible PVC: 25 per cent in closed systems; 49 per cent in partially open systems and 26 per cent in open systems.

If the same approximate breakdown applies to the use of LCCPs, then the total EU emissions from polymer processing can be estimated as 427 kg/year to air for C<sub>18-20</sub> liquid products (assuming an emission factor of 0.2 per cent from open systems and

0.04 per cent from partially open and closed systems). This figure assumes that no air emission control is applied. In Section 2.2.1 information is reported indicating that at least 50 per cent of the LCCPs are likely to be processed at sites with exhaust air treatment. The estimated emissions from these sites would be a factor of 10 lower, leading to total emissions from all sites of around 235 kg/year to air for C<sub>18-20</sub> liquid products, assuming that 50 per cent of the sites have such exhaust air treatment. The actual overall proportion of the industry with such controls is currently unknown, but the use of such equipment is relatively commonplace, particularly at large sites, and is becoming increasingly common at other sites. Based on this, the total EU emission from this source will be taken as 235 kg/year for the C<sub>18-20</sub> liquid chlorinated paraffins. The regional release will be taken as 10 per cent of the total EU release as recommended in the TGD.



**Table 3.4 Estimated worst case emissions of C<sub>18–20</sub> liquid chlorinated paraffins to air from PVC processing sites**

Process	Type of system	Release factor to air		Amount of chlorinated paraffin used per site (kg/day)	Number of days of use (days/year)	Release of LCCP per site <sup>b</sup>	
		Air emission control	No air emission control			Air emission control	No air emission control <sup>c</sup>
Calendering	open	0.02%	0.2%	370	33	0.074 kg/day (2.4 kg/year)	-
Extrusion	partially open	0.004%	0.04%	2,000	33	0.080 kg/day (2.6 kg/year)	-
	closed	0.004%	0.04%	170	33	-	0.068 kg/day (2.2 kg/year)
Injection moulding	closed	0.004%	0.04%	170	33	-	0.068 kg/day (2.2 kg/year)
Plastisol spread-coating <sup>a</sup>	open	0.02%	0.2%	250	33	0.050 kg/day (1.7 kg/year)	-

Notes: <sup>a</sup> Release from other plastisol processes such as dip coating and slush moulding is expected to be similar. Release from processes such as car underbody coating and sealing (if LCCPs are used), and rotational moulding are thought to be negligible.

<sup>b</sup> In the PEC calculations it will be assumed that 50 per cent of the air emissions eventually reach waste water at the site (see text).

<sup>c</sup> Taken to represent a small site using closed processing where fume reduction equipment may not always be used.

According to the OECD (2004b), the releases to air are as hot gases. For substances with low vapour pressures such as LCCPs, the possibility of condensation of the hot gases needs to be considered. This may lead to some of the releases initially entering other waste streams such as water due to cleaning etc. OECD (2004b) gives no guidance as to the fraction of the air release that could eventually end up in other effluent/waste streams. As a worst case approach, it could be assumed that 50 per cent of the release to air would eventually reach waste water. In the absence of other information, this assumption will be used later in the PEC calculations.

### 3.1.3 Release from use as a plasticiser/flame retardant in rubber

Information provided by industry indicates that both C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffin products are used as plasticisers/flame retardants in rubber and textiles.

LCCPs are used as flame retardant softeners (or process oils) in rubber. The estimated amount of rubber containing LCCPs produced in a region of the EU is estimated as 4,175–8,350 tonnes/year (C<sub>>20</sub> liquid chlorinated paraffin) and 207–414 tonnes/year (C<sub>>20</sub> solid chlorinated paraffins), assuming that production of rubber is widespread throughout the EU.

#### 3.1.3.1 Default release estimation

Appendix 1 of the TGD gives default release estimates for substances used in the polymers industry. No specific release factors are given for the rubber industry. However, since the processes involved for both rubber and plastic are generally similar (in that they both use a compounding step involving mixing of the flame retardant with plastic or rubber, followed by a shaping/curing operation involving heat), Table 3.11 of Appendix 1 of the TGD will be used for the default release estimation. From this table, the release factors for flame retardants (Use Category 22) during polymer processing for thermoplastics are 0.0005 (0.05 per cent) to air (boiling point  $\geq 300^{\circ}\text{C}$ ; vapour pressure  $< 1\text{ Pa}$ ) and 0.0005 (0.05 per cent) to waste water for both the C<sub>>20</sub> liquid and solid chlorinated paraffins. For thermosetting resins, the release factor to air is zero and the release factor to waste water is 0.0005 (0.05 per cent).

The estimated amount of rubber containing LCCPs produced in a region of the EU is estimated as 4,175–8,350 tonnes/year (C<sub>>20</sub> liquid chlorinated paraffin) and 207–414 tonnes/year (C<sub>>20</sub> solid chlorinated paraffins), assuming that production of rubber is widespread throughout the EU. Using Table B3.9 of Appendix 1 of the TGD, the amount of rubber containing LCCPs produced on a site would be 626–835 tonnes/year over 251–300 days/year for the C<sub>>20</sub> liquid chlorinated paraffins and 51.8–103.5 tonnes/year over 21–41 days/year for the C<sub>>20</sub> solid chlorinated paraffins. The amount of LCCP used to produce this amount of rubber would be 41.8 (over 300 days) or 62.6 tonnes/year (over 251 days) for the C<sub>>20</sub> liquid chlorinated paraffin and 5.2 tonnes/year (over 21–41 days) for the C<sub>>20</sub> solid chlorinated paraffin.

Based on the above figures, the following default release estimates can be made for the LCCPs emitted:

C <sub>&gt;20</sub> liquid	Local release:	20.9–31.3 kg/year or 0.070–0.12 kg/day to air 20.9–31.3 kg/year or 0.070–0.12 kg/day to waste water
	Regional release:	209 kg/year to air 209 kg/year to waste water
	Total EU release:	2,088 kg/year to air 2,088 kg/year to waste water
C <sub>&gt;20</sub> solid	Local release:	2.6 kg/year or 0.063–0.12 kg/day to air 2.6 kg/year or 0.063–0.12 kg/day to waste water
	Regional release:	10.4 kg/year to air 10.4 kg/year to waste water
	Total EU release:	104 kg/year to air 104 kg/year to waste water

### 3.1.3.2 Industry-specific release information

A recent survey of rubber manufacturers in the United Kingdom indicated that releases of chlorinated paraffins from the process were thought to be very low, although no quantitative data were provided (BRMA, 2001).

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

Another source of potentially useful information is the ESD on plastics additives (OECD, 2004b). This details possible releases to the environment from the use of flame retardants in plastics. Although the processing (curing/vulcanisation) of natural and synthetic rubber take place at lower temperatures (e.g. 125–150°C) than for many polymers, the same sorts of processes as for plastics (e.g. injection moulding, extrusion, calendaring etc.) can be used (Bouton, 1992; Kirk-Othmer, 1997). Therefore, as the compounding and subsequent processing of plastics are essentially similar to those of rubber, a similar (but possibly smaller) release would be expected from use of an additive in rubber than is found in plastics.

#### **Raw materials handling (formulation – step 1)**

Both C<sub>>20</sub> liquid and solid chlorinated paraffins may be used in rubber. Volatile losses to the atmosphere during handling at ambient temperatures are likely to be negligible for both types. According to the OECD (2004b), liquid additives are usually transported and handled in bulk, using enclosed storage systems and so minimal loss by spillage can occur. The worst case release figure for loss through spillage is estimated at 0.01 per cent.

For solid materials of particle size >40 µm a worst case release figure of 0.2 per cent to solid waste/water is recommended as a result of dust generation etc. The long-chain solid chlorinated paraffins are generally reported to be "waxy" solids and so the potential for dust generation may be lower than indicated by this figure. Initially these emissions will be to the atmosphere, but eventually the particles will be removed or settle and so ultimately losses will be to solid waste or waste water. As a worst case it could be assumed that all the release occurs to waste water.

### ***Compounding (formulation – step 2)***

Compounding is usually a dry process, where the base polymer and additives are mixed together. For plastics, the mixing process generates heat or is heated externally and so there is a potential for volatilisation from the process. This volatilisation loss is estimated at 0.002 per cent for organic flame retardants (OECD, 2004b). As this loss occurs as hot gas, there is a potential for subsequent condensation of the flame retardant and so it may also enter other waste streams as a result of cleaning etc. Similar to the case with PVC, it will be assumed that this loss is eventually split 50:50 between air and water, giving a release factor of 0.001 per cent to air and 0.001 per cent to waste water for both the solid and liquid LCCPs.

In addition to the loss by volatilisation, the solid LCCPs may be susceptible to dust generation during the compounding process. This loss is estimated at 0.01 per cent for powders of particle size >40 µm. Initially this loss will be to air, but ultimately it will be to solid waste or waste water as a result of settling/cleaning within the factory. As a worst case it could be assumed that all this loss eventually occurs to waste water.

### ***Conversion (processing)***

The OECD (2004b) gives the loss to the atmosphere of organic flame retardants from the conversion of plastics to be 0.01 per cent from open processes, 0.006 per cent from partially open processes and 0.002 per cent from closed processes. These releases will occur initially to air. Similar to the case with PVC, to take into account the possible condensation of the substance (and subsequent cleaning loss) it will be assumed that 50 per cent of the releases initially to air will enter into waste water and 50 per cent will remain in the air.

### ***Overall emission factor***

Based on the worst case emission figures derived from the OECD (2004b), the overall loss of LCCP from the production of rubber can be estimated at up to 0.016 per cent to waste water and 0.006 per cent to air for C<sub>>20</sub> liquid chlorinated paraffin products<sup>4</sup> and 0.206 per cent to waste water and 0.006 per cent to air for C<sub>>20</sub> solid chlorinated paraffins. The loss to waste water for the solid chlorinated paraffins is dominated by the solid losses (dust generation) at the raw materials handling stage. As indicated earlier, the solid chlorinated paraffins are generally described as "waxy" solids and so may be much less susceptible to dust generation than is indicated by these calculations.

The other emission factors available are <0.001 per cent (compartment unknown) reported by the Government of Canada (1993) and the default emission factors from the TGD of 0.05 per cent to air and 0.05 per cent to waste water. The basis of these figures is unknown. The figure reported by the Government of Canada (1993) is much lower than estimated using the approach outlined by the OECD (2004b) and may indicate that, due to the generally lower processing temperatures involved, the losses of flame retardant from rubber manufacturing are lower than those associated with the manufacture of plastic. However, it is not clear if this emission factor also includes the possible contribution from dust generation or spillage of raw materials and so the figures derived from the OECD (2004b) will be used in the risk assessment as a worst

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<sup>4</sup> These emission factors are those recommended in OECD (2004b) for a flame retardant. As discussed in Section 3.1.2, similar factors for the C<sub>>20</sub> liquid products could also be derived if based on the emissions as a plasticiser. In this case the factors would be 0.01 per cent to waste water from spillage; 0.001 per cent to air; 0.001 per cent to waste water from compounding; 0.001-0.005 per cent to air; and 0.001-0.005 per cent to waste water from conversion. The overall emission factor would again be 0.016 per cent to waste water and 0.006 per cent to air.

case, recognising the potential problems in extrapolating data on processing of plastics to rubber processing.

The previously estimated default amounts of LCCPs that are used on a rubber production site (62.6 tonnes/year over 251 days for the C<sub>>20</sub> liquid chlorinated paraffin and 5.2 tonnes/year over 21 days for the C<sub>>20</sub> solid chlorinated paraffin) are reasonably consistent with the available figures for the amounts of chlorinated paraffins that are used on sites in the United Kingdom (see Section 2.2.2), given that there appears to have been an increase in the use of LCCPs in this area in recent years. These values will be used as the basis for the realistic worst case release estimates. Using these data, the following release estimates can be obtained:

C <sub>&gt;20</sub> liquid	Local release:	3.8 kg/year or 0.015 kg/day to air 10.0 kg/year or 0.040 kg/day to waste water
	Regional release:	25.1 kg/year to air 66.8 kg/year to waste water
	Total EU release:	251 kg/year to air 668 kg/year to waste water
C <sub>&gt;20</sub> solid	Local release:	0.31 kg/year or 0.015 kg/day to air 10.7 kg/year or 0.51 kg/day to waste water
	Regional release:	1.2 kg/year to air 42.6 kg/year to waste water
	Total EU release:	12.4 kg/year to air 426 kg/year to waste water

### 3.1.4 Release from use as a plasticiser/flame retardant in sealants/adhesives

The main function of chlorinated paraffins in sealants/adhesives is as a plasticiser and/or flame retardant. The main types of LCCP used in sealants/adhesives are the C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid products. The estimated amount of sealant/adhesive containing LCCPs produced in a region in the EU is around 175–262 tonnes/year for the C<sub>18-20</sub> liquid chlorinated paraffins and 354–531 tonnes/year for the C<sub>>20</sub> liquid chlorinated paraffins.

#### 3.1.4.1 Default release estimation

No default release figures are given in the TGD for this use.

#### 3.1.4.2 Industry-specific information

Information on the manufacture of sealants containing medium-chain chlorinated paraffins was reported in the risk assessment of that substance (ECB, 2005a) and forms the basis for the assessment here along with information obtained from industry on LCCPs.

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

sealants are moisture sensitive (particularly the one-part sealants), water is unlikely to be used in the process and so release to waste water is likely to be very low.

Chlorinated paraffins are used in both one-part and two-part sealants, and similar methods are used to produce both types (ECB, 2005a). Typically, sealants are produced in a batch process of around 1,000 kg at a time. The process is simple mixing, sometimes under gentle heat (e.g. up to around 40°C) and is usually carried out under vacuum to avoid moisture entering the process. Once formulated, the sealant is pumped directly from the mixing vessel to fill cartridges (e.g. for one-part sealants) or tins (e.g. for two-part sealants).

Typically, one to two tonnes of sealant containing chlorinated paraffin would be manufactured at a site per week (ECB, 2005a). Losses to waste water during the manufacture of sealants are reported to be low or zero as water is not used in the process (most sealants are moisture sensitive). Solid waste can be generated during the process and this may be up to five per cent of the amount of sealant produced as a result of machine cleaning or scrap material. Cleaning between batches is minimised by the use of dedicated equipment or by starting with the formulation of light coloured product and progressing through to darker coloured products. Generally, the solid waste material is removed from the equipment by hand. Solvent cleaning of the equipment can also occur. These solvents are collected and disposed of at the end of their useful life by registered waste contractors.

Due to the physico-chemical properties of LCCPs, they are likely to be associated with the solid waste phases during the cleaning of equipment and so releases to waste water from the process are likely to be very low (the release to water due to leaching from the sealant is considered in Section 3.1.9).

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

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

Based on the above information, the major loss of sealant containing LCCPs during their production and use (application) will be as solid waste. It is estimated that this solid waste could contain up to 13 tonnes/year of C<sub>18–20</sub> liquid chlorinated paraffins and up to 27 tonnes/year of C<sub>>20</sub> liquid chlorinated paraffins in the EU.

### **3.1.5 Release from use as a plasticiser/flame retardant in paints**

LCCPs are used as plasticisers and/or flame retardants in paints. All three types of LCCPs considered in this report are used, and a paint may typically contain both liquid (either a C<sub>18–20</sub> or C<sub>>20</sub> liquid chlorinated paraffin) and solid C<sub>>20</sub> chlorinated paraffins. Based on the data reported in Section 2.2.4, the total LCCP content of the paint is typically in the range 10–15 per cent, with the C<sub>18–20</sub> or C<sub>>20</sub> liquid chlorinated paraffin content in the range 3–7 per cent and the C<sub>>20</sub> solid chlorinated paraffin content in the range 5–12 per cent.

The total amount of paint estimated to be manufactured in a region in the EU containing all LCCPs can be estimated as around 2,320–3,480 tonnes/year.

### 3.1.5.1 Default release estimation

Appendix 1 of the TGD gives default emission factors for both the formulation and use of paints.

#### **Formulation**

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

The amount of paint containing LCCPs formulated in a region is estimated to be between 2,320 and 3,480 tonnes/year, assuming that the paint formulation sites are numerous and widespread throughout the EU. From Table B2.3 of Appendix 1 of the TGD, the amount of paint formulated on one site can be estimated as 2,320 tonnes/year over 300 days or 3,480 tonnes/year over 300 days.

Based on the above information, the default release estimates for LCCP released during the formulation of paints can be estimated as:

All LCCPs	Local release:	348 kg/year or 1.2 kg/day to air
	comprising	~0.40 kg/day of either C <sub>18-20</sub> liquid or C <sub>&gt;20</sub> liquid
	<i>and</i>	~0.80 kg/day C <sub>&gt;20</sub> solid chlorinated paraffin
		1,044 kg/year or 3.5 kg/day to waste water
	comprising	~1.2 kg/day of either C <sub>18-20</sub> liquid or C <sub>&gt;20</sub> liquid
	<i>and</i>	~2.3 kg/day C <sub>&gt;20</sub> solid chlorinated paraffin

Regional and EU releases can be estimated as:

C <sub>18-20</sub> liquid	Regional release:	180 kg/year to air 540 kg/year to waste water
	Total EU release:	1,800 kg/year to air 5,400 kg/year to waste water
C <sub>&gt;20</sub> liquid	Regional release:	140 kg/year to air 420 kg/year to waste water
	Total EU release:	1,400 kg/year to air 4,200 kg/year to waste water
C <sub>&gt;20</sub> solid	Regional release:	28.0 kg/year to air 84.0 kg/year to waste water
	Total EU release:	280 kg/year to air 840 kg/year to waste water

#### **Processing (application of paints)**

The default emission factors from industrial use of paints are given in Table A3.15 of Appendix 1 of the TGD. The emission factors are 0 to air (Use Category 47; vapour pressure <10 Pa) and 0.001 (0.1 per cent) to waste water (solvent based paint; Use

Category 47; water solubility <10 mg/l). The amount of paint estimated to be used on an industrial site can be estimated at 348–522 tonnes/year over 300 days/year. This quantity of paint would contain a total of 52 tonnes of LCCP.

Based on these data, the following release estimates for LCCPs from industrial paints can be obtained.

All LCCPs	Local release:	52 kg/year or 0.17 kg/day to waste water
	comprising	~0.06 kg/day of either C <sub>18–20</sub> liquid or C <sub>&gt;20</sub> liquid
	<i>and</i>	~0.11 kg/day C <sub>&gt;20</sub> solid chlorinated paraffin
C <sub>18–20</sub> liquid	Regional release:	180 kg/year to waste water
	Total EU release:	1,800 kg/year to waste water
C <sub>&gt;20</sub> liquid	Regional release:	140 kg/year to waste water
	Total EU release:	1,400 kg/year to waste water
C <sub>&gt;20</sub> solid	Regional release:	28.0 kg/year to waste water
	Total EU release:	280 kg/year to waste water

Default emission factors for private (domestic/DIY) use of construction and maintenance paints are given in Table A4.5 of Appendix 1 of the TGD. Here the emission factor for air is 0 (Use Category 47; vapour pressure <10 Pa) and the emission factor for release to waste water is 0.001 (0.1 per cent) (Use Category 47; water solubility <10 mg/l; solvent based paint).

The extent of domestic usage of paint containing LCCPs is unknown but is likely to be very limited. The TGD indicates that for these types of paints the fraction used in domestic applications is of the order of 0.04–0.2 per cent of the total use. This value gives the amount of paint for domestic use in a region of 0.93 tonnes/year (assuming 15 per cent total LCCP content) or 7.0 tonnes/year (assuming a 10 per cent total LCCP content). The fraction of this paint used in the local scenario is 0.002 (0.2 per cent) and so the amount of paint used in the local scenario can be estimated as 1.9 kg/year (15 per cent total LCCP content) or 14 kg/year (10 per cent total LCCP content) over 300 days/year. Using the emission factor of 0.1 per cent, the worst case estimate for local release of total LCCPs to waste water from domestic use lies between  $2.9 \times 10^{-4}$  and  $1.4 \times 10^{-3}$  kg/year ( $9.7 \times 10^{-7}$  to  $4.7 \times 10^{-6}$  kg/day). These values can be considered as negligible.

### 3.1.5.2 Industry-specific information

#### **Formulation**

Information on the releases to the environment from formulation and use of chlorinated paraffins in paints has been obtained from industry (ECB, 2005a; BCF, 1999; BCF, 2001).

Chlorinated paraffins are generally only used in solvent-based paints, mainly for industrial applications. Releases to the environment from formulation and use are likely to be minimal (Government of Canada, 1993; ECB, 2005a) because the chlorinated paraffin is likely to be associated with the solid phase (e.g. dried paint) of any waste generated; it is very unlikely to enter into the aqueous effluent streams. The ESD for



paints, lacquers and varnishes industry in Chapter 7 of the TGD is also produced on this basis.

In addition to the above ESD, a further recent ESD on coatings is also available (Environment Agency, 2003). For formulation, this ESD indicates that emissions to air and water should be minimal for solvent-borne paints and coatings. Any solvent-borne paint/coating left in the manufacturing equipment at the end of the formulation of a batch is washed out with organic solvents and either recycled back to the process or disposed of (by incineration or as hazardous waste) and hence little or no release to the environment occurs from this process. Packaging waste will be disposed of in a similar fashion. The emission factors given in the ESD for formulation of solvent-borne coatings are summarised in Table 3.5.

**Table 3.5 LCCP emission factors for formulation of solvent-borne coatings (from Environment Agency ESD, 2003)**

Emission type	Emission factor	
	Standard size batch (~1,000 litres)	Large size batch (~10,000 litres)
Waste generation		
equipment leftovers	0.5% (recycled) 0.5% (to disposal)	0.25% (recycled) 0.25% (to disposal)
packaging waste	0.5% (to disposal)	0.5% (to disposal)
dust emissions	0.492% (to disposal)	0.493% (to disposal)
Emissions to air		
Low volatility liquids	0%	0%
Solids	0.005%	0.005%
Emissions to water		
Liquids	0%	0%
Solids	0.003%	0.002%

The main source of emission to water identified in the ESD is from wash-off of dust from workshop areas. This source of emission would only be relevant for C<sub>>20</sub> solid chlorinated paraffins but as these are waxy solids rather than dusty solids the amounts estimated to be emitted from this route are difficult to quantify.

On this basis, the local and regional emissions to waste water and air during the formulation of solvent-borne paints and coatings containing LCCPs can be assumed to be very low.

Other information on the possible releases to the environment during formulation of paints containing chlorinated paraffins has been obtained for the United Kingdom (BCF, 1999; BCF, 2001). This work confirmed that the releases to the atmosphere and waste water are expected to be very low during paint formulation. The amount of (solid) waste generated during the process was estimated as 0–2 per cent of the total amount of paint; the waste is disposed of to landfill or by incineration.

BCF (1999) indicated that paints and coatings containing chlorinated paraffins typically make up only a small fraction (typically <1–2 per cent, maximum five per cent) of the total amount of paint formulated on a site. The information obtained also indicated that the amount of chlorinated paraffin used at a site was generally small (the average usage per site was 2.8 tonnes/year) and that an estimated 30 sites in total in the United Kingdom manufactured paints containing chlorinated paraffins. Euro Chlor (1999) also

indicated that the number of sites manufacturing paints containing chlorinated paraffins around 10–50 in a country/region.

Assuming that there are only 10 sites formulating paints in a region, then the amount of paint containing LCCPs formulated on a site would be around 232–348 tonnes/year. Comparing these amounts with the default quantities estimated earlier suggests that only around 10 per cent of the total paint formulated at a site will contain LCCPs, which is consistent with the data available from sites in the UK (a maximum of five per cent was found in a survey of several sites in the UK (see above)).

Using the emission factors given by the Environment Agency (2003) and outlined in Table 3.5 (0 per cent to air and waste water for liquids, 0.005 per cent to air and 0.003 per cent to waste water for solids), the following local, regional and total EU releases can be estimated for paint formulation.

All LCCPs	Local release:	1.2 kg/year or 0.0039 kg/day to air
	comprising	~0 kg/day of either C <sub>18–20</sub> liquid or C <sub>&gt;20</sub> liquid
	<i>and</i>	~0.0039 kg/day C <sub>&gt;20</sub> solid chlorinated paraffin)
		0.70 kg/year or 0.0023 kg/day to waste water
	comprising	~0 kg/day of either C <sub>18–20</sub> liquid or C <sub>&gt;20</sub> liquid
	<i>and</i>	~0.0023 kg/day C <sub>&gt;20</sub> solid chlorinated paraffin
C <sub>18–20</sub> liquid	Regional release:	0 kg/year to air 0 kg/year to waste water
	Total EU release:	0 kg/year to air 0 kg/year to waste water
C <sub>&gt;20</sub> liquid	Regional release:	0 kg/year to air 0 kg/year to waste water
	Total EU release:	0 kg/year to air 0 kg/year to waste water
C <sub>&gt;20</sub> solid	Regional release:	1.4 kg/year to air 0.84 kg/year to waste water
	Total EU release:	14 kg/year to air 8.4 kg/year to waste water

### ***Processing (application of paints)***

During application of the paint, immediate losses of chlorinated paraffin to air should be minimal due to the low vapour pressure of the substance at ambient temperatures (losses over extended time periods are considered later). Losses to water are also expected to be low (owing to the low water solubility of the substance) from industrial application of paints. This is also indicated in the ESD for coatings (Environment Agency, 2003), and the default calculations given above.

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

The release from subsequent volatilisation and leaching from paint over long timescales is considered later in Section 3.1.9. It should be noted that the ESD on coatings (Environment Agency, 2003) indicates that a considerable amount of paint/coatings containing LCCPs may be disposed of during the application process (estimates range from 2.5 per cent to 60.8 per cent depending on the coating type and the mode of application), and this is taken into account in the estimate of lifetime losses from painted articles.

### **3.1.6 Release from use as an extreme pressure additive in metal cutting/working fluids**

The C<sub>>20</sub> liquid chlorinated paraffins are the main types of LCCPs used in metal cutting fluids in the EU, although it appears that a very small amount of C<sub>18–20</sub> liquid chlorinated paraffins are also used in this application.

Chlorinated paraffins in general are used in both oil-based and water-based (emulsion) metal cutting/working fluids, although LCCPs appear to be used primarily in fluids for the more difficult deep drawing operations. In most oil-based cutting fluids, the chlorinated paraffin content is around 5–10 per cent, but can be up to 70 per cent in some heavy drawing applications.

In water-based metal cutting/working fluids, the chlorinated paraffin may be present typically at around five per cent in the formulation. In use, this formulation is diluted (emulsified) in water to give the final metal cutting/working fluid. The typical dilution is around 1:20 with water. Thus if the chlorinated paraffin is present at five per cent in the formulation, the concentration in the fluid in use is around 0.25 per cent. Recent information from industry has indicated that LCCPs are not used in emulsifiable metalworking fluids (Euro Chlor, 2008), however the coverage of the survey is unclear (it is based on the customers of members of Euro Chlor but the percentage of customers responding is not reported).

The estimated amount of formulated fluid containing LCCPs produced in a region in the EU is around 515–1,030 tonnes/year, assuming formulation of such products is widespread throughout the EU. It will be assumed that LCCPs are used in both the oil-based and water-based lubricants and fluids.

#### **3.1.6.1 Default release information**

##### ***Formulation of metal cutting/working fluids***

The default release factors for the formulation of metal cutting/working fluids can be obtained from Table A2.2 of the TGD. For LCCPs these are 0.00005 ( $5 \times 10^{-3}$  per cent) to air and 0.002 (0.2 per cent) to waste water (Industry Category 8; Use Category 35; vapour pressure <1 Pa).

Assuming that 515–1,030 tonnes/year of metal cutting/working fluid are formulated in a region, the amount formulated on a site can be estimated to be 515–1,030 tonnes/year over 300 days (Table B2.3 of the TGD). The resulting default release estimates of C<sub>>20</sub> liquid chlorinated paraffins are:

C <sub>&gt;20</sub> liquid	Local release:	2.6 kg/year or 0.0086 kg/day to air 103 kg/year or 0.34 kg/day to waste water
	Regional release:	2.6 kg/year to air 130 kg/year to waste water
	Total EU release:	25.8 kg/year to air 1,030 kg/year to waste water

The equivalent calculations for C<sub>18-20</sub> liquid chlorinated paraffins are confidential but would lead to a maximum local release of a few grammes per day to air and waste water, and so are unlikely to be significant in terms of this risk assessment. The regional and total EU releases are confidential.

### ***Use in metal cutting/working fluids***

Appendix 1 of the TGD gives default emission factors to waste water for metal cutting fluid additives of 0.185 (18.5 per cent) from oil-based fluids and 0.316 (31.6 per cent) from water-based (emulsifiable) fluids (Table A3.7; Industry Category 8; Use Category 35). The default emission factors to air are 0.0002 (0.02 per cent) from both types of fluid.

The actual split of LCCP use between oil-based and emulsion fluids is unknown. Industry-specific information reported later indicates that this split is likely to be around 67:33 oil-based:water-based for chlorinated paraffins in general; this split will be assumed here. Although recent information from industry has indicated that LCCPs are not used in emulsifiable metalworking fluids (Euro Chlor, 2008), the coverage of the survey is unclear (it is based on the customers of members of Euro Chlor but the percentage of customers responding is not reported).

Based on this 2:1 oil-based:water-based ratio, the amount of oil-based fluid containing LCCPs used in a region in the EU can be estimated at around 345–690 tonnes/year assuming there are a large number of potential sites of use in the EU. From Table B3.5 of Appendix 1 of the TGD, the amount of fluid used on one site can be estimated as 345–690 tonnes/year for steel works and 276–552 tonnes/year for other applications, both over 300 days/year. These quantities of fluid would contain around 34.5 and 27.6 tonnes of LCCP for the two applications, respectively.

For water-based fluids, the amount of formulation (before dilution) containing LCCPs used in a region in the EU can be estimated as 340 tonnes/year. When this formulation is diluted 1:20 for use, the total amount of emulsion fluid used is around 6,800 tonnes/year. From Table B3.5 of Appendix 1 of the TGD, the amount of emulsion fluid used on one site can be estimated at 5,100 tonnes/year for steelworks and 2,040 tonnes/year for other uses, both over 300 days. These quantities of fluid would contain around 12.8 and 5.1 tonnes of LCCP for the two applications, respectively.

Based on these figures, the following default release estimates can be obtained for C<sub>>20</sub> liquid chlorinated paraffins:

$C_{>20}$ liquid	<i>Oil-based fluids</i>
Local release (steelworks):	6.9 kg/year or 0.023 kg/day to air 6,383 kg/year or 21.3 kg/day to waste water
Local release (other sites):	5.5 kg/year or 0.018 kg/day to air 5,160 kg/year or 17.0 kg/day to waste water
Regional release:	6.9 kg/year to air 6,383 kg/year to waste water
Total EU release:	69 kg/year to air 63,834 kg/year to waste water
	<i>Water-based (emulsion fluids)</i>
Local release (steel works):	2.6 kg/year or 0.0087 kg/day to air 4,045 kg/year or 13.5 kg/day to waste water
Local release (other sites):	1.0 kg/year or 0.0034 kg/day to air 1,610 kg/year or 5.4 kg/day to waste water
Regional release:	3.4 kg/year to air 5,370 kg/year to waste water
Total EU release:	34.0 kg/year to air 53,700 kg/year to waste water

The equivalent calculations for  $C_{18-20}$  liquid chlorinated paraffins are confidential, but result in a local emission of 0.11 kg/day or less to waste water and  $6.7 \times 10^{-5}$  kg/day or less to air. The regional and total EU emission estimates are confidential.

### 3.1.6.2 Industry-specific release information

#### **Formulation**

Information on the releases to the environment from this application is given in the ESD on lubricants and additives (OECD, 2004a). Formulation or blending of metal cutting/working fluids is normally carried out in a batch process. First, the base oils to be used are metered into the mixing vessel and the oils are blended together. This step is usually carried out at ambient temperature, but higher temperatures of up to 60°C can be used. Next, the additives are added to the base oil either by meter from a bulk storage tank or directly (either in neat form or diluted in base oil). Many additives are difficult to handle due to their high viscosity. Such additives may be pre-heated prior to blending. The blending vessels are normally mixed using paddle mixers or jet mixers, but other methods are sometimes used, such as air sparging, pulse-air mixing, high shear mixing and passing the fluid through a convoluted chamber to induce turbulence.

The general approach given in the ESD for estimating emissions from lubricant blending plants is outlined here. The ESD itself should be consulted for full details of the methods involved.

For emissions to air, the ESD assumes that the maximum concentration of lubricant in air within the blending plant is  $1 \text{ mg/m}^3$ . The ventilation rate of a representative plant is then used to estimate the amount of lubricant released in air. This assumes that there is no clean-up of the air before emission. Using the default parameters suggested in the emission scenario document, this results in an emission of 58 g/day to air of lubricant.

According to the ESD, a representative plant is one which blends 30,000 tonnes of lubricant per year. The ESD provides a formula to calculate the ventilation rate of other sizes of plant, and this has been used here to adjust the emissions to the actual amounts of lubricant containing  $C_{18-20}$  liquid or  $C_{>20}$  liquid chlorinated paraffins that are estimated to be produced at a site.

In order to estimate annual emissions from the plants the number of days of operation is needed. The ESD provides two methods to estimate this. One consistently results in a larger number of days than the other. For this assessment, both methods have been used and an intermediate value has been selected.

The emission estimated above relates to the base fluid, which will make up the majority of the lubricant in the vapour phase. For additives, the ESD calculates the mole fractions of additive and base fluid in the liquid phase and then estimates the mole fractions in the vapour phase using Raoult's law. The amount of additive in the vapour phase is then used to estimate the relevant emission.

Using this method the following emission estimates are obtained:

$C_{18-20}$ liquid	Local release	$4 \times 10^{-4}$ kg/day to air
	Regional release	Confidential (but very small)
	Total EU release	Confidential (but very small)
$C_{>20}$ liquid	Local release	$4 \times 10^{-5}$ kg/day to air
	Regional release	$3 \times 10^{-4}$ kg/year to air
	Total EU release	$3 \times 10^{-3}$ kg/year to air

For the emissions to water, the method in the ESD is based on the partitioning of additives between the oil phase and the aqueous phase in a separation system within the plant prior to the discharge of the waste water. It assumes that a maximum of 0.25 per cent of the lubricant is included in the water and oil which reaches the separator, and that the maximum content of oil in discharged water is 5 mg/l (the limit of visibility). The additive can be released in the oil phase and the water phase, with the relative importance depending on the partitioning properties of the specific chemical of interest. The number of days of operation estimated above is used to calculate the amount of lubricant blended each day.

The combined emission factors for the oil phase and water phase estimated using the method given in the emission scenario document are as follows:

$C_{18-20}$ liquid	emission factor to water = $5 \times 10^{-5}$ kg/tonne lubricant
$C_{>20}$ liquid	emission factor to water = $5 \times 10^{-5}$ kg/tonne lubricant

In the United Kingdom there are thought to be six large lubricant blending plants for all types of lubricants (OECD, 2004a). Assuming that each plant produces cutting fluids containing LCCPs (there is evidence to suggest that most formulators do, or have used chlorinated paraffins in the recent past (RPA, 1996)), the quantity of fluid containing C<sub>>20</sub> liquid chlorinated paraffin formulated at any one site can be estimated as a sixth of that estimated to be used in a country/region. The regional amount of fluid produced is estimated at 515–1,030 tonnes/year. Thus the amount of fluid containing LCCPs formulated at a large blending plant can be estimated at around 86–172 tonnes/year.

Using the methods outlined in OECD (2004a), this amount of lubricant will be formulated over 1–50 days. A midpoint value of 25 days will be used here. The amounts estimated to be emitted using this approach are summarised below:

C <sub>&gt;20</sub> liquid	Local release:	4.3×10 <sup>-3</sup> – 8.6×10 <sup>-3</sup> kg/year or 1.7×10 <sup>-4</sup> –3.4×10 <sup>-4</sup> kg/day to waste water
	Regional release:	0.026–0.052 kg/year to waste water
	Total EU release:	0.26–0.52 kg/year to waste water

For the C<sub>18–20</sub> chlorinated paraffins, the amounts used are very small and in this case it has been assumed that the total amount used is blended on a single site in the EU. The estimated emissions to water using this assumption are summarised below:

C <sub>18–20</sub> liquid	Local release:	5×10 <sup>-4</sup> kg day to waste water
	Regional release:	Confidential (but small)
	Total EU release:	Confidential (but small)

### ***Use in metal cutting/working fluids***

The major uses of LCCPs are as additives in oil-based metal cutting/working fluids (neat oils). However, they may also be used in water-based emulsions and so both types need to be considered<sup>5</sup>. It is recognised that many metalworking facilities have adopted fluid management techniques to reduce costs through less frequent fluid purchases and less frequent disposal; proper fluid management reduces machine downtime by optimising the intervals between fluid changes. However, since it cannot currently be said that *all* facilities use the latest fluid management systems, this assessment represents a “realistic worst case” throughout Europe.

### ***Oil-based fluids (neat oils)***

Information has been obtained on the use of, and release from, metalworking fluids in the United Kingdom (OECD, 2004a). Losses of fluid, and hence any additive contained within it, are dependent on the type of equipment available for separating the fluid from the swarf. In the United Kingdom it is thought that around 40 per cent of the metalworking activity is carried out in large machine shops with sophisticated swarf treatment, 30 per cent in medium-sized machine shops with basic swarf treatment and the remaining 30 per cent in small machine shops with no swarf treatment. Little information is available on the size distributions in other EU countries, although the distribution in Spain is thought to be similar to that in the United Kingdom, and in Italy

<sup>5</sup> Recent information from industry has indicated that LCCPs are not used in emulsifiable metalworking fluids (Euro Chlor, 2008), however the coverage of the survey is unclear (it is based on the customers of members of Euro Chlor but the percentage of customers responding is not reported).

the proportion of large machine shops is slightly higher (60 per cent in large machine shops, 30 per cent in medium-sized machine shops and 10 per cent in small machine shops) (RPA, 1996).

The estimated annual losses of cutting fluid, based on the replacement rates in the United Kingdom, are thought to be close to 50 per cent for a large machine shop, 75 per cent for a medium-sized machine shop and 100 per cent from a small machine shop (OECD, 2004a). Not all of this loss, however, is released to the environment. A breakdown of the total losses for a large and small machine shop using oil-based cutting fluids is shown in Table 3.6 (OECD, 2004a).

**Table 3.6 Total losses of oil-based cutting fluids in large and small metalworking shops**

Type of loss	Annual percentage fluid loss	
	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 <sup>a</sup>	3% to water <sup>a</sup>
Dragout/workpiece	1% to water	1% to water
	2% to chemical waste	2% to chemical waste
Internal reprocessing	1% to water <sup>a</sup>	not applicable
External reprocessing	10% (reused/discarded as waste oil)	not applicable
Dragout-swarf	30% (of which 90% burnt, 10% landfill)	90% (of which 90% burnt, 10% landfill)
<b>Total losses</b>	<b>48%</b>	<b>100%</b>

Notes: <sup>a</sup> The losses may be further minimised by collecting the cutting fluid for re-use.

The major losses of oil-based metal cutting/working fluids are associated with the swarf. It is thought that the vast majority (90 per cent) of swarf produced (and the adhering cutting fluid) is melted for re-use. Thus the cutting fluid and any additive will be destroyed in this process. In some situations, the swarf may undergo solvent cleaning prior to melting, and so some LCCP could end up in waste solvent in such sites. The remaining 10 per cent of swarf is thought to be disposed of to landfill (OECD, 2004a).

As can be seen from Table 3.6, the losses to waste water from a large and small machine shop can be estimated at four per cent and six per cent, respectively. However, some other losses have the potential for entering waste water. For instance, misting/evaporation losses are initially to air. However, these have the potential to settle within the facility and reach waste water as a result of cleaning equipment etc. The losses from external reprocessing of spent cutting fluid are due to line flushing etc. In a well controlled facility, flushings will be collected and re-used or discarded as waste oil. However, in a less well controlled facility, it is possible that this waste could be discharged to waste water.

Another source of loss is dragout of the cutting fluid on the workpiece. This is generally removed by either alkaline washing or solvent washing and it is thought that in both cases the remaining cutting fluid is distributed between emissions to water and



chemical waste. In a worst case it could be assumed that all this dragout loss ends up in waste water.

From the above information, a worst case loss from a metalworking facility would be around 18 per cent. Since these worst case loss figures are more likely to apply to a small facility than a large facility, where suitable reprocessing is usually carried out, an assessment will be made of both a large facility (release to waste water of four per cent) and a small facility (release to waste water of 18 per cent). The situation at a medium sized facility is likely to be between these two extremes.

It is thought that a typical large-scale metal cutting/working plant in the United Kingdom would contain around 50,000 litres of cutting oil. This volume will be used as the basis for the local emission scenario for a large site. Assuming that the LCCP makes up around five per cent of the cutting fluid, then 50,000 litres of cutting fluid would contain around 2,500 kg of LCCP. The possible emissions of LCCP to waste water can be estimated at 100 kg/year, using the four per cent release figure. These emissions are equivalent to 0.33 kg/day, assuming use on 300 days/year.

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

These estimates are obtained assuming a five per cent LCCP content in the cutting fluid. If a 10 per cent content is used then the emission estimates would be double these figures.

The local release estimates for use of C<sub>>20</sub> liquid chlorinated paraffins in oil-based cutting fluids are summarised below:

Local release (large site):     0.33 kg/day to waste water over 300 days  
  (assuming five per cent chlorinated paraffin content)  
  0.66 kg/day to waste water over 300 days  
  (assuming 10 per cent chlorinated paraffin content)

Local release (small site):     0.30 kg/day to waste water over 300 days  
  (assuming five per cent chlorinated paraffin content)  
  0.60 kg/day to waste water over 300  
  (assuming 10 per cent chlorinated paraffin content)

The daily emissions of C<sub>18-20</sub> liquid chlorinated paraffins from sites of use would be of a similar order to those estimated above, however, as the quantities involved are small (and hence the total amount of cutting fluid containing C<sub>18-20</sub> liquid chlorinated paraffins is small), such emissions from a small site are thought to be most relevant.

### ***Emulsifiable cutting fluids***

Similar to the situation with the neat oil cutting fluids, the losses of emulsifiable cutting fluids to the environment depend on the type of equipment available for separating the fluid from the swarf. However, there are some differences between the two types of fluids that have to be taken into account.

Firstly, losses by evaporation and by mist generation with emulsifiable fluids are higher than those associated with neat oils. However, since the emulsifiable cutting fluid is mainly water, which is more volatile than the additives present, the vapours and mists generated tend to have higher water contents than the bulk material. Thus the losses of additives may not be in proportion to the total losses of fluid. Also, the adhesion of emulsifiable cutting fluids to the swarf is less than that with neat cutting fluids (due to lower viscosity), although recovery of emulsifiable cutting fluids from swarf is not generally practised (OECD, 2004a).

A breakdown of the potential losses to the environment of emulsifiable metalworking/cutting fluids is shown in Table 3.7 (OECD, 2004a).

**Table 3.7 Potential losses to the environment of emulsifiable metalworking/cutting fluids**

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

In use, it is important to maintain the correct oil/water ratio and an average replenishment rate of around 10 per cent per week can be considered typical to compensate for loss of fluid by dragout and evaporative losses etc. Since there is preferential evaporative loss of water, the replenishment package used is often a diluted version of the original fluid, typically containing around 50 per cent of the normal working concentration of the oil component. In addition, emulsifiable cutting fluids are subject to degradation (largely bacterial) during use and the whole system has to be replenished at a much higher frequency than with neat oils, typically at intervals of between one and six months. A typical worst case volume of cutting fluid present in the holding tanks at a site using emulsifiable cutting fluids is around 10,000 litres of fluid (OECD, 2004a).

The emulsifiable metal cutting/working fluids are made by adding the oil component (containing the chlorinated paraffin at typically five per cent of the oil) to water at a dilution of around 1:20 oil:water. Thus, 10,000 litres of the emulsified fluid will contain 500 litres of oil and approximately 25 kg of chlorinated paraffin. These concentrations will be approximately maintained in the cutting fluid by weekly additions of half-strength emulsion (to take into account the preferential evaporation of the water phase), at a rate of around 10 per cent of the total cutting fluid volume present (i.e. 1,000 litres/week). The losses to water are likely to have a similar composition to the cutting fluid as used. From the loss figures reported in Table 3.7, the losses to water are estimated to be around six per cent (due to overalls, leaks and dragout from the workpiece). Thus the weekly loss of cutting fluid to waste water during use can be estimated as 60 litres/week. This volume of cutting fluid would contain around 0.15 kg/week or 0.025 kg/day of LCCP, assuming six working days/week (300 days/year) (OECD, 2004a).

In addition to the weekly loss of fluid during use, the whole system (10,000 litres of fluid containing 25 kg of LCCP) will be replaced every one to six months (OECD, 2004a). An

annual replenishment rate (or sometimes even longer) is thought to be typical for most facilities in the United States (CPIA, 2001). Before disposal, water-based (emulsion) cutting fluids can be treated before disposal by separating the oil and water phases by methods such as ultrafiltration. The oil phase can be collected for disposal (e.g. incineration) and the water phase then discharged to waste water.

Given the physical properties of LCCPs, it is likely that most of the chlorinated paraffin will be associated with the oil phase and so will not be released to the environment. However, it is thought that around 50 per cent of waste emulsion is discharged to the sewage treatment plant without any pre-treatment. Thus as a worst case, in addition to the 0.025 kg/day release of the LCCP from losses during use (as discussed above), an intermittent (2–6 times/year) discharge to waste water of 25 kg of LCCP at each discharge needs to be considered.<sup>6</sup>

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

The local release estimates for C<sub>>20</sub> liquid chlorinated paraffins from the use and disposal of emulsifiable cutting fluids are summarised below:

Local release:	Use of cutting fluid	0.025 kg/day to waste water over 300 days
	Disposal of cutting fluid	25 kg/day to waste water on 2–6 days/year

The emissions of C<sub>18–20</sub> chlorinated paraffins from use in emulsifiable cutting fluids would be expected to be similar to those estimated above. However, it should be noted that the tonnage involved is very small, and it is not clear if the C<sub>18–20</sub> chlorinated paraffins are used in emulsifiable cutting fluids.

### ***Total EU and regional release estimate for metal cutting/working fluids***

The differences in the loss and disposal patterns of oil-based and emulsion cutting fluids need to be taken into account in the estimation of the regional and continental release of LCCPs from use of metal cutting/working fluids.

The split between the use of LCCPs in oil-based and emulsion fluids is not known. The OECD (2004a) indicates that the amount of base oil used to produce oil-based and emulsion fluids in the United Kingdom is in the ratio 15,750:7,700 tonnes/year. Since the LCCP is present at similar concentrations in both the oil-based and emulsifiable cutting fluids (before dilution to the working strength), the same ratio could be used to determine the relative amounts of chlorinated paraffin used in each type. Thus, it can be assumed that, of the 515–1,030 tonnes/year of fluid containing C<sub>>20</sub> liquid

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<sup>6</sup> According to an analysis by Entec (2004), intermittent disposal of such emulsified metal cutting/working fluids to drain is not necessarily prohibited under existing legislation in the United Kingdom, provided the site operator obtained relevant permission from the sewerage undertaker. However, most companies are expected to separate the oil phase from the emulsified fluid prior to disposal to drain (with the oil being disposed of by processes such as incineration). Therefore this scenario is not relevant to the vast majority of sites using emulsifiable metal cutting/working fluids containing LCCPs.

chlorinated paraffins estimated to be used in a region in the EU, approximately 346–692 tonnes/year can be expected to be used in oil-based fluids and 169–338 tonnes/year can be expected to be used in emulsion-based fluids prior to dilution to working strength.

The total worst case regional release from emulsion-based fluids can be estimated assuming that 50 per cent of the fluid is eventually released to waste water without any pre-treatment (OECD, 2004a). Thus the total regional release of C<sub>>20</sub> liquid chlorinated paraffins from emulsion-based fluids is estimated at 8,455 kg/year.

For the oil-based fluids, the release to the environment depends on the size of the facility. As discussed above, around 60 per cent of oil-based fluids can be assumed to be used in large (and medium) facilities with swarf reprocessing, and the realistic worst case release to waste water from such facilities is estimated at four per cent. This gives a total regional release of LCCPs from large sites using oil-based fluids of 830 kg/year. For the remaining 40 per cent of oil, this will be assumed to be used in small and medium facilities, where little or no swarf reprocessing is carried out. For both these facilities, a worst case release figure of 18 per cent to waste water will be assumed. This gives a total regional release of LCCPs from small and medium sized facilities using oil-based fluids of 2,491 kg/year. Thus the overall regional release of LCCPs to waste water from use in oil-based cutting fluids is 3,321 kg/year.

The total regional emissions from use of C<sub>18–20</sub> liquid chlorinated paraffins have been estimated using a similar approach but the details of the calculation are confidential.

### **3.1.7 Release from use in leather fat liquors**

Both C<sub>18–20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins are used in the EU in the formulation of leather fat liquors.

The amount of leather fat liquor containing LCCPs formulated in a region in the EU is estimated at approximately 240 tonnes. The EU is an exporter of leather fat liquors containing chlorinated paraffins (around 50 per cent of the leather fat liquors containing medium-chain chlorinated paraffins are exported from the EU (ECB, 2005a)), but the extent of this export for fat liquors containing LCCPs is unknown and so is not taken into account in this assessment.

#### **3.1.7.1 Default release estimation**

Appendix 1 of the TGD provides default release estimates for the formulation and processing (use) of substances used in the leather processing industry (Industry Category 7).

##### **Formulation**

For the formulation stage, Table A2.1 of the Appendix is appropriate. The default emission factors for this process are 0.001 (0.1 per cent) to air (vapour pressure <10 Pa; produced in dedicated equipment) and 0.003 (0.3 per cent) to waste water. The amount of leather fat liquor formulated on one site can be estimated from Table B2.3. Assuming a regional production of 240 tonnes of leather fat liquors, all of this 240 tonnes of fat liquor is estimated to be used on one site over 300 days. The following figures can therefore be estimated for release of total LCCPs from the formulation step:

Local release:	24 kg/year or 0.08 kg/day to air split 0.055 kg/day C <sub>18-20</sub> liquid chlorinated paraffin and 0.025 kg/day C <sub>&gt;20</sub> liquid chlorinated paraffin
	72 kg/year or 0.24 kg/day to waste water split 0.15 kg/day C <sub>18-20</sub> liquid chlorinated paraffin and 0.075 kg/day C <sub>&gt;20</sub> liquid chlorinated paraffin
Regional release:	24 kg/year to air split 16.5 kg/year C <sub>18-20</sub> liquid chlorinated paraffin and 7.5 kg/year C <sub>&gt;20</sub> liquid chlorinated paraffin
	72 kg/year to waste water split 49.3 kg/year C <sub>18-20</sub> liquid chlorinated paraffin and 22.6 kg/year C <sub>&gt;20</sub> liquid chlorinated paraffin
Total EU release:	240 kg/year to air split 165 kg/year C <sub>18-20</sub> liquid chlorinated paraffin and 75 kg/year C <sub>&gt;20</sub> liquid chlorinated paraffin
	720 kg/year to waste water split 493 kg/year C <sub>18-20</sub> liquid and 226 kg/year C <sub>&gt;20</sub> liquid chlorinated paraffin

These estimates assume that a site formulates leather fat liquors using both C<sub>18-20</sub> and C<sub>>20</sub> liquid chlorinated paraffins.

### ***Processing (use of leather fat liquors)***

The assessment assumes that around 240 tonnes of leather fat liquors containing LCCPs are used in a region in the EU each year. According to Table B3.4 of Appendix 1 of the TGD, the amount used at a site is 100 tonnes/year of leather fat liquor containing C<sub>18-20</sub> liquid chlorinated paraffin over 100 days or 46 tonnes of leather fat liquor containing C<sub>>20</sub> liquid chlorinated paraffin over 46 days.

Table A3.6 of Appendix 1 of the TGD gives default emission factors for the use of substances during the processing step. For LCCPs the emission factors are 0.001 (0.1 per cent) to air (solubility <100 mg/l; vapour pressure <100 Pa) and 0.05 (5 per cent) to waste water (Main Category 2 (inclusion into matrix; solubility <100 mg/l)).

The following figures can therefore be estimated for release of LCCPs from the leather fat liquoring (i.e use of leather fat liquors) step:

C <sub>18-20</sub> liquid	Local release:	10 kg/year or 0.10 kg/day to air 500 kg/year or 5 kg/day to waste water
	Regional release:	16.7 kg/year to air 830 kg/year to waste water
	Total EU release:	166 kg/year to air 8,300 kg/year to waste water
C <sub>&gt;20</sub> liquid	Local release:	4.6 kg/year or 0.1 kg/day to air 230 kg/year or 5.0 kg/day to waste water
	Regional release:	7.6 kg/year to air 380 kg/year to waste water
	Total EU release:	76 kg/year to air 3,800 kg/year to waste water

### 3.1.7.2 Industry-specific release estimation

#### **Formulation of fat liquors**

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

A small amount of chlorinated paraffin may also be sold directly to tanneries which then make their own fat liquors. The emissions from this process are likely to be small compared to the emissions associated with the fat liquoring process itself (default release factor for formulation is 0.3 per cent compared with the release factor for fat liquoring of two per cent (see later)); these emissions are not considered any further.

#### **Processing (fat liquoring)**

An ESD is available for the leather industry (Chapter 7 of the TGD). This recommends a value of 15 tonnes/day as a reasonable worst case for the mass of leather processed at a site, based on production data for Germany. Figures for typical water use are also available. These figures depend on whether the site carries out all stages of leather production (from processing of raw skins to production of the final leather), where a water consumption of 35 l/kg raw hide is typical, or is specialised in the refining of “wet blue” (leather produced after the tanning step), where a water consumption of 18 l/kg leather is typical. Processing of one tonne of raw hides produces a maximum of 250 kg of “wet blue”. Since the fat liquoring step follows the tanning stage, both types of site have the potential to use fat liquors containing LCCPs.

Information on the amount of fat liquor used in treating leather has been provided previously (Euro Chlor, 1998). The typical application rate is around 70–120 g of fat liquor/kg of leather treated. Since the fat liquor typically contains around 10 per cent by weight of the chlorinated paraffin, the amount of the chlorinated paraffin used in this process is around 7–12 g/kg leather treated. The amount of chlorinated paraffin present in the treatment solution at the end of the process is thought to be around two

per cent of that used (Euro Chlor, 1998). This residual amount will be discharged to waste water.

Using this information, the following site release estimates can be made, using the methods outlined in Chapter 7 of the TGD:

Complete processing:

Mass of raw leather processed/day = 15 tonnes

Mass of "wet blue" leather produced = 3.75 tonnes/day

Mass of LCCPs used = 12 kg/tonne "wet blue" = 45 kg/day

Percentage released to waste water = 2 per cent

Mass of LCCPs released to waste water = 0.9 kg/day

Processing of "wet blue":

Mass of "wet blue" processed/day = 15 tonnes

Mass of LCCPs used = 12 kg/tonne "wet blue" = 180 kg/day

Percentage released to waste water = 2 per cent

Mass of LCCPs released to waste water = 3.6 kg/day

These release estimates are appropriate for both types of LCCP used in the process. The default estimated number of days of use at a local site are 100 days/year for the C<sub>18-20</sub> chlorinated paraffin and 46 days/year for the C<sub>>20</sub> chlorinated paraffin. Since the calculations are based on the total amount of leather processed at a site, if both types of LCCP are used at the same site, then the figures would refer to the combined amount of the chlorinated paraffins used.

The calculation for processing of "wet blue" scenario assumes that 15 tonnes/day are processed at a site as recommended in the ESD in the TGD. However, a draft update to this ESD indicates that the typical mass of "wet blue" processed at a site may be around 3.2 tonnes/day (UBA, 1998). This would reduce the calculated emissions by a factor of around four, and would lead to similar calculated PECs as obtained for the complete processing scenario. Therefore, the PECs obtained for complete processing only will be taken forward to the risk characterisation.

The overall release estimate to waste water from the process in the EU is 3,320 kg/year of C<sub>18-20</sub> liquid chlorinated paraffins and 1,520 kg/year of C<sub>>20</sub> liquid chlorinated paraffins. The estimated regional release will be 10 per cent of these figures.

### 3.1.8 Release from use in textiles

Information provided by industry indicates that both C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffin products may have been used in the past as plasticisers/flame retardants for textiles, where they were applied as a backcoating. However this use no longer occurs in the EU.

However a small amount of C<sub>18-20</sub> liquid chlorinated paraffins is used for waterproofing textiles in the EU. Few details of the process used are available and so the default methods in the TGD have been used to estimate the following emissions from this use. Details of the calculations are considered confidential.

C <sub>18-20</sub> liquid	Local release	8.3 kg/day to air. 4.3 kg/day to waste water
	Regional release	Confidential
	Total EU release	Confidential

### 3.1.9 Release from articles over their service life

Although LCCPs are of low vapour pressure at ambient temperatures, the vapour pressure is not so low as to preclude the possibility of volatilisation from plastics, paints, rubber, textiles and sealants during their service life. This is particularly true of the C<sub>18-20</sub> liquid chlorinated paraffins with lower chlorine contents (see Appendix B for estimates of how vapour pressure varies with chlorine content).

#### 3.1.9.1 Volatilisation

The ESD on plastics additives (OECD, 2004b) summarises the work that has been carried out on plasticiser leaching and volatilisation from PVC products.

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

$$\text{rate of volatilisation (\% per year)} = 1.1 \times 10^6 \times \text{vapour pressure (mmHg)}.$$

In Section 1.4.4, it was shown that the vapour pressure of LCCPs depends markedly on the carbon chain length and degree of chlorination. Using the representative vapour pressures for the various LCCP products, rates of volatilisation can be estimated using the above equation (see Table 3.8).

**Table 3.8 LCCP rates of volatilisation**

LCCP	Vapour pressure	Estimated volatilisation rate
C <sub>18-20</sub> liquid	1.9×10 <sup>-6</sup> mmHg (2.5×10 <sup>-4</sup> Pa)	2 per cent/year
C <sub>&gt;20</sub> liquid	1.9×10 <sup>-7</sup> mmHg (2.5×10 <sup>-5</sup> Pa)	0.2 per cent/year
C <sub>&gt;20</sub> solid	1.1×10 <sup>-16</sup> mmHg (1.5×10 <sup>-14</sup> Pa)	1×10 <sup>-10</sup> per cent/year

These estimates apply to losses from thin film applications. These estimated rates are highly uncertain because they are dependent on the vapour pressure. As discussed in Section 1.4.4, there are some uncertainties over the actual vapour pressures of these substances.

For general articles an emission factor of 0.05 per cent of the annual consumption of plasticiser is recommended for losses over the lifetime of articles (OECD, 2004b). This figure is appropriate for a plasticiser such as DEHP, and is based on the estimated amount volatilised (approximately 140 tonnes/year) from the major applications, related



to the annual consumption of the substance. Thus, although the amount of the substance present in articles will be higher than the annual consumption (the lifetime of many products more than one year), this is accounted for in the way the emission factor has been estimated. The figure of 140 tonnes/year for the amount of DEHP volatilised was estimated from the results of theoretical and semi-experimental studies on the volatilisation rate from PVC, along with the estimated surface area of PVC articles and products present in the EU, taking into account the lifetime of the product.

As discussed earlier, the C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid products appear to be around 2.5 and five times less volatile than DEHP from products; a general emission factor of 0.02 per cent and 0.01 per cent, respectively, is appropriate for the loss of these LCCPs over the lifetime of the products, (related to the annual consumption of LCCPs incorporated in the products). The volatile loss of C<sub>>20</sub> solid chlorinated paraffins over the articles' lifetime is expected to be very low.

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

Other products, such as paints, rubber, textiles, sealants, etc., can also be expected to lose LCCP by volatilisation. A similar rate of volatilisation to that in PVC will be assumed.

The estimated loss rate of two per cent per year for C<sub>18-20</sub> liquid chlorinated paraffins and 0.2 per cent per year for C<sub>>20</sub> liquid chlorinated paraffins from thin films may be appropriate for paints (although as paints form a surface skin of low permeability, this should reduce the emissions compared to those from a thin film of plastic). However, this value will overestimate the releases from sealants, rubber and textiles, so a loss rate of 0.01–0.02 per cent over the lifetime would appear more appropriate here.

The release figure for thin films should be applied to the total amount LCCP present in painted articles in the EU, rather than the yearly consumption figure in this area. The releases from paints using this figure have been estimated based on a 5–7 year lifetime for painted surfaces. It is likely that the actual releases from painted surfaces will be lower than this figure due to formation of a surface skin of low permeability.

Table 3.9 summarises the possible volatilisation losses from articles containing LCCPs.

**Table 3.9 Estimated volatilisation losses of LCCPs from polymeric materials over their lifetimes**

Use	Release to air		
	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
PVC (over lifetime)	105 kg/year	NA	NA
Rubber	NA	418 kg/year	negligible
Textile	Confidential	NA	NA
Paints (over 5–7 year lifetime)	180,400–252,560 kg/year	13,940–19,516 kg/year	negligible
Sealants and adhesives (over lifetime)	52	53 kg/year	NA
Total EU	~180,600–~252,700 kg/year	14,411–19,987 kg/year	negligible
Regional total	~18,060–~25,270 kg/year	1,411–1,999 kg/year	negligible

Note: NA = not applicable (i.e. no major use in the application).

An alternative approach to estimating the volatilisation losses of LCCPs from PVC use is considered in Appendix F. This method gives a release to air over the products' lifetime of around 126–139 kg/year for C<sub>18-20</sub> liquid chlorinated paraffins (and 3.0–3.3 kg/year for C<sub>>20</sub> liquid chlorinated paraffins, based on their use in the past in this application). These estimates are in good agreement with the figures derived in Table 3.9. The approach taken in Appendix F requires a large number of assumptions and so there is considerable uncertainty in the figures derived. Therefore the figures from Table 3.9 will be used in the environmental modelling to estimate the regional concentrations.

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

### 3.1.9.2 Leaching

Information has been reported on the leaching of plasticiser from PVC flooring during washing (OECD, 2004b). Again, this information has generally been generated for a phthalate plasticiser such as DEHP. Since leaching losses are likely to depend to some extent on the water solubility of LCCPs, the difference in solubility between DEHP (recommended value taken from Draft DEHP ESR Assessment: 3 µg/l) and LCCPs (≤5 µg/l) needs to be considered. Thus, based on these water solubilities, the potential for leaching of LCCPs appears to be similar to that determined for DEHP.

The worst case losses to water were estimated at 0.05 per cent for washing of interior products and 0.7 per cent for exterior products such as roofing (OECD, 2004b). The factor of 0.05 per cent for washing interior products is the estimated loss over the products' lifetime, and applies to the annual consumption of plasticiser rather than the total amount present in articles (this is accounted for in the way the emission factor was

derived). Information provided by industry indicates that a polyurethane coating is typically applied to around 50–60 per cent of cushioned PVC flooring. These coatings may reduce the potential for leaching loss from washing of the flooring.

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

Since a major use of chlorinated paraffins is likely to be in indoor applications such as flooring (see Appendix F) the 0.05 per cent release factor over the products' lifetime is appropriate. As indicated above, some cushioned PVC products may have coatings that reduce the potential for leaching loss from the product, but the extent of this reduction is unknown and so adds further uncertainty to the estimates presented, and is considered further in Appendix F.

For paints and, to a lesser extent, sealants, the external release factor may be more appropriate, as they are sometimes used in applications where significant exposure to water may occur (e.g. marine paints, masonry paints). A 5–7 year lifetime will be assumed for paints and a 10–30 year lifetime will be assumed for sealants.

For textile applications, there will be the potential for loss to water during washing or exposure to rain etc. There are no data available on the possible emissions from this process. In the absence of any further information the 0.05 per cent loss factor for washing of interior products will be used in the assessment for textile products over their lifetime.

For the other applications, e.g. leather, the potential for exposure to water appears to be limited. The worst case release to the environment from leaching of LCCPs from products is shown in Table 3.10.

An alternative approach to estimating the leaching losses from PVC use is considered in Appendix F. This gives a release to water of around 429–530 kg/year to waste water, 298 kg/year to surface water (plus a loss of around 298 kg/year to soil, and 51 kg/year to waste water from leaching from landfills) for C<sub>18-20</sub> liquid chlorinated paraffins (the equivalent figures for the past use of C<sub>>20</sub> liquid chlorinated paraffins are around 20–25 kg/year to waste water, 14 kg/year to surface water, 14 kg/year to soil and 2 kg/year to waste water from leaching from landfills). These estimates are in reasonable agreement with the figures derived in Table 3.10.

The approach taken in Appendix F requires a large number of assumptions and so there is a large degree of uncertainty in the figures derived. Therefore the figures from Table 3.10 will be used in the environmental modelling to estimate the regional concentrations. The estimate for the historic use of C<sub>>20</sub> liquids in PVC is very small compared with the estimates for leaching from other uses of the substance and so has not been considered significant in this risk assessment.

**Table 3.10 Estimated leaching losses of LCCPs from polymeric materials over their lifetime**

Use	Release to water		
	C <sub>18-20</sub> liquid (kg/year)	C <sub>&gt;20</sub> liquid (kg/year)	C <sub>&gt;20</sub> solid (kg/year)
PVC over lifetime	262 <sup>a</sup>	NA	NA
Rubber over lifetime	NA	2,088 <sup>b</sup>	104 <sup>b</sup>
Textiles over lifetime	Confidential	NA	NA
Paints over 5–7 years lifetime	13,530–18,942 <sup>b</sup>	10,455–14,637 <sup>b</sup>	2,100–2,940 <sup>b</sup>
Sealants and adhesives over 10–30 years lifetime	3,930–11,790 <sup>b</sup>	7,965–23,895 <sup>b</sup>	NA
Total EU	~18,000–~31,000 • 105 to waste water • 8,810–15,500 to surface water • 8,810–15,500 to soil	20,508–40,620 • 10,254–20,310 to surface water • 10,254–20,310 to soil	2,204–3,044 • 1,102–1,522 to surface water • 1,102–1,522 to soil
Regional total	1,800–3,100 • 10 to waste water, • 881–1,550 to surface water • 881–1,550 to soil	2,051–4,062 • 1,025–2,031 to surface water • 1,025–2,031 to soil	220–304 • 110–152 to surface water • 110–152 to soil

Notes: NA = not applicable (i.e. no use in the application).

<sup>a</sup> The emission is assumed to be split 40 per cent to waste water treatment plants, 30 per cent direct to surface water and 30 per cent direct to industrial/urban soil.

<sup>b</sup> The emission is assumed to be split 50 per cent direct to surface water and 50 per cent direct to industrial/urban soil.

The losses from leaching are likely to be released either to waste water, surface water directly or to industrial/urban soil. In the assessment a 50:50 split between surface water and industrial/urban soil will be used for the emissions from paints and sealants. For PVC emissions to waste water treatment plants are also likely and it will be assumed here that the emissions are split approximately 40 per cent to waste water, 30 per cent direct to surface water and 30 per cent to industrial/urban soil, in line with the analysis in Appendix F.

The figures estimated for the leaching loss are likely to overestimate the actual loss as not all the PVC, paint, sealants or textiles containing LCCP will come into contact with water. There are also uncertainties in determining representative lifetimes of products such as sealants, which have a large bearing on the resulting release estimates. In addition, some of the emission factors used also include losses of particulates etc. due to weathering effects and erosion, as well as leaching loss. The environmental behaviour of LCCPs in these particulates is unknown.

### 3.1.9.3 Waste in the environment and ultimate disposal

#### **“Waste remaining in the environment”**

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

No agreed method is currently included in the TGD for addressing these potential sources of release. These emissions were considered in the EU risk assessment for medium-chain chlorinated paraffins (ECB, 2005a). Appendix F uses a similar approach to that taken in ECB (2005a) to derive the following overall release figures for LCCPs as particulates.

Release to air	= 81–83 kg/year of C <sub>18–20</sub> liquid + 238 kg/year of C <sub>&gt;20</sub> liquid + 19 kg/year of C <sub>&gt;20</sub> solid
Release to surface water	= 19,857–20,719 kg/year of C <sub>18–20</sub> liquid + 59,643–59,913 kg/year of C <sub>&gt;20</sub> liquid + 4,779 kg/year of C <sub>&gt;20</sub> solid
Release to waste water	= 865–1,570 kg/year of C <sub>18–20</sub> liquid + 41–74 kg/year of C <sub>&gt;20</sub> liquid
Release to urban/industrial soil	= 59,813–62,410 kg/year of C <sub>18–20</sub> liquid + 179,647–180,457 kg/year of C <sub>&gt;20</sub> liquid + 14,393 kg/year of C <sub>&gt;20</sub> solid

As these releases of LCCP are essentially bound within a polymer matrix, the actual bioavailability and environmental behaviour of the LCCP are unknown. There are no agreed methods available in the current TGD for dealing with these types of releases in the risk assessment. In this assessment they have been taken to represent a bioavailable source of LCCPs in the environment and have been included in the regional and continental models.

#### **Ultimate disposal**

Since LCCPs have not generally reacted or changed during their lifecycle, ultimately all the chlorinated paraffin used in products will be disposed of at the end of the products' useful lives. Disposal by landfill or incineration is likely to be the ultimate destination of much of the chlorinated paraffin. For some applications, e.g. metalworking fluids, some of the chlorinated paraffin could be destroyed in processes such as recycling of metal swarf. For other processes, the LCCP present is likely to end up in the sludge produced in the process, which will again most likely be disposed of by incineration or landfill.

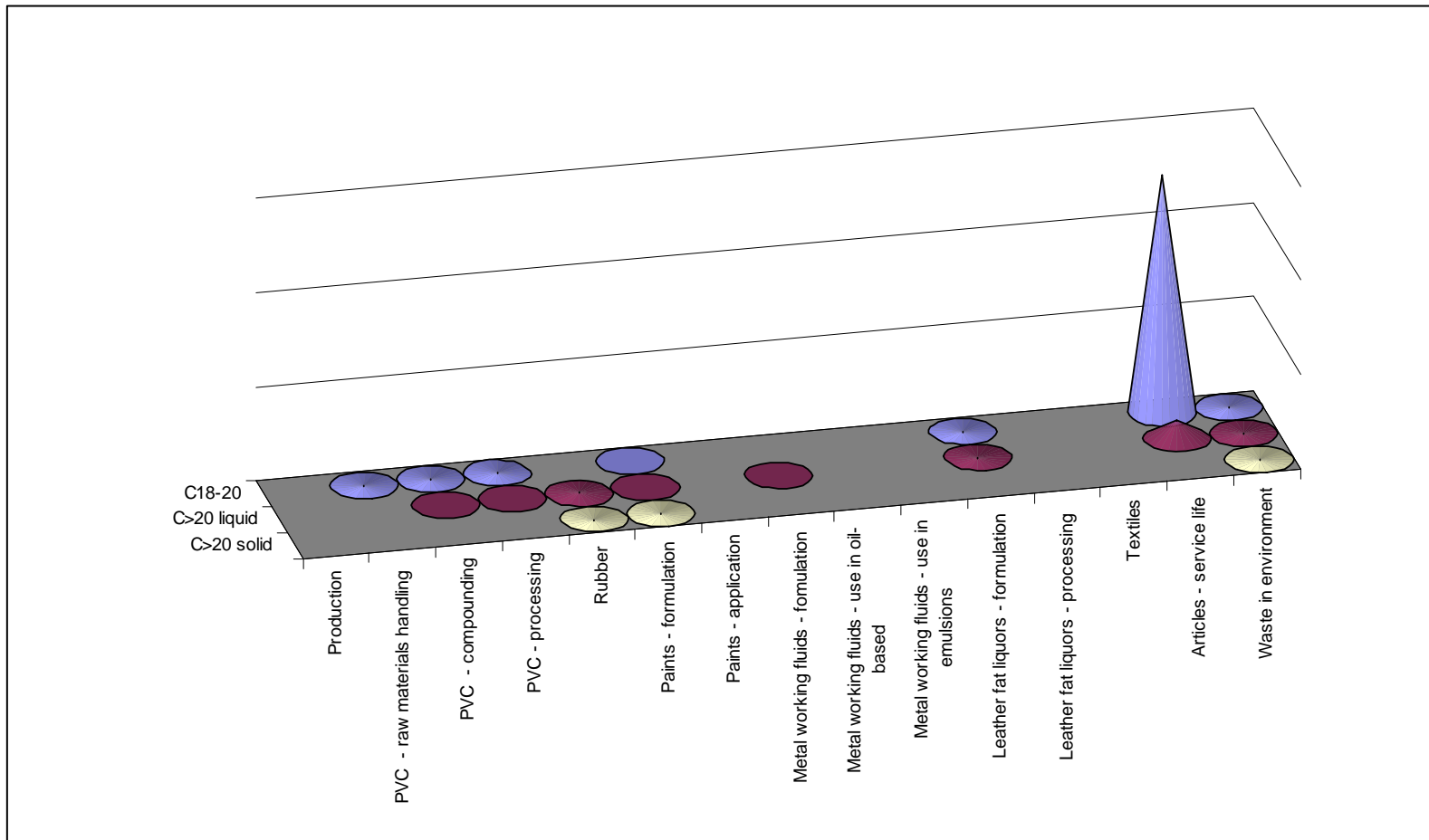
As a first approximation, it can be assumed that the annual consumption of LCCP is used to replace the articles disposed of each year, thus the amount of LCCPs disposed of to landfill and incineration each year is of the order of up to 5,000–10,000 tonnes.

Of the possible disposal methods, incineration is likely to completely destroy the LCCP. In landfills, chlorinated paraffins are expected to be relatively stable for a number of years and so could be subject to leaching or volatilisation from the landfill. It is currently not possible to quantify these releases. However, LCCPs are expected to adsorb strongly onto soil and so leaching and volatilisation from landfill would not be expected to be significant processes compared with other sources of release (see Section 3.1.9 and Appendix F).

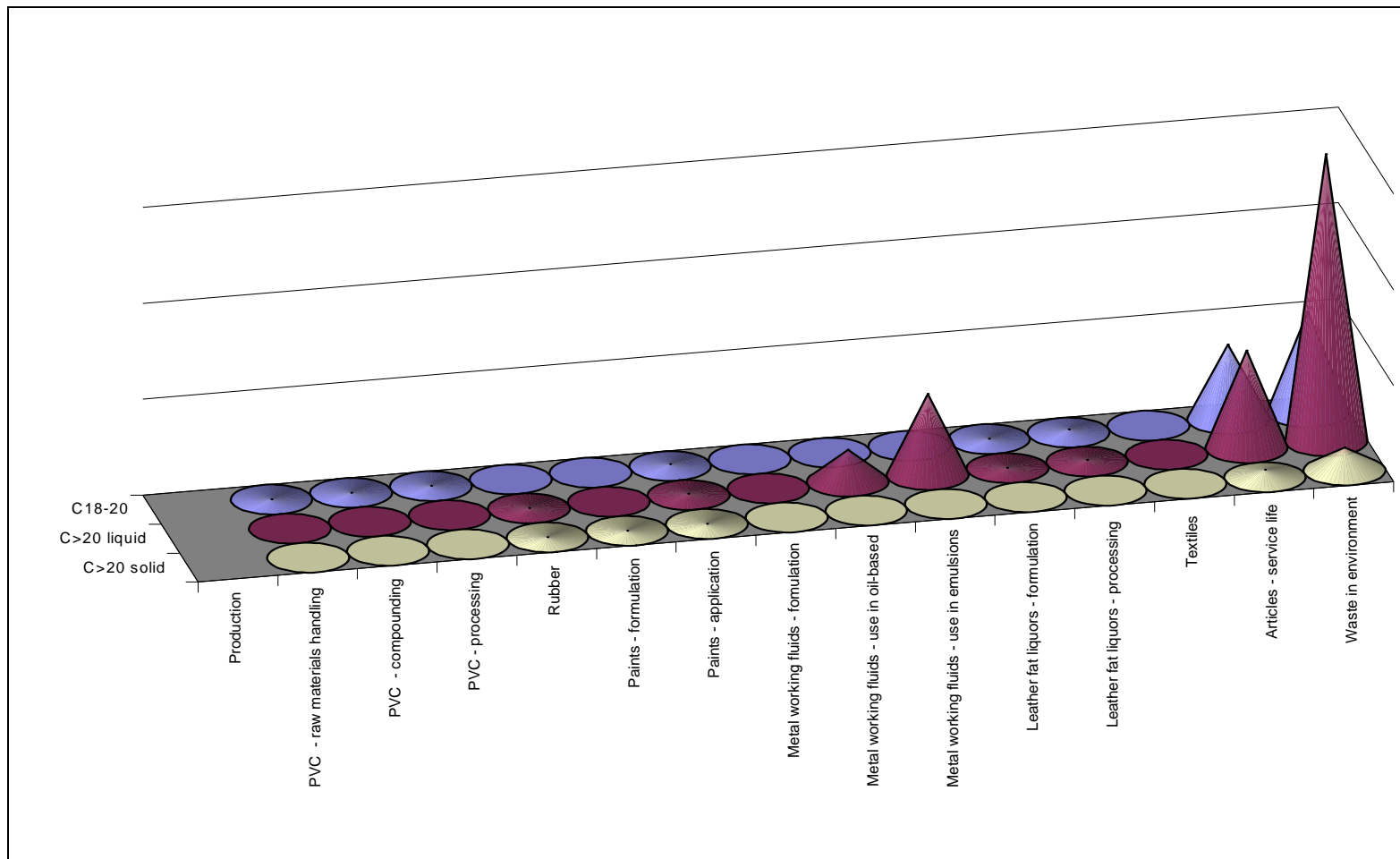
### **3.1.10 Summary of release estimates**

The releases of LCCPs to the environment are summarised in Table 3.11. In most cases the releases are based on some information specific to the industry, supplemented with default release estimates from the TGD where appropriate.

The relative contributions of the various sources to the total regional emissions are shown in the following charts (Figure 3.1 to Figure 3.3).

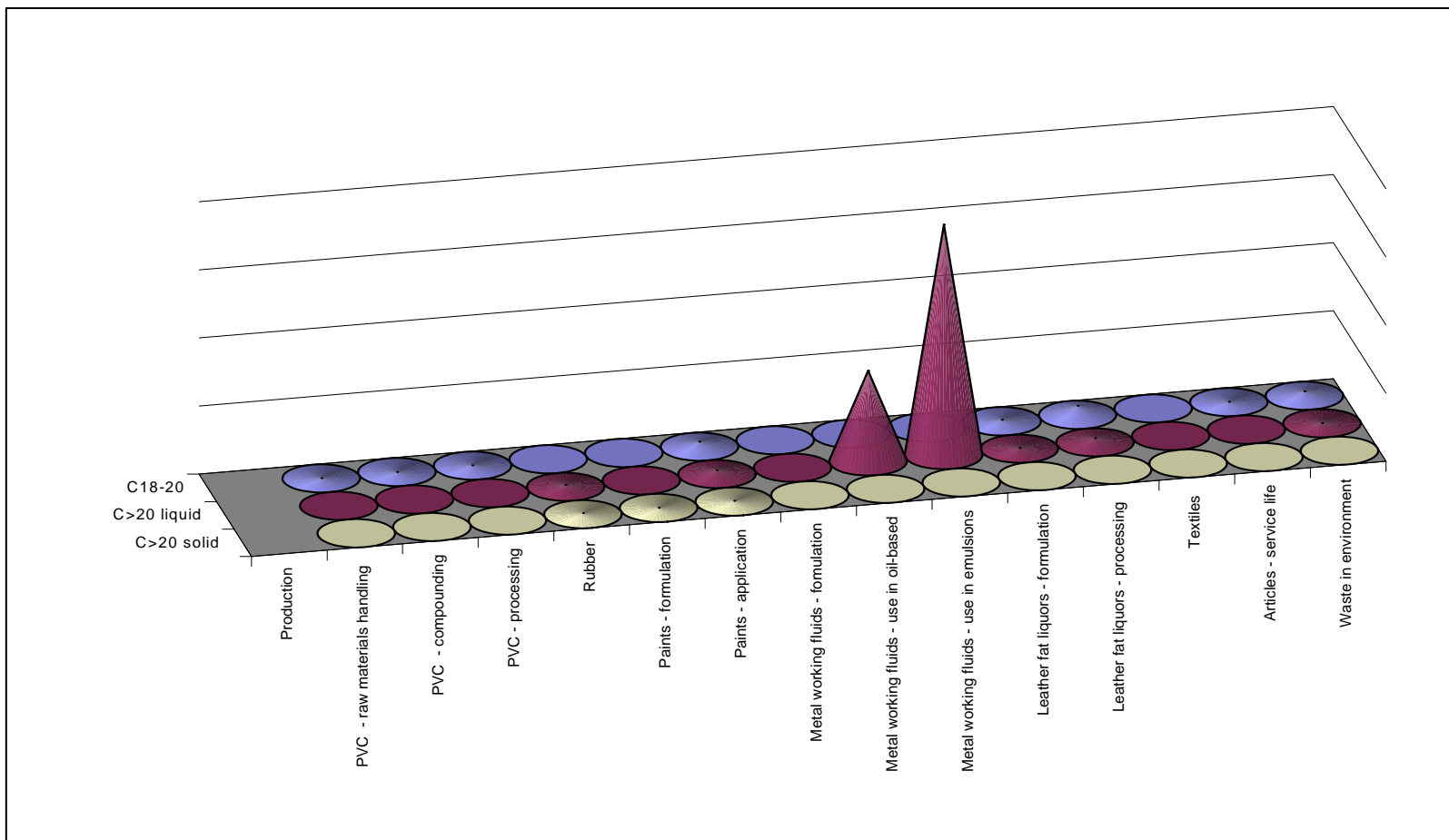


**Figure 3.1 Contribution to total air emissions**



**Figure 3.2 Contribution to total emissions direct to surface water**





**Figure 3.3 Contribution to total emissions via waste water treatment plant**

**Table 3.11 Summary of environmental release estimates for LCCPs**

Use	Comment	Type of LCCP	Estimated local release (kg/day)		No of days <sup>l</sup>	Estimated regional release (kg/year)			Estimated continental release <sup>d</sup> (kg/year)		
			air	waste water		air	waste water <sup>g</sup>	soil <sup>o</sup>	air	waste water <sup>g</sup>	soil <sup>o</sup>
Production	Generic calculation	C <sub>18-20</sub> liquid		0.063	300	n	n	n	n	n	n
		C <sub>&gt;20</sub> liquid		0.32	300						
		C <sub>&gt;20</sub> solid		0.0063	300						
Use in PVC <sup>e</sup> – plastisol coating <sup>h</sup>	Compounding site (formulation) Conversion site (processing) Combined compounding and conversion site	C <sub>18-20</sub> liquid		0.025 <sup>a</sup>	33						
		C <sub>18-20</sub> liquid	0.025 <sup>a</sup>	0.025 <sup>a</sup>	33						
		C <sub>18-20</sub> liquid	0.025 <sup>a</sup>	0.050 <sup>a</sup>	33						
Use in PVC <sup>e</sup> – extrusion/other	Compounding site (formulation) Conversion site (processing)	C <sub>18-20</sub> liquid	0.0075 <sup>a</sup> 0.040 <sup>b</sup> 0.0034 <sup>c</sup>	0.0445 <sup>a</sup> 0.24 <sup>b</sup> 0.0204 <sup>c</sup>	33						
		C <sub>18-20</sub> liquid	0.037 <sup>a</sup> 0.040 <sup>b</sup> 0.034 <sup>c</sup>	0.037 <sup>a</sup> 0.040 <sup>b</sup> 0.034 <sup>c</sup>	33						

Table 3.11 continued overleaf

**Table 3.11** continued

Use	Comment	Type of LCCP	Estimated local release (kg/day)		No of days <sup>l</sup>	Estimated regional release (kg/year)			Estimated continental release <sup>d</sup> (kg/year)		
			air	waste water		air	waste water <sup>g</sup>	soil <sup>o</sup>	air	waste water <sup>g</sup>	soil <sup>o</sup>
Use in PVC <sup>e</sup> – extrusion/other	Combined compounding and conversion site	C <sub>18-20</sub> liquid	0.0445 <sup>a</sup> 0.080 <sup>b</sup> 0.0374 <sup>c</sup>	0.0815 <sup>a</sup> 0.28 <sup>b</sup> 0.0544 <sup>c</sup>	33						
Use in PVC – regional and continental releases	Raw materials handling (formulation)	C <sub>18-20</sub> liquid					5.2			47	
	Compounding (formulation)	C <sub>18-20</sub> liquid				0.7	0.7		6.6	6.6	
	Conversion <sup>f</sup> (processing)	C <sub>18-20</sub> liquid				12	12		106	106	
Rubber	Formulation/processing site	C <sub>&gt;20</sub> liquid	0.015	0.040	251	25	67		226	601	
		C <sub>&gt;20</sub> solid	0.015	0.51	21	1.2	43		11	383	
Sealants/adhesives	Formulation/use	C <sub>18-20</sub> liquid	negligible								
Paints and varnishes	Formulation	C <sub>&gt;20</sub> liquid	negligible								
		C <sub>18-20</sub> liquid	negligible								
		C <sub>&gt;20</sub> liquid	negligible								
		C <sub>&gt;20</sub> solid	0.0039	0.0023	300	1.4	0.84		13	7.6	

Use	Comment	Type of LCCP	Estimated local release (kg/day)		No of days <sup>l</sup>	Estimated regional release (kg/year)			Estimated continental release <sup>d</sup> (kg/year)		
			air	waste water		air	waste water <sup>g</sup>	soil <sup>o</sup>	air	waste water <sup>g</sup>	soil <sup>o</sup>
Industrial application of paints (Processing)	C <sub>18-20</sub> liquid		{0.06}			300		{180}			{1,620}
	C <sub>&gt;20</sub> liquid		{0.06}			300		{140}			{1,260}
	C <sub>&gt;20</sub> solid		{0.11}			300		{28}			{252}
Metal cutting/working fluids	Formulation	C <sub>18-20</sub> liquid	4×10 <sup>-4</sup>	5×10 <sup>-4</sup>	<10	n	n		n	n	
		C <sub>&gt;20</sub> liquid	4×10 <sup>-5</sup>	3.4×10 <sup>-4</sup>	25	3×10 <sup>-4</sup>	0.052		3×10 <sup>-3</sup>	0.47	
		Use in oil based fluids (processing; large site)	C <sub>&gt;20</sub> liquid		0.33 <sup>i</sup> or 0.66 <sup>j</sup>	300		830			7,472
		Use in oil based fluids (processing; small site)	C <sub>18-20</sub> liquid		0.30 <sup>i</sup> or 0.60 <sup>j</sup>	300		n			N
			C <sub>&gt;20</sub> liquid		0.30 <sup>i</sup> or 0.60 <sup>j</sup>	300		2,491			22,415
		Use in emulsifiable fluids (processing)	C <sub>18-20</sub> liquid		0.025 (plus an intermittent discharge of 25 kg/event)	300		n			n
		C <sub>&gt;20</sub> liquid		0.025 (plus an intermittent discharge of 25 kg/event)	300		8,455			76,095	

Table 3.11: continued

Use	Comment	Type of LCCP	Estimated local release (kg/day)		No of days <sup>l</sup>	Estimated regional release (kg/year)			Estimated continental release <sup>d</sup> (kg/year)		
			air	waste water		air	waste water <sup>g</sup>	soil <sup>o</sup>	air	waste water <sup>g</sup>	soil <sup>o</sup>
Leather fat liquors	Formulation	C <sub>18-20</sub> liquid	{0.055}i	{0.15}i	300	{17}	{49}		{149}	{444}	
		C <sub>&gt;20</sub> liquid	{0.025}i	{0.075}i	300	{7.5}	{23}		{68}	{203}	
	Use – complete processing of raw hides	C <sub>18-20</sub> liquid		0.9	100			332			2,988
		C <sub>&gt;20</sub> liquid		0.9	46			152			1,368
		Use – processing of “wet blue”	C <sub>18-20</sub> liquid		3.6	100					
C <sub>&gt;20</sub> liquid			3.6	46							
Textiles	Processing	C <sub>18-20</sub> liquid	{8.3}	{4.3}	300	n	n		n	n	
Articles – volatile and leaching loss	Service life	C <sub>18-20</sub> liquid				18,060–25,270	10 + 881–1,550 <sup>m</sup>	881–1,550	162,540–227,430	95 + 7,929–13,950 <sup>m</sup>	7,929–13,950
		C <sub>&gt;20</sub> liquid				1,411–1,999	1,025–2,031 <sup>m</sup>	1,025–2,031 <sup>m</sup>	12,970–17,988	9,229–18,279 <sup>m</sup>	9,229–18,279
		C <sub>&gt;20</sub> solid				negligible	110-152 <sup>m</sup>	110-152	negligible	992–1,370 <sup>m</sup>	992–1,370

**Table 3.11: continued**

Use	Comment	Type of LCCP	Estimated local release (kg/day)		no of days <sup>1</sup>	Estimated regional release (kg/year)			Estimated continental released (kg/year)		
			air	waste water		air	waste water <sup>g</sup>	soil <sup>o</sup>	air	waste water <sup>g</sup>	soil <sup>o</sup>
"Waste" remaining in the environment	Service life and disposal	C <sub>18-20</sub> liquid			8	1,986–2,072 <sup>m</sup> + 87–157	5,981–6,241		73–75	17,871–18,647 <sup>m</sup> + 779–1,413	53,832–56,169
		C <sub>&gt;20</sub> liquid			24	5,964–5,991 <sup>m</sup> + 4–7	17,965–18,046		214	53,679–53,922 <sup>m</sup> + 37–67	161,682–162,411
		C <sub>&gt;20</sub> solid			2	478 <sup>m</sup>	1,439		17	4,301 <sup>m</sup>	12,954
Total emissions		C <sub>18-20</sub> liquid			18,098	541–597 via wwtp	6,862–7,791		162,875–227,767	4,868–5,376 via wwtp	61,761–70,119
					25,308	3,002–3,771 direct to surface water				27,017–33,941 direct to surface water	
		C <sub>&gt;20</sub> liquid			1,468–2,056	9,730–9,732 via wwtp	18,990–20,077		13,478–18,496	87,561–87,585 via wwtp	170,911–180,690
						9,421–10,455 direct to surface water			84,798–94,097 direct to surface water		

C <sub>&gt;20</sub> solid	4.6	57 via wwtp 602–644 direct to surface water	1,549– 1,591	41	514 via wwtp 5,422– 5,800 direct to surface water	13,946– 14,324
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- Notes: <sup>a</sup> Open systems (as defined in OECD, 2004b).  
<sup>b</sup> Partially open systems (as defined in OECD, 2004b).  
<sup>c</sup> Closed systems (as defined in OECD, 2004b).  
<sup>d</sup> Continental release = total EU release-regional release.  
<sup>e</sup> Releases estimated from OECD, 2004b assuming that 50 per cent of the initial release to air will condense and eventually reach waste water.  
<sup>f</sup> Regional and continental releases from conversion assume 50 per cent of sites have air emission control. The actual overall proportion of the industry with such controls is unknown, but is likely to be higher than this figure.  
<sup>g</sup> A 80 per cent connection rate to waste water treatment plants will be assumed.  
<sup>h</sup> Releases from car underbody coating and sealing, and rotational moulding are thought to be negligible during the processing step.  
<sup>i</sup> Industry-specific release information is also available and has been used to estimate the PEC<sub>local</sub> in preference to these default values.  
<sup>j</sup> Figure assumes a 5 per cent chlorinated paraffin content in the cutting fluid.  
<sup>k</sup> Figure assumes a 10 per cent chlorinated paraffin content in the cutting fluid.  
<sup>l</sup> Number of days/year over which the local emission occurs.  
<sup>m</sup> Emissions occur directly to surface water.  
<sup>n</sup> Confidential information – the regional and continental releases from this source are small compared with the total releases from other sources.  
<sup>o</sup> Direct emissions to urban/industrial soil.  
{ } Denotes estimates are based on the TGD default values only.

## 3.2 Environmental fate and distribution

### 3.2.1 Atmospheric degradation

LCCPs will react with hydroxyl radicals in the atmosphere. Second order rate constants ( $k_{OH}$ ) for this reaction can be estimated from chemical structure using the Syracuse Research Corporation AOP (version 1.86; the program is based on the Atkinson method recommended in the TGD), and example calculations have been given in Table 3.12. The estimated atmospheric half-lives are based on an atmospheric hydroxyl radical concentration of  $5 \times 10^5$  molecule/cm<sup>3</sup>.

**Table 3.12** Estimated atmospheric half-lives for LCCPs

Formula	Chlorine content (% wt. Cl)	$k_{OH}$ (cm <sup>3</sup> /molecule s)	Atmospheric half-life
C <sub>18</sub> H <sub>33</sub> Cl <sub>5</sub>	41.6	$1.27 \times 10^{-11}$	30.3 hours
C <sub>18</sub> H <sub>30</sub> Cl <sub>8</sub>	53.6	$9.83 \times 10^{-12}$	39.2 hours
C <sub>20</sub> H <sub>36</sub> Cl <sub>6</sub>	43.6	$1.47 \times 10^{-11}$	26.2 hours
C <sub>20</sub> H <sub>33</sub> Cl <sub>9</sub>	53.9	$1.05 \times 10^{-11}$	36.7 hours
C <sub>25</sub> H <sub>45</sub> Cl <sub>7</sub>	41.9	$1.88 \times 10^{-11}$	20.5 hours
C <sub>25</sub> H <sub>42</sub> Cl <sub>10</sub>	50.9	$1.53 \times 10^{-11}$	25.2 hours
C <sub>25</sub> H <sub>29</sub> Cl <sub>23</sub>	71.3	$3.43 \times 10^{-12}$	112 hours
C <sub>30</sub> H <sub>53</sub> Cl <sub>9</sub>	43.6	$2.14 \times 10^{-11}$	18.0 hours
C <sub>30</sub> H <sub>49</sub> Cl <sub>13</sub>	53.0	$1.79 \times 10^{-11}$	21.5 hours
C <sub>30</sub> H <sub>35</sub> Cl <sub>27</sub>	70.8	$5.51 \times 10^{-12}$	69.9 hours

The predicted data indicate that for a given chlorine content, the half-life in air would be expected to decrease with increasing carbon chain length. Conversely, for a given carbon chain length, the predicted half-life increases with increasing chlorine content.

### 3.2.2 Aquatic degradation

#### 3.2.2.1 Abiotic degradation

In aqueous systems, LCCPs are not expected to degrade significantly by abiotic processes such as hydrolysis or direct photolysis.

#### 3.2.2.2 Biodegradation

The biodegradation of a C<sub>20-30</sub>, 42% wt. Cl product has been determined in a prolonged Biochemical Oxygen Demand (BOD) test (Madeley and Birtley, 1980). The test was carried out using an emulsion of the chlorinated paraffin. First, a concentrated emulsion was prepared in distilled water. This was left to stand for 24 hours and a sub-sample of the emulsion was taken and the concentration of chlorinated paraffin in the emulsion



analysed by infrared spectrophotometry after solvent extraction. The emulsion was then added to BOD dilution water at concentrations of 2, 10, and 20 mg/l and the microbial seed was added. Two microbial populations were used in the study: firstly a culture from soil collected close to a chlorinated paraffins production plant that was acclimatised over an eight week period to a concentration of 20–50 mg/l of the chlorinated paraffin; and secondly, a non-acclimatized culture obtained from the effluent of a laboratory activated sludge unit treating domestic sewage. Replicate BOD bottles were used for each test concentration and the concentration of dissolved oxygen remaining at various times was measured. The results are shown in Table 3.13 (it is not clear to which test concentration the results refer). The results indicate some potential for degradation with acclimated microorganisms.

**Table 3.13 BOD values for LCCPs (Madeley and Birtley, 1980)**

Substance	Microorganism source	BOD (g O <sub>2</sub> /g substance)				Approx. % biodegradation <sup>a</sup> at day 25
		Day 10	Day 15	Day 20	Day 25	
C <sub>20–30</sub> , 42% wt. Cl.	non-acclimated	0.16	0.18	0.31	0.14	7.5 per cent
	acclimated	0.01	0.14	0.37	0.43	23 per cent

Note: <sup>a</sup> The approximate percentage biodegradation has been estimated from the BOD/ThOD ratio. The ThOD (theoretical oxygen demand) has been estimated (ThOD (g O<sub>2</sub>/g substance) = 16[2×c+0.5×(h-cl)]/mw; where c=number of carbon atoms, h=number of hydrogen atoms, cl=number of chlorine atoms and MW = molecular weight) for an example formula of the commercial substance as follows: 42% wt. Cl (C<sub>25</sub>H<sub>45</sub>Cl<sub>7</sub>), ThOD=1.86 g O<sub>2</sub>/g substance. Slightly different degradation percentages would be obtained if other example formulae were used.

To investigate the potential for degradation further, Madeley and Birtley (1980) carried out a series of experiments using a <sup>14</sup>C-labelled pentacosane (radiolabelled on the central carbon) mixed with the same C<sub>20–30</sub>, 42% wt. Cl product in Hach respirometers with non-acclimated microorganisms. After eight weeks incubation, around 11 per cent of the <sup>14</sup>C was collected as <sup>14</sup>CO<sub>2</sub>, indicating that where degradation had occurred it was extensive enough to release the central carbon atom of the C<sub>25</sub> chain.

In addition to the above studies, Madeley and Birtley (1980) also reported preliminary studies investigating the degradation of the C<sub>20–30</sub>, 42% wt. Cl product under anaerobic conditions. The anaerobic bacteria were obtained from anaerobic sludge digesters. Gas production (methane and CO<sub>2</sub>) in the presence of increasing quantities of an emulsion of the chlorinated paraffin was determined over 30 days and compared with controls.

No significant increase or decrease in bacterial activity was seen at concentrations of the chlorinated paraffin of up to 10 per cent by weight of dry sludge solids. It was concluded that the substance was not toxic to the bacterial population present but also was not actively degraded under these conditions.

Howard *et al.* (1975) report the results of unpublished biodegradation studies on LCCPs carried out by Hildebrecht (1972). The degradation (determined by oxygen consumption) was studied over 20 hours using a Warburg respirometer or over five days using a BOD method. The sewage seed used was acclimated to up to 100 mg/l of chlorinated paraffins before use in the test. The details of the substances tested and the results obtained are shown in Table 3.14. The validity of these results is questionable as the test solutions contained a surfactant (and in some cases other carbon sources) that

may have been biodegradable under the conditions of the test. Unidentified nutrients were also added to the test which may also have contributed to the BOD seen if they were biodegradable. In addition, the extent of degradation was determined by the authors by comparing the oxygen consumption in the test with the theoretical oxygen demand (ThOD) based on oxidation to CO<sub>2</sub> of the total organic carbon present in the solution from all sources. Howard *et al.* (1975) also indicates that the estimation of ThOD by this method is only approximate as it does not account for any oxygen consumed in the formation of water from available hydrogen. Therefore, the results refer to the biodegradability of the formulation tested rather than the actual chlorinated paraffin component of the formulation and so it is not possible to draw definite conclusions as to the degradability of the chlorinated paraffins in these tests.

**Table 3.14 Biodegradation results of Hildebrecht (1972)**

Chlorinated paraffin	Formulation tested	Warburg respirometry		BOD dilution method	
		Oxygen consumption (mg/l)	Degradation <sup>a</sup>	BOD (mg/l)	Degradation <sup>a</sup>
C <sub>&gt;20</sub> , 40–42% wt. Cl	500 mg/l of a mixture containing 75% chlorinated paraffin, 5% surfactant and 20% water.	83	17.2%	120	25%
C <sub>&gt;20</sub> , 70% wt. Cl	500 mg/l of a mixture containing 37.5% chlorinated paraffin, 37.5% perchloroethylene, 5% surfactant and 20% water.	298	17.2%	30	2%
	500 mg/l of the surfactant.	377	46.5%	530	65%

Note: <sup>a</sup> Degradation was estimated by the authors as the percentage of the theoretical oxygen demand based on the total carbon content of the test solution. Substances other than the chlorinated paraffin contribute to this total carbon content.

Hoechst AG (1976 and 1977) reported five-day biochemical oxygen demand (BOD<sub>5</sub>) values for various LCCPs. Few details of how the tests were carried out are given. The results are reported in Table 3.15 and show little or no biodegradation when compared with the measured chemical oxygen demand (COD) values.

**Table 3.15 BOD<sub>5</sub> and COD values for various LCCPs (Hoechst AG, 1976 and 1977)**

Chemical	COD (mg O <sub>2</sub> /g)	BOD <sub>5</sub> (mg O <sub>2</sub> /g)	Percentage biodegradation
C <sub>18-20</sub> , 35% wt. Cl	1,720	12	0.7%
C <sub>18-20</sub> , 44% wt. Cl	820	<10	<1.2%
C <sub>18-20</sub> , 49% wt. Cl	440 <sup>a</sup>	<10	<2.3%
C <sub>18-20</sub> , 52% wt. Cl	1,620	<10	<0.6%

Note: <sup>a</sup> The COD value was not reproducible.

The removal of LCCPs has been studied using non-adapted activated sludge. Few experimental details of the test conditions used are reported. However, removal was determined by chemical oxygen demand determination, presumably of effluent or water in the system. The substances tested were a C<sub>18-20</sub>, 35% wt. Cl product, a C<sub>18-20</sub>, 44% wt. Cl product, a C<sub>18-20</sub>, 49% wt. Cl product and a C<sub>18-20</sub>, 52% wt. Cl product. In all cases, removal was reported to be >90 per cent over five and 10 days, but it was also indicated that the majority of the removal was by adsorption onto the sludge rather than biodegradation (Hoechst AG, 1976 and 1977).

The degradation of several LCCPs has been studied by Omori *et al.* (1987) using a variety of bacterial cultures. The LCCPs studied had average chemical formulae of C<sub>24.5</sub>H<sub>44.5</sub>Cl<sub>6.5</sub> (40.5% wt. Cl), C<sub>24.5</sub>H<sub>41</sub>Cl<sub>10</sub> (50% wt. Cl) and C<sub>24.5</sub>H<sub>30</sub>Cl<sub>21</sub> (70% wt. Cl) and degradation was studied by monitoring the release of chloride ion. First, degradation of the 40.5% and 70% wt. Cl chlorinated paraffin was studied using resting cell cultures of *Pseudomonas aeruginosa*, *Achromobacter delmarvae*, *A. cycloclastes*, *Micrococcus* sp. and *Corynebacterium hydrocarboclastus* grown on glycerol. These bacteria had previously been shown to degrade 1-chlorohexadecane as well as some other mono- and dichlorinated alkanes.

Little or no degradation (chloride release) was observed when the 70% wt. chlorinated paraffin was incubated with the bacteria for 24 hours at 30°C. However, chloride was found to be released from the 40.5% wt. Cl chlorinated paraffin, with the highest amounts being seen with *A. delmarvae* and *A. cycloclastes* (36 and 25 mg/l respectively) and lower amounts from *Micrococcus* sp. (17 mg/l), *C. hydrocarboclastus* (12 µg/l) and *P. aeruginosa* (4–5 mg/l). The initial chlorinated paraffin concentration in these incubations was 10 mM, which for the 40.5% wt. Cl substance corresponds to 5.7 g/l (or 2.3 g/l of chlorine), and so 36 mg/l of chloride released represents around 1.6 per cent of the total available.

For the co-metabolic degradation studies, bacterial strains (designated HK-3, HK-6, HK-8 and HK-10) were isolated from soil using an enrichment culture containing n-hexadecane as the sole carbon source. The co-metabolic biodegradation experiments were carried out using the single bacterial strains (HK-3, HK-6 or HK-8) incubated at 30°C for 48 hours in mineral medium containing 0.05 per cent (i.e. 500 mg/l) n-hexadecane and 0.1 per cent (i.e. 1,000 mg/l) of either the 40.5%, 50% or 70% wt. Cl chlorinated paraffin. In addition, biodegradation of both the 40.5% wt. Cl and 70% wt. Cl products (concentration equivalent to 180 mg Cl in 1.2 litres) was studied under similar conditions (36 hour incubations) using a mixed bacterial inoculum (containing all four strains) previously exposed to 5,000 mg/l of n-hexadecane. A final study was carried out by inoculating the co-metabolic culture broth from bacterial strain HK-3 (after autoclaving) with another bacterium (strain H15-4) that had been shown to release chlorine from 2-chlorinated fatty acid (a possible metabolite of the chlorinated paraffins). The results of these test are shown in Table 3.16.

The authors concluded that the degradation seen was consistent with that previously observed for other chlorinated alkanes in that a variety of enzymes are required to degrade chlorinated paraffins and that the most likely mode of degradation involves firstly dechlorination of the terminal methyl groups, with subsequent oxidation to form chlorinated fatty acids, which are then broken down to 2- or 3-chlorinated fatty acids via  $\beta$ -oxidation.

**Table 3.16 Results of dechlorination experiments (Omori *et al.*, 1987)**

Chlorinated paraffin (average formula)	Chloride release over 48 hours incubation (mg/l)				
	Bacterial strain HK-3	Bacterial strain H15-4	Bacterial strain HK-6	Bacterial strain HK-8	Mixed bacterial culture (HK-3, HK-6, HK-8 and HK-10)
C <sub>24.5</sub> H <sub>44.5</sub> Cl <sub>6.5</sub> (40.5% wt. Cl)	40 (9.9%) <sup>a, b</sup>	13% <sup>a</sup>	9 (2.2%) <sup>a</sup>	14 (3.5%) <sup>a</sup>	50 (33%) <sup>a</sup>
C <sub>24.5</sub> H <sub>41</sub> Cl <sub>10</sub> (50% wt. Cl)	15 (3.0%) <sup>a</sup>	9% <sup>a</sup>	9 (1.8%) <sup>a</sup>	13 (2.6%) <sup>a</sup>	
C <sub>24.5</sub> H <sub>30</sub> Cl <sub>21</sub> (70% wt. Cl)	18 (2.6%) <sup>a</sup>	12% <sup>a</sup>	10 (1.4%) <sup>a</sup>	12 (1.7%) <sup>a</sup>	22 (15%) <sup>a</sup>

Notes: <sup>a</sup> Chloride release expressed as a percentage of the total present in the chlorinated paraffin.

<sup>b</sup> The pH of the culture medium fell as dechlorination proceeded and may have inhibited growth of the microorganism and hence further dechlorination.

Allpress and Gowland (1999) identified a bacterium (*Rhodococcus* sp.) that was able to grow using various chlorinated paraffins as sole source of carbon and energy. The bacterium was isolated from stream water from an industrial area of the United Kingdom using a minimal salts medium containing one per cent by volume of a C<sub>14-17</sub>, 45% wt. Cl chlorinated paraffin product. The ability of this bacterium to utilise LCCPs was investigated by inoculating minimal salts medium containing one of two LCCPs (a C<sub>18-20</sub>, 48% wt. Cl product and a C<sub>>20</sub>, 42% wt. Cl product) at a concentration of one per cent by volume and determining the chloride release compared with controls over 71 days of incubation at 20°C. The test media also contained anti-bumping granules to aid dispersion of the test substance within the media.

Both of the LCCPs tested were used by the bacterium and 11 per cent (C<sub>18-20</sub>, 48% wt. Cl product) and 14 per cent (C<sub>>20</sub>, 42% wt. Cl product) of the chlorine present in the chlorinated paraffins was released as chloride after 71 days. Several other chlorinated paraffins were tested using this system and it was concluded that the *Rhodococcus* sp. identified in the study was able to utilise chlorinated paraffins as sole source of carbon and energy, but little or no utilisation occurred with chlorinated paraffins with high degrees of chlorination (at or above around 59–60% wt. Cl).

Zitko and Arsenault (1974 and 1977) reported the results of a study to determine the biodegradation of two LCCPs in spiked estuarine sediments under both aerobic and anaerobic conditions. The substances tested were a C<sub>>20</sub>, 42% wt. Cl product and a C<sub>>20</sub>, 70% wt. Cl product. The tests were carried out in flasks containing 25 g of sediment, 300 ml of sea water and 10 ml of a suspension of decomposing organic matter in sea water. Three flasks were used in the experiment, one for each of the two products tested, and a third acting as control. The flasks were incubated at 19–22°C with aeration for 28 days (the volume of water was kept constant by adding distilled

water during the test). In addition to these, another identical set of three flasks were kept stoppered over the exposure period. Samples of sediments were collected at various times during the experiment and analysed for the presence of the chlorinated paraffins. The results are shown in Table 3.17.

**Table 3.17 Biodegradation in sediments (Zitko and Arsenault, 1974 and 1977)**

Time	Concentration of chlorinated paraffin (mg/kg dry weight)			
	Aerated flasks		Stoppered flasks	
	C <sub>&gt;20</sub> , 42% wt. Cl	C <sub>&gt;20</sub> , 70% wt. Cl	C <sub>&gt;20</sub> , 42% wt. Cl	C <sub>&gt;20</sub> , 70% wt. Cl
0 days	596	357	596	357
10 days	257	76	80	41
21 days	147	128	194	33
28 days	377	72	98	50

The analytical method used in the degradation experiments was based on microcoulometry. This method detects the presence of chlorine and so will detect all chlorinated compounds present, but may also suffer from interference from sulphur and nitrogen compounds. Interferences were found to occur in the control and the sediment spiked with the C<sub>>20</sub>, 42% wt. Cl product, but these were found to be reasonably volatile and could be effectively removed by drying the sediment at 46°C at reduced pressure (27 psi) overnight. The effect of this treatment on the recoveries of the chlorinated paraffins is not given, but the concentrations reported are corrected for overall recovery and background measurements in the control.

After 30 days, all the remaining sediments were dried and analysed for chlorinated paraffins and breakdown products using thin layer chromatography and infra-red spectrophotometry. Only trace amounts of the chlorinated paraffins could be detected, and there was evidence for more polar metabolites (as shown by thin layer chromatography) being present.

The results from this experiment show that primary degradation of LCCPs occurred to some extent in these tests. The extent of primary degradation appears to have been greater in the stoppered flasks than in the aerated flasks. The paper interprets this as representing a higher rate of degradation in anaerobic conditions than aerobic conditions. However, this interpretation should be treated with caution as it assumes that the stoppered flasks were anaerobic, but no information is given in the paper to show that this was the case (i.e. for instance the flasks had effectively 200 ml of headspace, and the actual oxygen content of the stoppered flasks is not given).

### 3.2.2.3 Degradation products

Little information is available on the possible degradation products of LCCPs. Of possible concern for the environment would be if the LCCPs were broken down to give the more bioavailable short- and medium-chain chlorinated paraffins in the environment. This possibility is unlikely to be significant for the reasons outlined below.

The two main forms of biodegradation possible are aerobic and anaerobic degradation. Under aerobic conditions, the most likely mechanism for degradation would be  $\beta$ -oxidation, which would lead to chain shortening by two carbon units each time, but more

importantly would also lead to oxidation of the terminal carbon, usually forming an acid group. Also, such processes tend to progress step-wise down the carbon chain and there is no reason why, if degradation did occur, it would stop at a carbon chain length of C<sub>10-13</sub>.

The co-metabolic degradation experiments carried out by Omori *et al.* (1987), mentioned in the preceding section, indicated that  $\beta$ -oxidation to form initially chlorinated fatty acids which are then broken down to 2- or 3-chlorinated fatty acids was the most likely degradation mechanism for chlorinated paraffins. It is unlikely that short- or medium-chain chlorinated paraffins themselves would be formed under such conditions from LCCPs.

Under anaerobic conditions, most chlorinated compounds appear to degrade by reductive dechlorination, which removes chlorine from the molecule but would not be expected to alter the carbon chain length. This sort of reaction has been most extensively studied for halogenated aromatics, but substances such as tetrachloroethylene and trichloroethylene appear to degrade in a similar way. Again, even if chain shortening did occur as well, there is no reason why the reaction would stop at C<sub>10-13</sub> and so it is unlikely that short- or medium- chain chlorinated paraffins would be formed as a result of these types of reactions.

### 3.2.3 Degradation in soil

No data are available on the degradation of LCCPs in soil systems.

### 3.2.4 Evaluation of environmental degradation data

No standard-ready or inherent biodegradation test results are available for LCCPs. From the available data, LCCPs can be considered as not biodegradable in such systems and so a biodegradation rate constant of 0 day<sup>-1</sup> will be used for all types of LCCPs in the risk assessment.

There is evidence that some microorganisms may be capable of degrading LCCPs in the environment in acclimated or co-metabolic systems. The potential for biodegradation appears to increase with decreasing chlorine content. There is also some evidence that biodegradation may occur under anaerobic conditions, although it is not clear whether anaerobic conditions were actually maintained in the test. It is not possible to derive rate constants for biodegradation in soil, surface water and sediment systems from the available data. As a worst case approach, no biodegradation will be assumed in these media in the PEC calculations. The actual biodegradation rate used in the assessment has little effect on the local PECs, but has a major effect on the predicted regional and continental concentrations. This issue is considered further in Appendix E.

Hydrolysis and aquatic photolysis is not expected to be a significant degradation process for LCCPs in the environment.

LCCPs are predicted to react with hydroxyl radicals in the atmosphere. For this assessment, the atmospheric half-lives given in Table 3.18 will be taken as being representative of the various subgroups considered.

**Table 3.18 Atmospheric half-lives of LCCPs**

Subgroup	Best estimates
C <sub>18-20</sub> liquids (typically 40–52% wt CI)	30 hours
C <sub>&gt;20</sub> liquids (typically 40–54% wt. CI)	25 hours
C <sub>&gt;20</sub> solids (typically 70% wt. CI)	110 hours

For the marine environment, experiments have been carried out to investigate the biodegradation of two LCCPs in a sea water/estuarine sediment system. These provide some indication of degradation but it is not possible to derive any biodegradation rates applicable to the marine environment from these data.

### 3.2.5 Environmental partitioning

The potential environmental distribution of LCCPs has been studied using a generic level III fugacity model. The model used was a four compartment model (EQC version 1.01, May 1997) that has been circulated for use within the OECD HPV program. The model was run four times with a nominal release rate of 1,000 kg/hour, initially entering the air, soil or water compartments in different proportions. A summary of the results is given in Table 3.19. Further details of the input values used and the model output are given in Appendix C.

The results of the fugacity modelling indicate that LCCPs are likely to be associated with the soil and sediment compartments. When the substances are released to air, the model predicts that they will end up mainly in soil, probably as a result of atmospheric deposition processes. When the substances are released to water, the model predicts that the vast majority of the substance will be associated with sediment, but some would also be expected to occur in the water phase. When the substance is released to soil, it is predicted to remain mainly in the soil compartment, but a small amount may also enter the sediment compartment, possibly as a result of wash-off from the soil to water.

Very little of the substance released to water is predicted to enter the soil phase, indicating that transport processes such as volatilisation to the atmosphere and subsequent deposition are not likely to occur for these substances. However, the key input parameter into this prediction is the Henry's Law constant. The model estimates this value from the vapour pressure and water solubility of the substance. As discussed in Section 1.4.8.3 there are large uncertainties in the reliability of the Henry's Law constants estimated for LCCPs from the available vapour pressure and water solubility data. The "best" estimates for the Henry's Law constants are 16 Pa m<sup>3</sup>/mole for C<sub>18-20</sub> liquid chlorinated paraffins, 15 Pa m<sup>3</sup>/mole for C<sub>>20</sub> liquid chlorinated paraffins and 1×10<sup>-6</sup> Pa m<sup>3</sup>/mole for the C<sub>>20</sub> solid chlorinated paraffins. These values indicate that transport from water to the atmosphere is not likely to be significant for the C<sub>>20</sub> solid chlorinated paraffins, but may be more significant than predicted here for the C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins.

From the fugacity modelling results it is clear that most of the LCCP in the environment would be expected to be associated with the soil and sediment phases.

**Table 3.19 Results of level III fugacity modelling for LCCPs**

Release compartment	Percentage distribution (%)											
	Air			Water			Soil			Sediment		
	<b>C<sub>18-20</sub> liquid</b>	<b>C<sub>&gt;20</sub> liquid</b>	<b>C<sub>&gt;20</sub> solid</b>	<b>C<sub>18-20</sub> liquid</b>	<b>C<sub>&gt;20</sub> liquid</b>	<b>C<sub>&gt;20</sub> solid</b>	<b>C<sub>18-20</sub> liquid</b>	<b>C<sub>&gt;20</sub> liquid</b>	<b>C<sub>&gt;20</sub> solid</b>	<b>C<sub>18-20</sub> liquid</b>	<b>C<sub>&gt;20</sub> liquid</b>	<b>C<sub>&gt;20</sub> solid</b>
100% to air	1.14 ×10 <sup>-3</sup>	4.45 ×10 <sup>-4</sup>	3.68 ×10 <sup>-4</sup>	3.40 ×10 <sup>-3</sup>	3.35 ×10 <sup>-3</sup>	3.34 ×10 <sup>-3</sup>	99.6	99.6	99.6	0.393	0.387	0.386
100% to water	7.12 ×10 <sup>-6</sup>	2.78 ×10 <sup>-7</sup>	8.08 ×10 <sup>-24</sup>	0.853	0.857	0.858	0.625	0.062	2.19 ×10 <sup>-18</sup>	98.5	99.1	99.1
100% to soil	7.05 ×10 <sup>-8</sup>	2.35 ×10 <sup>-9</sup>	6.37 ×10 <sup>-24</sup>	3.01 ×10 <sup>-3</sup>	3.01 ×10 <sup>-3</sup>	3.01 ×10 <sup>-3</sup>	99.6	99.6	99.6	0.348	0.348	0.348
50% to air and 50% to water	1.12 ×10 <sup>-3</sup>	4.41 ×10 <sup>-4</sup>	3.66 ×10 <sup>-4</sup>	0.018	0.012	8.45 ×10 <sup>-3</sup>	97.9	98.6	99.0	2.06	1.35	0.976



## 3.2.6 Adsorption

### 3.2.6.1 Experimental data

No experimental adsorption coefficients appear to be available for LCCPs.

### 3.2.6.2 Predicted data

Organic carbon-water partition coefficients (Koc) can be estimated from log Kow using the methodology outlined in the TGD. The equation given for predominantly hydrophobic chemicals is:

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

Definitive determinations of Koc values using short-chain chlorinated paraffins have indicated that the above equation is applicable to chlorinated paraffins (Thompson *et al.*, 1998). Using this equation, the following values for Koc can be estimated:

C <sub>18-20</sub> liquid chlorinated paraffin	log Kow = 9.7	Koc = 9.06×10 <sup>7</sup> l/kg
C <sub>&gt;20</sub> liquid chlorinated paraffin	log Kow = 10.3	Koc = 2.77×10 <sup>8</sup> l/kg
C <sub>&gt;20</sub> solid chlorinated paraffin	log Kow = 17	Koc = 7.4×10 <sup>13</sup> l/kg

The validity of the equation for very high log Kow values is not known.

Koc values for several LCCPs have also been estimated using the Syracuse Research Corporation PCKOC (version 1.63) program. This estimates Koc values from chemical structure using a molecular connectivity index approach. The values obtained for several example structures are shown in Table 3.20. These estimates are reasonably consistent to those obtained above from log Kow.

**Table 3.20 Estimated Koc values for LCCPs from structure**

Formula	% wt. Cl	Koc (l/kg)
C <sub>18</sub> H <sub>33</sub> Cl <sub>5</sub>	41.6	2.93×10 <sup>6</sup>
C <sub>18</sub> H <sub>30</sub> Cl <sub>8</sub>	53.6	1.27×10 <sup>7</sup>
C <sub>20</sub> H <sub>36</sub> Cl <sub>6</sub>	43.6	1.61×10 <sup>7</sup>
C <sub>20</sub> H <sub>33</sub> Cl <sub>9</sub>	53.9	7.00×10 <sup>7</sup>
C <sub>25</sub> H <sub>45</sub> Cl <sub>7</sub>	41.9	5.58×10 <sup>8</sup>
C <sub>25</sub> H <sub>42</sub> Cl <sub>10</sub>	50.9	2.42×10 <sup>9</sup>
C <sub>25</sub> H <sub>29</sub> Cl <sub>23</sub>	71.3	1×10 <sup>10</sup> <sup>a</sup>
C <sub>30</sub> H <sub>53</sub> Cl <sub>9</sub>	43.6	1×10 <sup>10</sup> <sup>a</sup>
C <sub>30</sub> H <sub>49</sub> Cl <sub>13</sub>	53.0	1×10 <sup>10</sup> <sup>a</sup>
C <sub>30</sub> H <sub>35</sub> Cl <sub>27</sub>	70.8	1×10 <sup>10</sup> <sup>a</sup>

Note: <sup>a</sup> Upper limit of estimation method.

The high Koc value estimated for LCCPs indicates that the substance is expected to be relatively immobile in soil and would not be expected to leach from soil into

groundwater. Vertical movement of LCCPs adsorbed onto soil particulates via macropores may provide a transport mechanism in soil.

### 3.2.6.3 Summary of adsorption data

No experimental data are available for LCCPs. The following estimated values will be considered in the risk assessment:

C <sub>18-20</sub> liquid chlorinated paraffin	Koc = $9.06 \times 10^7$ l/kg
C <sub>&gt;20</sub> liquid chlorinated paraffin	Koc = $2.77 \times 10^8$ l/kg
C <sub>&gt;20</sub> solid chlorinated paraffin	Koc = $>1 \times 10^{10}$ l/kg

The very high values for Koc indicate that LCCPs will adsorb strongly onto sediments and soil and will not leach significantly from soil.

Appendix E considers the effects of varying the log Kow value (and hence predicted Koc) on the overall outcome of the risk assessment.

No data are available specific to the marine environment. The estimated Koc values are considered to be representative.

### 3.2.7 Volatilisation

LCCPs have low, but measurable, vapour pressures at ambient temperatures. Therefore they are predicted to volatilise only slowly from articles in use (although volatilisation could be more extensive at elevated temperatures). Once in the environment, LCCPs could also volatilise slowly from water or soil etc., but in these compartments volatilisation is likely to be mediated to a large extent by strong adsorption of the LCCPs to sediment and soil. The potential for volatilisation is expected to reduce with both increasing carbon chain length and increasing chlorine content (i.e. in line with the expected trends in the decrease in vapour pressure and increase in adsorption to soil and sediment).

### 3.2.8 Precipitation

LCCPs have a very low water solubility and so are unlikely to be significantly removed from the atmosphere in precipitation in the dissolved phase. However, LCCPs are expected to adsorb strongly onto atmospheric particulates which could then be washed out of the atmosphere by precipitation (or deposited by dry deposition processes). Thus transfer from the atmosphere to soil and surface water could occur via atmospheric particulates.

### 3.2.9 Bioaccumulation and metabolism

#### 3.2.9.1 Bioconcentration from water

Bengtsson *et al.* (1979) studied the uptake of an LCCP by bleak (*Alburnus alburnus*). The chlorinated paraffin tested was a C<sub>18-26</sub>, 49% wt. Cl substance. The tests were performed at 10°C using a semi-static procedure in which the test solutions containing

125 µg/l of the test substance were renewed every two to three days over the 14-day exposure period. A seven-day depuration period followed the 14-day exposure period. The water used in the experiment was Baltic Sea water with a salinity of 7‰, and acetone was present in all aquaria, including controls, at a concentration of 0.1 ml/l. The fish used in the experiment had an average weight of 4.5 g and were not fed during the exposure period. Six groups of 15 fish were used for both the exposure and control solutions.

No mortalities or effects on behaviour were seen in fish exposed to the LCCP during the test. Very little uptake of the chlorinated paraffin occurred during the exposure period, with whole body levels of the LCCP of around 1–2 mg/kg fresh body weight (read from graph) being determined at 14 days. From this value a BCF of around 8–16 l/kg can be estimated. A reduction in the body concentration occurred during the seven-day depuration period. The analytical method used (neutron activation analysis) is not specific for the chlorinated paraffin and so may also include any chlorinated metabolites present in the fish, which may result in an overestimate of the actual chlorinated paraffin concentration in the fish if substantial metabolism was occurring.

In this experiment the concentration tested was above the water solubility of the substance in pure water, leading to the possibility that not all the test substance was present in true solution in the experiment. Also, the exposure period in the study is relatively short and so it is not certain that equilibrium would have been reached.

The accumulation of two LCCPs has been studied in rainbow trout (*Oncorhynchus mykiss*) over 60 days in GLP studies (Madeley and Maddock, 1983a and b). The investigations were carried out as part of a long-term toxicity test, and the bioconcentration factors were determined only at the end of the study. The substances tested were commercial products (either a C<sub>22–26</sub>, 43% wt. Cl product or a C<sub>>20</sub>, 70% wt. Cl product) mixed with a n-pentacosane-13-<sup>14</sup>C that had been chlorinated to a similar degree. A flow-through system was used for each test and the concentrations of chlorinated paraffin were measured by both radioactivity measurements and parent compound analysis (using a thin layer chromatography (TLC) method). The tests were carried out at a temperature of 12±1°C. Fish were fed with a proprietary trout food throughout the test at a rate of two per cent of body weight/day. Further details of the test system used can be found in Section 4.1.1.

For the C<sub>22–26</sub>, 43% wt. Cl substance (Madeley and Maddock, 1983a), two nominal exposure concentrations of 1.0 mg/l and 3.2 mg/l were used. In order to provide stable test solutions/suspensions, acetone at a concentration of 500 ppm (0.5 ml/l) was also present in the tests. The actual mean measured concentrations found during the test were 0.97 and 4.0 mg/l at the two exposure concentrations respectively, based on regular <sup>14</sup>C-measurements. On five occasions during the tests parent compound analyses were also carried out. These gave mean measured concentrations of 0.76 mg/l and 2.2 mg/l for the two exposure concentrations respectively, and were in general agreement with the <sup>14</sup>C-measurements. No treatment-related mortalities occurred during the test. The BCFs determined were 17.9–37.6 l/kg, based on <sup>14</sup>C measurements in whole fish and 3.6–9.0 l/kg based on parent compound analysis in whole fish, with the higher BCF values being found at the higher exposure concentrations.

For the C<sub>>20</sub>, 70% wt. Cl substance (Madeley and Maddock, 1983b) three nominal exposure concentrations of 1.0 mg/l, 2.1 mg/l and 4.2 mg/l were used. In order to provide stable test solutions/suspensions, acetone at a concentration of 500 ppm (0.5 ml/l) for the two lower concentrations or 1,000 ppm (1 ml/l) for the highest concentration was also present in the test. Monitoring of the actual test concentrations by <sup>14</sup>C-measurements indicated that the mean measured concentrations were 0.84 mg/l, 1.9

mg/l and 3.8 mg/l at the three test concentrations respectively. Parent compound analysis of the exposure concentrations on five occasions during the test gave similar results (mean measured levels were 0.6 mg/l, 1.0 mg/l and 2.1 mg/l at the three concentrations respectively). No treatment-related mortalities occurred during the test, although some behavioural effects were seen in both the control and exposed populations during the test. The BCFs determined were 5.7–53.8 based on <sup>14</sup>C-measurements in whole fish, and 1.0–42.8 mg/l based on parent compound analysis of the levels in whole fish.

In this experiment, the highest BCF values were obtained in the experiments with the lowest exposure concentration. The BCF determined in the 1.9 mg/l exposure groups (5.7 based on <sup>14</sup>C-measurements and 1.0 based on parent compound measurements) was lower than that found at the other two concentrations (32.5–53.8 based on <sup>14</sup>C-measurements and 31.6–42.8 based on parent compound analysis). The results of the Madeley and Maddock (1983a and 1983b) studies are summarised in Table 3.21.

Madeley and Thompson (1983a and 1983b) determined bioconcentration factors in mussels (*Mytilus edulis*) at the end of a 60-day toxicity study using the same two LCPCs as used in the *Oncorhynchus mykiss* studies above (GLP study). The test substances were dissolved in acetone before dilution with sea water (salinity 34.0–35.5‰, pH 8.0–8.3, dissolved oxygen 6.1–8.25 mg/l, temperature 15°C). The test used a flow-through system in order to maintain the concentration in the exposure vessels but, as the study was actually designed to determine the toxicity to mussels, relatively high nominal concentrations of the test substances were used and the BCFs were only determined at the termination of the study. The organisms were fed with algae (*Platymonas suecica*) at a rate of 1.0–1.1×10<sup>9</sup> cells/day. The algae were continuously added to the in-flowing dilution water.

The mussels were exposed to the chlorinated paraffin via the water phase. However, adsorption to the algae with subsequent ingestion or direct ingestion of undissolved test substance could also have occurred. For the C<sub>22–26</sub>, 43% wt. Cl substance (Madeley and Thompson, 1983a), two nominal test concentrations of 0.32 and 3.2 mg/l were used. Acetone, at a concentration of 500 ppm (0.5 ml/l), was also present in the test solutions in order to produce stable solutions/dispersions. The highest test solution was reported to be cloudy in appearance, and some fine white deposits were observed occasionally on the surface. The mean measured exposure concentrations were determined to be 0.12 and 2.18 mg/l based on frequent <sup>14</sup>C-measurements throughout the test period. The mean exposure concentrations determined by parent compound (TLC) analysis on four occasions were 0.09 mg/l and 2.85 mg/l respectively, which are in reasonable agreement with the <sup>14</sup>C-measurements.

**Table 3.21 Results of the 60-day rainbow trout bioconcentration studies (Madeley and Maddock (1983a and 1983b))**

Substance tested	Measured exposure concentrations (mg/l)	Measured concentration in whole fish after 60 days exposure (mg/kg wet wt.)		Measured bioconcentration factor (concentration in fish/concentration in water) (l/kg)	
	<sup>14</sup> C-measurements	<sup>14</sup> C-measurements	Parent compound measurements	<sup>14</sup> C-measurements	Parent compound measurements
C <sub>22-26</sub> , 43% wt. Cl	0 (control)	-	1.2	-	-
	0 (solvent control)	-	1.1	-	-
	0.97	17.4	3.5	17.9	3.6
	4.0	150.2	36	37.6	9.0
C <sub>&gt;20</sub> , 70% wt. Cl	0 (control)	-	1.2	-	-
	0 (solvent control)	-	0.8-1.1	-	-
	0.84	45.2	36	53.8	42.8
	1.9	10.9	2.0	5.7	1.0
	3.8	123.6	120	32.5	31.6

No treatment-related mortality occurred during the test, however reduced filter feeding behaviour of the mussels compared with control organisms was consistently observed at the higher exposure concentration from day 7 onwards. The BCFs ((mg/kg wet mussel)/(mg/l test solution)) determined were 261–1,158 l/kg, based on <sup>14</sup>C measurements in the mussels and 87.2–1,000 l/kg based on parent compound analysis in the mussels (Madeley and Thompson, 1983a); the BCF was found to be lower at the higher exposure concentration. The similarity between the values obtained by the two analytical methods indicates that the majority of the <sup>14</sup>C present in the organism must have been as parent compound rather than metabolites.

For the C<sub>>20</sub>, 70% wt. Cl substance (Madeley and Thompson, 1983b), two nominal concentrations of 0.56 and 1.8 mg/l were used. Acetone, at a concentration of 500 ppm (0.5 ml/l) was again present in the test solutions in order to produce stable solutions/dispersions. Some deposition of the test substance was observed at the higher concentration tested, indicating that the maximum solubility in the test system had been exceeded. The mean measured exposure concentrations were 0.46 mg/l and 1.33 mg/l respectively, based on frequent <sup>14</sup>C-measurements. The mean exposure concentrations determined by parent compound (TLC) analysis on four occasions were 0.51 mg/l and 0.9 mg/l respectively, which are in reasonable agreement with the <sup>14</sup>C-measurements.

No treatment-related mortality or effect on filter feeding activity was observed during the test. The BCFs determined were 223–341 l/kg based on <sup>14</sup>C measurements in the mussels and 105–167 l/kg based on parent compound analysis in the mussels. Again, the BCF was found to be lower at the higher exposure concentration. There was also reasonable agreement between the values obtained by the two analytical methods, indicating that the majority of the <sup>14</sup>C found in the mussels must have been as parent compound rather than metabolites.

The results of the Madeley and Thompson (1983a and 1983b) studies are summarised in Table 3.22.

**Table 3.22 Summary of the 60-day mussel bioconcentration studies (Madeley and Thompson (1983a and 1983b))**

Substance tested	Measured exposure concentrations (mg/l)	Measured concentration in mussels after 60 days exposure (mg/kg wet wt.)		Measured bioconcentration factor (concentration in mussels/concentration in water) (l/kg)	
	<sup>14</sup> C-measurements	<sup>14</sup> C-measurements	Parent compound measurements	<sup>14</sup> C-measurements	Parent compound measurements
C <sub>&gt;20</sub> , 43% wt. Cl	0 (control)	-	0.63	-	-
	0 (solvent control)	-	1.3	-	-
	0.12	138.9	120	1,158	1,000
	2.18	569.7	190	261	87.2
C <sub>22-26</sub> , 70% wt. Cl	0 (control)	-	1.1	-	-
	0 (solvent control)	-	1.2	-	-
	0.46	157	77	341	157
	1.33	297.1	140	223	105

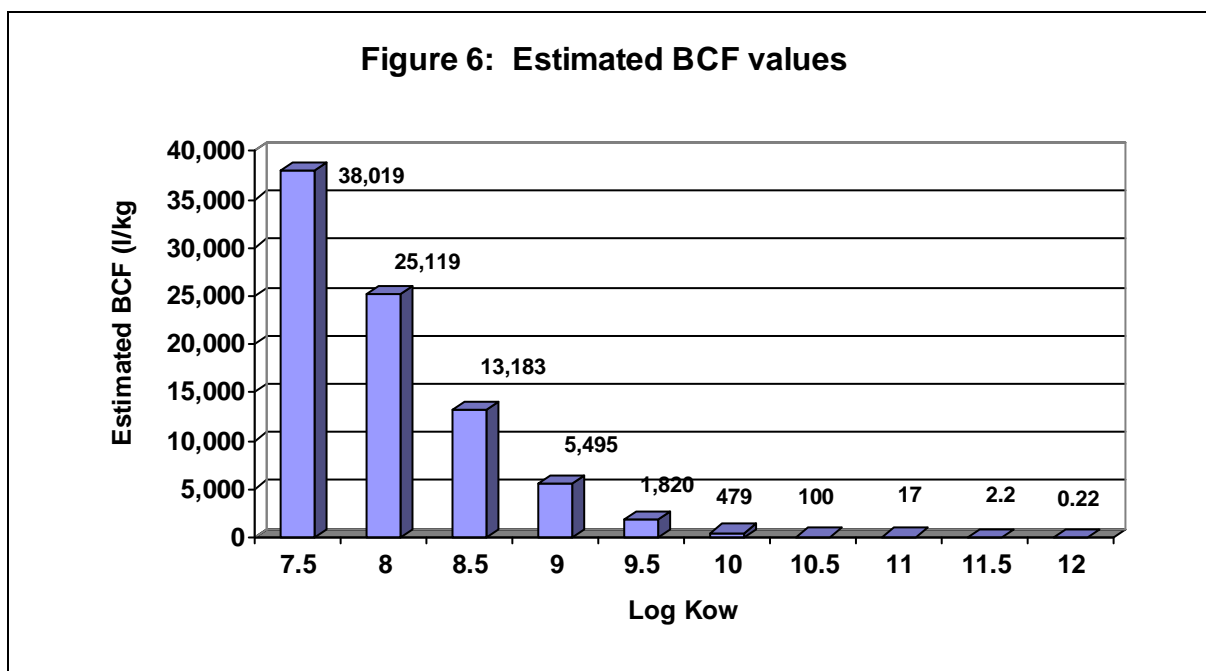
### Discussion of bioconcentration data

None of the available bioconcentration studies can be considered fully valid. All of the studies have used exposure concentrations in excess of the water solubility of the substance and indeed some of the tests appear to have been carried out using suspensions. In addition, there is no indication in the available studies that a steady state had been reached during the uptake phase. This means that these experiments may underestimate the true BCF of the substance.

According to the TGD, the bioconcentration factor (BCF) for fish can be estimated from the following equation.

$$\log \text{BCF} = -0.20 \times (\log \text{Kow})^2 + 2.74 \times \log \text{Kow} - 4.72$$

The equation applies to substances with  $\log \text{Kow} > 6$  and molecular weights  $< 700$  g/mole. The  $\log \text{Kow}$  values for LCCPs range from around 7.5 to  $> 12$  (see Section 1.4.6). The BCF values estimated using this equation over this range of  $\log \text{Kow}$  values are shown in Figure 3.4.



**Figure 3.4 Estimated BCF values**

These data indicate that the BCF value is predicted to decrease with increasing  $\log \text{Kow}$ , reaching a value of  $< 100$  when the  $\log \text{Kow}$  value becomes  $> 10.5$ . Thus, it is clear that at least some LCCPs are not expected to bioconcentrate to a significant extent. As discussed in Section 1.4.6, the  $\log \text{Kow}$  values of LCCP are likely to increase with increasing carbon chain length and increasing degree of chlorination.

This trend in the predicted BCF for LCCPs continues the trend found with the available fish BCF data for short-chain and medium-chain chlorinated paraffins. Here, reliable BCFs of 7,816 and 1,087 l/kg were determined for short-chain ( $\log \text{Kow} \sim 6$ ) and medium-chain ( $\log \text{Kow} \sim 7$ ) chlorinated paraffins respectively. Thus, based on comparison with the available data for other chlorinated paraffins, the fish BCF for LCCPs would be expected to further reduce with increasing carbon chain length.



One explanation for the apparent fall-off of BCF with log Kow is that the molecule becomes too large to pass through cell membranes and so cannot be effectively taken up. This phenomenon is considered to occur when the diameter of the molecule reaches a certain size, and as a rough approximation this generally occurs at molecular weights of 700–800 g/mole and above.

Since all chlorinated paraffins conform to the general formula  $C_nH_{2n+2-y}Cl_y$ , it is relatively straight forward to determine the chlorine content for each value of n where this 800 g/mole molecular weight limit may be reached. These values are shown in Table 3.23.

Based on these theoretical considerations, it is unlikely that the highly chlorinated (i.e. 70% wt. Cl) LCCPs will undergo significant bioconcentration in fish.

The BCF values selected for use in the assessment are summarised in Section 3.2.9.

**Table 3.23** Approximate chlorine contents resulting in a molecular weight of 800 g/mole

Number of carbon atoms (n)	Calculated number of chlorine atoms/molecule	Chlorine content of chlorinated paraffin
18	15.0	66.0% wt. Cl
19	14.6	64.7% wt. Cl
20	14.2	63.0% wt. Cl
21	13.8	61.3% wt. Cl
22	13.4	59.6% wt. Cl
23	13.0	57.9% wt. Cl
24	12.7	56.2% wt. Cl
25	12.3	54.5% wt. Cl
26	11.9	52.8% wt. Cl
27	11.5	51.1% wt. Cl
28	11.1	49.4% wt. Cl
29	10.7	47.7% wt. Cl
30	10.4	46.0% wt. Cl

### 3.2.9.2 Accumulation from sediment and soil

The risk assessment methodology in the TGD considers uptake from soil into earthworms and into plants (root crops).

#### **Earthworms**

For earthworms, no measured BCF or uptake data are available for LCCPs and so a predicted value is used in the assessment. A number of approaches have been considered for predicting the BCF for earthworms. Firstly, the methodology outlined in the TGD has been used to estimate the BCF for earthworms from log Kow. The resulting BCF values are shown below. These BCF values relate the uptake in earthworms to the soil pore water concentrations of the substance.

	BCF <sub>earthworm</sub>
C <sub>18-20</sub> liquid	6.0×10 <sup>7</sup> l/kg
C <sub>&gt;20</sub> liquid	2.4×10 <sup>8</sup> l/kg
C <sub>&gt;20</sub> solid	1.2×10 <sup>15</sup> l/kg

It should be noted that the method used for earthworms within the current TGD and EUSES is only valid for substances with log Kow of up to around 8. All three types of LCCPs considered in this assessment have log Kow values significantly above this value and so the above estimates are of questionable value to the assessment. In addition, as was noted earlier, the bioaccumulation potential of LCCPs appears to be lower than would be expected based on the high log Kow value alone.

The reliability of the above TGD method has recently been studied in detail (Brooke and Crookes, 2007). In this study, the predictions obtained using the TGD method were compared with available experimental data from laboratory or field studies for a range of chemicals for both exposure via water only and exposure in whole soils.

For the water only exposure, test data were available for 11 substances (pesticides and chlorobenzenes) covering a log Kow range from -0.47 to 5.50. For this test set, generally good agreement was found between the predicted earthworm BCF and the experimentally determined BCF. However, it should be noted that the test set did not include substances with log Kow values >6.

A much larger test set of experimental data was available for whole soil exposure (both from field studies and laboratory studies). The test set contained 488 data points for around 107 substances covering an approximate log Kow range of 1 to 9.5. In this case, a comparison was made between the predicted accumulation and that actually measured by converting both datasets to a bioaccumulation factor (BAF<sub>earthworm</sub>) based on the concentrations in earthworms (mg/kg wet weight)/concentration in soil (mg/kg wet weight). This analysis showed the current TGD method consistently overpredicted the BAF<sub>earthworm</sub> (and hence the concentration in earthworms) for substances with a log Kow above about 4 to 5. Further, the overprediction appeared to increase linearly with increasing log Kow above this range. Based on these findings, Brooke and Crookes (2007) determined the following correction to the BAF<sub>earthworm</sub> by linear regression that is applicable to all substances with log Kow values in the range 1 to 9.5 provided that the Koc value is estimated using the QSAR for predominantly hydrophobic substances<sup>7</sup>.

$$\log \text{BAF}_{\text{earthworm\_corrected}} = \log \text{BAF}_{\text{earthworm\_predicted}} - (0.39 \times \log \text{Kow}) + 1.72.$$

In order to use this correction it is necessary to convert the earthworm BCF to a BAF<sub>earthworm</sub> value. This conversion is achieved using the default worm and soil properties laid out in the TGD. Brooke and Crookes (2007) showed that the BAF<sub>earthworm</sub> can be related to the BCF<sub>earthworm</sub> and the organic carbon-water partition coefficient (Koc) using the following equation:

<sup>7</sup> The methodology used by Brooke and Crookes (2007) required an estimate of the Koc value from log Kow. The analysis was carried out using both the TGD default QSAR for Koc ( $\log \text{Koc} = 0.52 \times \log \text{Kow} + 1.02$ ), and the QSAR for predominantly hydrophobic chemicals ( $\log \text{Koc} = 0.81 \times \log \text{Kow} + 0.10$ ). Similar results were obtained in both cases, but the final equation for the correction is slightly different when the TGD default QSAR is used rather than the QSAR for predominantly hydrophobic chemicals. For LCCPs, the QSAR for predominantly hydrophobic chemicals has been used to estimate the Koc values used in the assessment (see Section 3.2.6).

$$\text{BAF}_{\text{earthworm}} = \frac{\left[ \left( \frac{1.7 \times \text{BCF}_{\text{earthworm}}}{0.2 + (0.03 \times \text{Koc})} \right) + 0.1133 \right]}{1.1133}$$

Using these equations values for the  $\text{BAF}_{\text{earthworm\_predicted}}$  and  $\text{BAF}_{\text{earthworm\_corrected}}$  can be estimated for LCCPs (Table 3.24).

**Table 3.24 Estimated LCCP earthworm BAF**

Property	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
Log Kow	9.7	10.3	17
Koc (Section 3.2.6)	9.06×10 <sup>7</sup> l/kg	2.77×10 <sup>8</sup> l/kg	7.4×10 <sup>13</sup> l/kg (>1×10 <sup>10</sup> l/kg)
BCF <sub>earthworm</sub> (TGD prediction – see above)	6.0×10 <sup>7</sup> l/kg	2.4×10 <sup>8</sup> l/kg	1.2×10 <sup>15</sup> l/kg
BAF <sub>earthworm_predicted</sub>	33.9 kg/kg	44.1 kg/kg	825.5 kg/kg
BAF <sub>earthworm_corrected</sub>	0.29 kg/kg	0.22 kg/kg	0.010 kg/kg

For comparison, a measured  $\text{BAF}_{\text{earthworm}}$  is available for the related medium-chain chlorinated paraffins (ECB, 2005a). The BAF measured was around 5.6 (on a wet worm (mg/kg)/wet soil (mg/kg) basis; this value is extrapolated to the default properties of soil used in the TGD). The value of the  $\text{BAF}_{\text{earthworm\_predicted}}$  that would be estimated using the TGD methodology for medium-chain chlorinated paraffins (log Kow of 7) would be around 11 and using the above correction this would lead to a  $\text{BAF}_{\text{earthworm\_corrected}}$  of around 1. In this case, both the predicted and corrected BAFs are of a similar order to the measured BAF.

A third possibility for the estimation of the BCF for earthworms is to use an older method that was included in a previous version of the TGD. This method was used for medium-chain chlorinated paraffins (ECB, 2005a) and was found to give reasonable agreement with the measured data for that substance. The relevant equation, which relates the  $\text{BAF}_{\text{earthworm}}$  (on a wet worm (mg/kg)/wet soil (mg/kg) basis), the octanol-water partition coefficient (Kow) and the soil-water partition coefficient ( $K_{\text{soil-water}}$ ) is given below (see ECB (2000a) for further details).

$$\text{BAF}_{\text{earthworm}} = 0.25 \times \text{Kow} \times 0.16 \times \frac{1,700 \times 10^{-3}}{K_{\text{soil-water}}}$$

The method was recommended for log Kow values in the range 1.0–6.5. For substances with a log Kow above this range, the method recommended that a Kow of 3.16×10<sup>6</sup> (i.e. a log Kow of 6.5) was used. For medium-chain chlorinated paraffins, the  $\text{BAF}_{\text{earthworm}}$  predicted using this method was 12.2 which compares reasonably with the experimental value of 5.6. The BAF values estimated for LCCPs using this method (assuming a Kow of 3.16×10<sup>6</sup> for all three substances) are summarised in Table 3.25 below.

**Table 3.25 Estimates for BAF<sub>earthworm</sub> using alternative TGD method**

LCCP subgroup	K <sub>soil-water</sub> (m <sup>3</sup> /m <sup>3</sup> ) <sup>8</sup>	BAF <sub>earthworm</sub>
C <sub>18-20</sub> liquid	2.72×10 <sup>6</sup>	0.080
C <sub>&gt;20</sub> liquid	8.31×10 <sup>6</sup>	0.026
C <sub>&gt;20</sub> solid	>3.0×10 <sup>8</sup>	<7.2×10 <sup>-4</sup>

The estimates for the earthworm BAF for LCCPs obtained using the older TGD method are much lower (by a factor of around 400–1×10<sup>6</sup>) than those obtained using the current TGD methodology, but only about a factor of four to eight lower than those obtained by applying the correction to the current TGD method discussed above.

A final method suggested by industry for estimating the earthworm BAF for LCCPs is to scale the measured BAF of 5.6 kg/kg determined for medium-chain chlorinated paraffins to LCCPs using the predicted BCF for fish as a scaler. Using a predicted fish BCF of 45,700 l/kg<sup>9</sup> for medium-chain chlorinated paraffins, 1,096 l/kg for C<sub>18-20</sub> liquid chlorinated paraffins, 192 l/kg for C<sub>>20</sub> liquid chlorinated paraffins and <1 l/kg for C<sub>>20</sub> solid chlorinated paraffins, the following scaled earthworm BAF values can be estimated.

	BAF <sub>earthworm_scaled</sub>
C <sub>18-20</sub> liquid	0.13 kg/kg
C <sub>&gt;20</sub> liquid	0.024 kg/kg
C <sub>&gt;20</sub> solid	<1.2×10 <sup>-4</sup> kg/kg

This approach gives a similar value to the corrected TGD approach and the “old” TGD approach for the C<sub>18-20</sub> liquid chlorinated paraffins, but a lower value than both methods for the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins. However, the reliability of this “scaling” method can be questioned as it relies on the earthworm BAF being directly proportional to the predicted fish BCF. For example, the fish BCF estimates made using the TGD method rise with increasing log Kow, up until log Kow is around 7, and then decrease with increasing log Kow above this value. It is not known if the earthworm BAF actually follows the same trend.

The values below (obtained using the correction to the current TGD methodology) will be used to estimate the uptake and accumulation in earthworms. These have been chosen because:

- the methodology used for estimating the uptake into earthworms in the current TGD was designed to improve upon the methodology in the older versions of the TGD;
- an extensive validation exercise has been carried out on the current TGD methodology and this identified a correction that could be applied to substances with very high log Kow values;

<sup>8</sup> Values estimated from the organic carbon-water partition coefficient using the methods in the TGD.

<sup>9</sup> Estimated using the TGD methodology for a substance with a log Kow of 7. The actual fish BCF for medium-chain chlorinated paraffins has been measured as 1,087 l/kg (ECB, 2005a).

- that there are uncertainties with the older methodology for substances with log Kow values above 6.5;
- the uncertainty in using a fish BCF to “scale” the available data for medium-chain chlorinated paraffins to LCCPs.

The values for  $BAF_{\text{earthworm\_corrected}}$  are:

	$BAF_{\text{earthworm\_corrected}}$
$C_{18-20}$ liquid	0.29 kg/kg
$C_{>20}$ liquid	0.22 kg/kg
$C_{>20}$ solid	0.010 kg/kg

### **Plant roots**

No experimental information is currently available on the uptake of LCCPs into plant roots and so predicted data are considered in the assessment.

The partition coefficient between plant roots and water ( $K_{\text{plant-water}}$ ) and the root-soil accumulation factors ( $BAF_{\text{root}}$ , which can be defined as the concentration in root (mg/kg wet weight)/concentration in soil (mg/kg wet weight)) that are predicted by the TGD methodology are summarised below for the LCCPs.

	$K_{\text{plant-water}}$ ( $\text{m}^3/\text{m}^3$ )	$BAF_{\text{root}}$ (kg/kg)
$C_{18-20}$ liquid	$1.6 \times 10^7$	14.6
$C_{>20}$ liquid	$6.1 \times 10^7$	17.9
$C_{>20}$ solid	$1.4 \times 10^{14}$	$<1.1 \times 10^6$

When these values are used in the calculation of the total daily uptake in humans via the food chain the resulting estimated daily dose is dominated by the predicted concentration in root crops (root crops account for >99 per cent of the total daily dose; calculations not shown). However, the concentrations in root crops predicted by the model are in most cases unrealistically high and so the use of these default accumulation factors may lead to significant overestimation of the total daily intake. For example, in the regional calculations for the  $C_{>20}$  solid chlorinated paraffins the concentration predicted in root crops using the TGD default method is  $1.9 \times 10^4$  mg/kg, meaning that the root crop is essentially two per cent LCCP by weight – a value that is clearly unrealistic.

A recent validation exercise of the methodology used in the TGD to estimate the uptake of chemicals into food has been carried out by Brooke *et al.* (2007). The study compared the predicted root uptake with that seen in studies using whole soil or nutrient solutions using a dataset consisting of around 122 datapoints for around 47 chemicals covering a log Kow range between -0.5 and 9.1.

The chemicals used in the study included various pesticides along with polycyclic aromatic hydrocarbons and chlorinated and brominated hydrocarbons, including a data point for medium-chain chlorinated paraffins. The analysis found that the current TGD methodology predicts the uptake into roots well for substances with a log Kow value up to around three. For substances with a log Kow value between three and four, there was a tendency for the TGD method to overpredict the actual uptake, but this overprediction was generally less than a factor of 10. For substances with log Kow values above four, the overprediction of the uptake became progressively worse with increasing log Kow.

In particular, it was evident that the TGD method predicts the value for  $BAF_{root}$  increases with increasing log Kow in this region, whereas the available experimental data shows a decreasing trend in the  $BAF_{root}$  with increasing log Kow. By normalising the available experimental data to a standard soil organic carbon content of two per cent, Brooke *et al.* (2007) derived the following equation relating the  $BAF_{root}$  to log Kow:

$$\log BAF_{root} = -0.38 \times \log Kow + 0.67$$

However, it should be noted that there was considerable scatter in the data, and the correlation coefficient for the above regression equation was low ( $R^2 = 0.41$ ). The estimated  $BAF_{root}$ , and the equivalent  $K_{plant-water}$  obtained using this equation for LCCPs are summarised below (Table 3.26). As can be seen, these values are considerably smaller than predicted above using the TGD methodology.

**Table 3.26**  $BAF_{root}$  and  $K_{plant-water}$  estimates for LCCP subgroups obtained using equation from Brooke *et al.* (2007)

LCCP subgroup	log Kow	$BAF_{root}$ (kg/kg)	$K_{plant-water}$ ( $m^3/m^3$ )
$C_{18-20}$ liquid	9.7	$9.6 \times 10^{-4}$	$1.1 \times 10^3$
$C_{>20}$ liquid	10.3	$5.7 \times 10^{-4}$	$2.0 \times 10^3$
$C_{>20}$ solid	17	$1.6 \times 10^{-6}$	200

Also relevant to the discussion here are the experimental data available on uptake from soil into root crops for the medium-chain chlorinated paraffins. These data are discussed in ECB (2007a). Here experiments carried out with carrot roots showed that the actual  $BAF_{root}$  for medium-chain chlorinated paraffins was 0.045 kg/kg and the equivalent  $K_{plant-water}$  of  $330 m^3/m^3$ , was around 136 times lower than would be predicted using EUSES. The log Kow value for medium-chain chlorinated paraffins is around 7 and using this log Kow value in the above equation derived would lead to an estimated  $BAF_{root}$  of 0.010 which is of a similar order to that determined experimentally.

Although it is not possible to extrapolate the measured  $BAF_{root}$  value for medium-chain chlorinated paraffins directly to LCCPs (the  $BAF_{root}$  depends on both the plant-water partition coefficient and the soil-water partition coefficient) it is reasonable to expect the actual bioaccumulation factor for LCCPs to be lower than that determined for medium-chain chlorinated paraffins. Therefore, it can be concluded that the contribution from root crops to the total daily intake for LCCPs is likely to be much lower than the default calculations predicted using the TGD methodology.

Based on the above discussion, the values for the plant-water partition coefficient to be used in the risk assessment are given in Table 3.27. These values are derived from the analysis of the TGD methodology carried out by Brooke *et al.* (2007). Although there was considerable uncertainty in the regression equation used, it should be noted that these values for the  $K_{plant-water}$  are similar to (in the case of the  $C_{>20}$  solid chlorinated paraffins) or higher than (for the liquid LCCPs) the equivalent value for medium-chain chlorinated paraffins ( $K_{plant-water} = 330 m^3/m^3$ ) derived from laboratory studies and so there appears to be some conservatism built in to the use of these  $K_{plant-water}$  values.

**Table 3.27 Values for the plant-water partition ( $K_{\text{plant-water}}$ ) to be used in the assessment**

LCCP subgroup	log Kow	BAF <sub>root</sub> (kg/kg)	$K_{\text{plant-water}}$ (m <sup>3</sup> /m <sup>3</sup> )
C <sub>18-20</sub> liquid	9.7	$9.6 \times 10^{-4}$	$1.1 \times 10^3$
C <sub>&gt;20</sub> liquid	10.3	$5.7 \times 10^{-4}$	$2.0 \times 10^3$
C <sub>&gt;20</sub> solid	17	$1.6 \times 10^{-6}$	200

### 3.2.9.3 Dietary/oral accumulation

The accumulation of a C<sub>18</sub>, 49% wt. chlorinated paraffin has been studied in juvenile rainbow trout (*Oncorhynchus mykiss*) (Fisk *et al.*, 2000). The substance tested was a single carbon chain length product synthesised by the free-radical chlorination of a <sup>14</sup>C-labelled C<sub>18</sub>-alkane with SO<sub>2</sub>Cl<sub>2</sub>. The product had an average formula of C<sub>18</sub>H<sub>30.3</sub>Cl<sub>6.7</sub>, but the position of the radio-label in the carbon chain was not stated. The food used during the test was a commercial fish food (41 per cent protein, 14 per cent lipid and three per cent fibre). The chlorinated paraffin was added to the food as a suspension in hexane followed by evaporation of the solvent.

Two chlorinated paraffin concentrations were tested: 1.6 mg/kg wet wt. food and 15 mg/kg wet wt. food. During the test, groups of 36 juvenile fish in flow-through tanks (initial weight 1–5 g, final weight 23–69 g) were fed the contaminated food (daily feeding rate was 1.5 per cent of mean weight of fish) over a 40-day period, followed by a 160-day depuration period using clean food. At various times during the experiment fish were sampled for <sup>14</sup>C levels in the carcass (whole fish minus liver and gastrointestinal tract). All measured concentrations were corrected for growth dilution. At day 40 of the uptake phase and day 40 of the depuration phase the amount of non-toluene-extractable <sup>14</sup>C-label present in carcass was also determined. This measurement was assumed to reflect the extent of biotransformation of the substance in fish. No effect on body and liver growth rates or liver somatic indices were seen between exposed and control populations during the test.

The results indicated that the chlorinated paraffin uptake had not reached steady state by day 40 of the uptake phase and so the bioconcentration factor for uptake from food was determined kinetically. The assimilation efficiencies (based on lipid corrected concentrations in fish and food) were determined to be 13–22 per cent, and the depuration rate constant was estimated to be 0.0076–0.0088 d<sup>-1</sup> (depuration half-life ~79–91 days). There was little evidence for biotransformation of the chlorinated paraffin by the fish. Based on the measured kinetic parameters, the bioaccumulation factor (concentration in fish (lipid normalised)/concentration in food (lipid normalised)) was around 0.81–0.93.

The uptake and accumulation of a C<sub>20-30</sub>, 42% wt. Cl product has been studied using both rainbow trout (*Oncorhynchus mykiss*) and mussel (*Mytilus edulis*) (Madeley and Birtley, 1980). The chlorinated paraffin used was a <sup>14</sup>C-pentacosane (radiolabel on the central carbon atom of the C<sub>25</sub> chain) which had been chlorinated to 42 per cent by weight. This was then mixed with a commercial C<sub>20-30</sub>, 42% wt. product before use. The food used in the test was suspended yeast cells for mussel and a commercial trout diet for trout. The food was dosed with the chlorinated paraffin mixture prior to feeding of the organisms.

In the trout studies, three groups of 40 fish were fed diets containing chlorinated paraffins at doses of either 0 mg/kg dry food (control group), 47 mg/kg dry food or 385

mg/kg dry food for 35 days. After the 35 day exposure period, all three groups were fed the control diet for a further 49 days (depuration period). The temperature during the experiment was maintained at  $12\pm 3^{\circ}\text{C}$ . No treatment related adverse effects were seen in any of the fish during the experiment.

The resulting tissue concentrations (as determined by  $^{14}\text{C}$ -measurements) are shown in Table 3.28. The uptake of radioactivity was found to be highest in the liver and gut, with the concentrations found approaching those in the administered food. The levels in all tissues were found to increase with time during the exposure phase, but were all approaching a plateau level by day 35 of the exposure. During the depuration phase, the  $^{14}\text{C}$ -activity in both gut and liver was found to rapidly diminish. Based on the ratio of the concentration in fish at day 35 and the concentration in food, the bioaccumulation factor can be estimated to be 0.22–0.26 on a dry weight basis in this study.

**Table 3.28 Tissue concentrations of  $^{14}\text{C}$  in fish fed a diet of  $^{14}\text{C}$ -labelled 42% wt. CI LCCP (Madeley and Birtley, 1980)**

Dose	Exposure phase	Tissue concentration (based on $^{14}\text{C}$ -measurements) (mg/kg dry weight)				
		Liver	Gut	Flesh	Remains	Total body burden
47 mg/kg dry food	End of 35-day uptake period	29.5	36.4	2.5	6.8	10.3
	End of 49-day depuration period	2.8	4.8	1.4	3.1	3.3
385 mg/kg dry food	End of 35-day uptake period	263	353	23.1	66.3	100.6
	End of 49-day depuration period	21.8 (6.5) <sup>a</sup>	47.3 (5.4) <sup>a</sup>	17.2 (3.7) <sup>a</sup>	29.8 (5.7) <sup>a</sup>	31.6

Note: <sup>a</sup> Concentration of chlorinated paraffin determined directly by TLC analysis.

In addition to the  $^{14}\text{C}$ -analyses, some fish in the 385 mg/kg dry food dose group were also analysed for the parent chlorinated paraffin directly by a thin layer chromatography (TLC) method at the end of the depuration phase. These results are also shown in Table 3.28 for comparison with the  $^{14}\text{C}$ -measurements. The levels measured by this direct method were generally much lower than those obtained by the  $^{14}\text{C}$ -method, indicating that chlorinated paraffin had been metabolised in the fish to some extent.

In the mussel study the dry yeast was dosed with the chlorinated paraffin at a concentration of 524 mg/kg dry weight and the exposure period was 47 days, followed by a depuration period of 56 days. The tissue concentrations measured at various times during the experiment are shown in Table 3.29. During the test, seven control animals and 10 exposed mussels died. The total number of mussels used in the study is not given in the paper but was at least 84 and so this difference in death rate is probably not significant.

In addition to the  $^{14}\text{C}$ -analyses, some mussels were also analysed for the parent chlorinated paraffin directly by a thin layer chromatography (TLC) method at the end of both the exposure phase and the depuration phase. These results are also shown in Table 3.29 for comparison with the  $^{14}\text{C}$ -measurements. The levels measured by this direct method were generally in agreement with those obtained by the  $^{14}\text{C}$  method,



indicating that little or no metabolism of the chlorinated paraffin had occurred in the experiment.

**Table 3.29 Uptake of <sup>14</sup>C-labelled long-chain (42% wt. Cl) chlorinated paraffin by mussels (Madeley and Birtley, 1980)**

Time	Tissue concentration (based on <sup>14</sup> C-measurements) (mg/kg dry weight)					
	Digestive gland	Foot	Gonad	Gill	Remaining tissues	Total body burden
<b>Uptake phase</b>						
Day 5	-	-	-	-	-	1.8
Day 9	-	-	-	-	-	2.4
Day 12	-	-	-	-	-	4.2
Day 19	-	-	-	-	-	5.1
Day 26	155.2	2.6	2.8	3.5	1.8	4.3
Day 33	36.6	1.3	1.9	5.3	2.9	5.9
Day 42	100.7	2.2	3.5	4.4	4.6	6.6
Day 47	80.5	5.4	1.9	7.0	6.8	11.2
						(3–16) <sup>a</sup>
<b>Depuration phase</b>						
Day 7	35.1	1.8	1.4	3.3	1.7	5.5
Day 21	37.0	3.3	2.0	3.1	1.7	2.9
Day 28	42.2	3.1	1.0	1.9	1.5	2.0
Day 39	15.8	2.9	2.0	3.6	1.7	2.2
Day 49	11.3	1.7	1.5	2.5	1.3	3.1
Day 56	7.0	0.9	0.9	1.5	0.6	1.2
						(<1–7) <sup>a</sup>

Note: <sup>a</sup> Concentration of chlorinated paraffin determined directly by TLC analysis.

Zitko (1974) studied the uptake of two LCCPs in the diet of juvenile Atlantic salmon (*Salmo salar*) over 181 days. The weekly amount of contaminated food added was 8 g per tank, with each tank containing 20 fish (fish weight was approximately 5–7 g/fish). In addition, shorter experiments were carried out to investigate the uptake of chlorinated paraffins by fish from suspended solids (silica). The chlorinated paraffins studied were a C<sub>>20</sub>, 42% wt. Cl product and a C<sub>>20</sub>, 70% wt. Cl product. A positive control (polychlorinated biphenyl (Aroclor 1254)) was also used in the study. The concentrations in the fish were expressed on a whole fish body weight as chlorine. Mortalities occurred in the exposed fish and also in the control group during the feeding studies. These findings are discussed further in Section 4.1.1. The results are shown in Table 3.30.

**Table 3.30 Uptake of LCCPs by juvenile Atlantic salmon (Zitko, 1974)**

Substance	Exposure concentration	Exposure time	Lipid content of fish	Concentration in fish (wet weight basis)
<b>Studies using suspended solids</b>				
Control		48 hours	0.99%	0.34 mg Cl/kg
C <sub>&gt;20</sub> , 42% wt. Cl	1 g/kg solid	48 hours	1.10%	0.44 mg Cl/kg
		144 hours	1.33%	0.75 mg Cl/kg
C <sub>&gt;20</sub> , 70% wt. Cl	1 g/kg solid	48 hours	1.56%	0.22 mg Cl/kg
		144 hours	2.10%	0.46 mg Cl/kg
Positive control (Aroclor 1254)	1 g/kg solid	24 hours	1.52%	19.9 mg Aroclor 1254/kg
		48 hours	1.86%	28.3 mg Aroclor 1254/kg
		144 hours	1.78%	134 mg Aroclor 1254/kg
<b>Feeding studies</b>				
Control		33 days	1.03%	0.30 mg Cl/kg
		109 days	0.65%	<0.05 mg Cl/kg
		181 days	0.47%	<0.05 mg Cl/kg
C <sub>&gt;20</sub> , 42% wt. Cl	10 mg/kg food	33 days	1.30%	0.11 mg Cl/kg
		109 days	0.69%	<0.05 mg Cl/kg
		181 days	0.49%	<0.05 mg Cl/kg
	100 mg/kg food	33 days	1.22%	0.51 mg Cl/kg
		109 days	0.49%	<0.05 mg Cl/kg
		181 days	0.34%	<0.05 mg Cl/kg
C <sub>&gt;20</sub> , 70% wt. Cl	10 mg/kg food	33 days	1.13%	0.29 mg Cl/kg
		109 days	0.40%	<0.05 mg Cl/kg
		181 days	0.29%	<0.05 mg Cl/kg
	100 mg/kg food	33 days	1.30%	0.49 mg Cl/kg
		109 days	0.56%	<0.05 mg Cl/kg
		181 days	0.92%	<0.05 mg Cl/kg
Positive control (Aroclor 1254)	10 mg/kg food	33 days	5.09%	3.86 mg Aroclor 1254/kg
		109 days	3.10%	3.80 mg Aroclor 1254/kg
		181 days	2.07%	3.80 mg Aroclor 1254/kg
	100 mg/kg food	33 days	5.30%	13.9 mg Aroclor 1254/kg
		109 days	2.73%	24.0 mg Aroclor 1254/kg
		181 days	2.69%	30.0 mg Aroclor 1254/kg

The results indicate that very little uptake of the chlorinated paraffins occurred from suspended solids or from food over the time period of the experiments.

A further feeding study with fish has been carried out by Bengtsson and Baumann Ofstad (1982). In this experiment, bleak (*Alburnus alburnus*) were exposed to a C<sub>18-26</sub>, 49% wt. Cl product via food for 91 days, followed by a 316-day depuration period. The fish used in the study had a body weight of around 4 g at the start of the experiment and the experiments were carried out in glass tanks with a continuous flow of brackish

water (~7‰). The temperature of the water varied between 3.5–16°C following the natural fluctuations in the bay from which the water was extracted.

During the exposure phase, the chlorinated paraffin was added to the fish food (flakes) at a concentration of 3,400 mg/kg food and this was added to the exposure tank (containing 30 fish) in 0.25 g portions twice daily on weekdays and once daily at weekends. The fish in three tanks were fed non-contaminated food at the same rate, and acted as the control groups for the experiment. Throughout the test, the dissolved oxygen was measured to be >90 per cent of saturation. Fish were sampled on days 14, 28, 56 and 91 of the exposure phase and on days 7, 35, 133 and 316 of the depuration phase. These fish were starved for two days (to avoid contributions of chlorinated paraffin from undigested food) prior to whole body analysis for levels of total chlorine using neutron activation analysis.

No significant increase in mortality was seen in the exposed fish during the experiment. Only a small amount of the LCCP appeared to be accumulated by the fish. The estimated concentration of chlorine (assumed to be chlorinated paraffin) in fish reached 24 mg/kg at the end of the 91-day exposure period (the bioaccumulation factor is therefore  $24/3,400 = 0.007$ ). The authors estimated that the uptake efficiency was around two per cent. The total chlorine levels in the fish were found to be reduced by around 50 per cent during the first four to five weeks of the depuration period, then the level appeared to remain constant for the remainder of the depuration period (40 weeks).

Yang *et al.* (1987) investigated the oral uptake of a radio labelled C<sub>18</sub>, 50–53% wt. Cl chlorinated paraffin in Sprague-Dawley rats. The chlorinated paraffin used in the study was synthesised by chlorination of 1-<sup>14</sup>C-octadecane. A single oral dose of 0.5 g/kg body weight was given to the rats and the amount of radioactivity excreted was monitored over 96 hours. At the end of the experiment the radioactivity remaining in the body tissues was also determined. The results are shown in Table 3.31.

**Table 3.31 Excretion of a C<sub>18</sub>, 50–53% wt. chlorinated paraffin in rats (Yang *et al.*, 1987)**

Recovered radioactivity	Time (hours)			
	24	48	72	96
Urine	1.0±0.3%	1.5±0.3%	1.9±0.5%	1.9±0.6%
Feces	22.2±21.5%	41.5±17.3%	70.2±7.1%	76.4±2.8% <sup>a</sup>
Air (as <sup>14</sup> CO <sub>2</sub> )	1.5±0.6%	3.1±1.7%	4.0±2.0%	4.5±2.3%
Tissues	not determined	not determined	not determined	3.3±2.7%
Total	24.7±22.0%	46.1±16.2%	76.1±6.1%	86.2±5.6%

Note: <sup>a</sup> Unabsorbed material accounted for approximately 16 per cent of the applied dose.

Other information on the uptake, distribution and excretion of LCCPs is summarised in other reviews (BUA, 1992; WHO, 1996). For example, BUA (1992) reports the results of studies using C<sub>22–26</sub>, 43% wt. Cl and C<sub>22–26</sub>, 70% wt. Cl products in rats. Both products contained <sup>14</sup>C-labelled chlorinated paraffin (the <sup>14</sup>C was in the centre of the carbon chain) and were administered to rats by gavage at concentrations of 100 and 3,750 mg/kg bw/day in corn oil. For the C<sub>22–26</sub>, 43% wt. Cl product, 82–96 per cent of the radio label was excreted in feces after seven days, with 0.1–0.8 per cent being excreted in urine and 0.1–1.6 per cent being exhaled. Similar results were found with

the C<sub>22-26</sub>, 70% wt. Cl product, with 76–88 per cent of the radiolabel being excreted in feces, 0.1–1.6 per cent being excreted in urine and 0.1–0.6 per cent being exhaled, again after seven days. The high rate of excretion via feces found in these studies indicate that the test substances were poorly absorbed.

### 3.2.9.4 Summary of accumulation

The available bioconcentration results on LCCPs are not reliable as much of the data were obtained using exposure concentrations well in excess of the water solubility of the substance. It is generally unclear if the length of the studies was sufficient for steady state to be reached. Therefore, although these studies show that uptake does occur, it is not possible to obtain a reliable BCF value from them. As a result, the estimated data for the fish bioconcentration factor will be considered in the assessment as a precautionary approach. The following values will be used for the fish bioconcentration factor:

C <sub>18-20</sub> liquid	BCF = 1,096 l/kg
C <sub>&gt;20</sub> liquid	BCF = 192 l/kg
C <sub>&gt;20</sub> solid	BCF <1 l/kg

Appendix E considers the effects of varying the log Kow value (and hence predicted BCF) on the overall outcome of the risk assessment.

For the marine environment, there are data available on the accumulation of LCCPs by mussels in salt water and fish in brackish water. These show similar patterns of uptake as found for freshwater species. Again, no reliable BCF can be derived from the data, and so the estimated BCFs are considered the most relevant for the marine environment as a precautionary approach.

In addition to bioconcentration, the TGD also provides methods to take into account biomagnification in the assessment of secondary poisoning. The method requires a biomagnification factor (BMF) for fish, preferably expressed on a lipid normalised basis. According to the TGD, an appropriate BMF for LCCPs would be 1 for all three types of LCCP considered, based on the fish BCF being <2,000 l/kg and the log Kow being >9.

There is evidence from feeding studies that the LCCPs can be taken up via the diet, but in all cases the concentrations reached in the animals were less than those in the diet. This indicates that although uptake of the substance can occur via food, the levels should not increase through the food chain. These findings support the default BMF of 1 determined above. Uptake via diet or the undissolved phase may also explain some of the uptake seen in the available bioconcentration studies.

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

There is a fundamental difference in biomagnification/accumulation factors obtained from field studies/measurements and those obtained in laboratory feeding studies. Field-derived factors will take into account accumulation from water and by food, whereas laboratory feeding studies only consider the food route. No distinction is made

in the methods given in the TGD between these two types of factors (this is considered further in Section 3.3.4).

The data obtained in the Fisk *et al.* (2000) study are lipid normalised. The fish food used in this study had a lipid content of 14 per cent, which was generally higher than that in the fish (e.g. 6–11 per cent). Thus if the accumulation factors were expressed in terms of a whole fish and whole food basis, they would be lower by around a factor of 1.3–2.3 times. However, conversely, it could be argued that in the environment the food for a predatory species would be generally of lower lipid content than found in laboratory fish food (and may be of lower lipid content than the predatory species itself). It is therefore not possible to infer from these results (or other laboratory-based results using proprietary food of high lipid content) that the accumulation factor on a whole body and food basis would be lower in the environment than found in the laboratory studies. In terms of the TGD, the methods suggest that the lipid-normalised BMFs should be used.

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

Some of the studies (notably Fisk *et al.*, 2000) have been corrected for growth dilution. The TGD is unclear on whether this is an appropriate basis on which to calculate accumulation or biomagnification factors. It could be argued that such a correction, in some circumstances, may make it virtually impossible for a steady state to be reached in fish that are growing. It is possible, for example, to have a situation where the actual concentrations in the fish remain constant from one sampling period to the next (i.e. steady state may have been reached) but if the fish grew by 10 per cent over the same sampling period, then the growth corrected concentrations would appear to increase by 10 per cent due to the calculation method involved. The Environment Agency has reanalysed the growth corrected data for the C<sub>18</sub> chlorinated paraffin from the Fisk *et al.* (2000) study and estimated that the non-growth-corrected fish accumulation factors from the study would be in the range 0.10–0.11 on a lipid basis. It should be noted, however, that since the original raw concentration-time data were lacking in the paper (only the derived kinetic parameters were reported) the reanalysis is only approximate and may be subject to large errors.

Some of the studies measuring accumulation are based on the concentration in fish at the end of the exposure period, where either a steady state was not reached or where there is no information as to whether or not a steady state was reached. These data may therefore underestimate the actual accumulation factor. Accumulation factors determined by kinetic methods do not suffer from this problem.

Many of the results have been obtained using <sup>14</sup>C-measurements and will include contributions from metabolites and so overestimate the accumulation of the LCCPs themselves.

In summary, the measurement of the bioaccumulation/biomagnification factor is very difficult for complex substances such as LCCPs and so there are some uncertainties associated with many of the experiments. Taking into account all of the factors described above, it is not possible to determine reliable BMF values suitable for use in the risk assessment, based on the current understanding of the methods used in the available studies. Indeed many of the points outlined above are not specific to LCCPs.

Rather, they relate to how such data should be generated and treated within the current framework for secondary poisoning outlined in the TGD – an issue that is probably best addressed outside of this specific assessment.

The available data for LCCPs do show that uptake into fish from food occurs in the laboratory, and that this uptake can be significant in some cases. The degree of uptake appears to be highest for the C<sub>18-20</sub> liquid chlorinated paraffins, but uptake of C<sub>>20</sub> liquid chlorinated paraffins has also been demonstrated. The uptake of the highly chlorinated C<sub>>20</sub> solid chlorinated paraffins from food appears to be minimal. Based on the available data, a fish accumulation factor from food of around 1 on a lipid basis (based on the available laboratory studies) will be considered as a worst case in this risk assessment for both the C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins. For the C<sub>>20</sub> solid chlorinated paraffins the fish accumulation factor from food will be assumed to be <<1.

For uptake and accumulation in earthworms, the following accumulation factors will be used in the PEC calculations. These are based on the TGD default methodology but take into account the results of recent validation exercises.

	BAF <sub>earthworm</sub> (related to bulk soil concentration)	K <sub>plant-water</sub> (related to porewater)
C <sub>18-20</sub> liquid	0.29 kg/kg	1.1×10 <sup>3</sup> m <sup>3</sup> /m <sup>3</sup>
C <sub>&gt;20</sub> liquid	0.22 kg/kg	2.0×10 <sup>3</sup> m <sup>3</sup> /m <sup>3</sup>
C <sub>&gt;20</sub> solid	0.010 kg/kg	200 m <sup>3</sup> /m <sup>3</sup>

### 3.3 Environmental concentrations

#### 3.3.1 Aquatic compartment (surface water, sediment and waste water treatment plant)

##### 3.3.1.1 Calculation of PEC<sub>local</sub>

Using the emission data given in Table 3.11 for the estimated amounts released at a site for production and the various uses of LCCPs, it is possible to estimate a PEC for surface water by assuming that the amount released per site enters into waste water and this enters into a waste water treatment plant. The TGD suggests that the size of the waste water treatment plant should be around 2,000 m<sup>3</sup>/day, and the effluent from the plant will be diluted by a factor of 10 in the receiving water. It is assumed that no biodegradation occurs during waste water treatment.

Based on the physico-chemical properties of LCCPs, the predicted behaviour of the substance during waste water treatment (as estimated in EUSES 2.0.3) is shown in Table 3.32. These results show that all types of LCCPs would be expected to behave similarly during waste water treatment.

**Table 3.32 Predicted behaviour during waste water treatment**

	<b>C<sub>18-20</sub> liquid</b>	<b>C<sub>&gt;20</sub> liquid</b>	<b>C<sub>&gt;20</sub> solid</b>
% to air	0%	0%	0%
% to sludge	92%	92%	92%
% degraded	0%	0%	0%
% to water	8%	8%	8%

Information on the short-chain chlorinated paraffins indicates that the removal by adsorption onto sludge may be higher than predicted by EUSES 2.0.3 – around 93 per cent, based on the results of a coupled unit test (ECB, 2000). Since LCCPs are likely, if anything, to adsorb more strongly onto sludge, then the results obtained for the short-chain chlorinated paraffins will be used in preference to the values obtained by EUSES, i.e. for the PEC calculations in the following sections, 93 per cent adsorption onto sludge and seven per cent release to surface water from the waste water treatment plant will be assumed.

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

$$C_{local\ water} = \frac{C_{local\ eff}}{(1 + K_{p\ susp} \times SUSP_{water} \times 10^{-6}) \times DILUTION}$$

where  $C_{local\ water}$  = local concentration in surface water during an emission episode  
 $C_{local\ eff}$  = concentration in effluent from waste water treatment plant  
 $SUSP_{water}$  = concentration of suspended matter in surface water = 15 mg/l  
 $DILUTION$  = dilution factor for effluent in receiving water = 10 for generic scenarios.  
 $K_{p\ susp}$  = solids-water partition coefficient for suspended matter  
=  $9.06 \times 10^6$  l/kg for  $C_{18-20}$  liquid chlorinated paraffins  
=  $2.77 \times 10^7$  l/kg for  $C_{>20}$  liquid chlorinated paraffins  
=  $>1 \times 10^9$  l/kg for  $C_{>20}$  solid chlorinated paraffins.

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

$$PEC_{local(water)} = C_{local\ water} + PEC_{regional(water)}$$

Where  $PEC_{regional(water)}$  =  $3.9 \times 10^{-4}$  µg/l for  $C_{18-20}$  liquid chlorinated paraffins  
=  $4.8 \times 10^{-4}$  µg/l for  $C_{>20}$  liquid chlorinated paraffins  
=  $8.5 \times 10^{-7}$  µg/l for  $C_{>20}$  solid chlorinated paraffins  
(based on the EUSES calculation: see later in this section)

Finally the PEC for sediment  $PEC_{local(sed)}$  is estimated from:

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

Where  $RHO_{susp}$  = bulk density of suspended matter = 1,150 kg/m<sup>3</sup>

- $K_{\text{susp-water}}$  = suspended matter-water partition coefficient  
 =  $2.27 \times 10^6 \text{ m}^3/\text{m}^3$  for  $C_{18-20}$  liquid chlorinated paraffin  
 =  $6.93 \times 10^6 \text{ m}^3/\text{m}^3$  for  $C_{>20}$  liquid chlorinated paraffin  
 =  $>2.5 \times 10^8 \text{ m}^3/\text{m}^3$  for  $C_{>20}$  solid chlorinated paraffin

### Production sites

Site specific information is currently available for several of the current production sites in the EU. This information is confidential, but has been used to derive emissions from a generic production site. The resulting PECs are shown in Table 3.33.

**Table 3.33 Summary of PECs estimated for a generic production site**

	$C_{18-20}$ liquid	$C_{>20}$ liquid	$C_{>20}$ solid
Local release to waste water (kg/day)	0.063	0.32	0.0063
No of days of release/year	300	300	300
Size of WWTP ( $\text{m}^3/\text{day}$ )	2,000	2,000	2,000
Influent concentration ( $\mu\text{g/l}$ )	32	160	3.2
% to water during WWTP	7	7	7
$C_{\text{local}}_{\text{eff}}$ ( $\mu\text{g/l}$ )	2.2	11	0.22
Dilution factor	10	10	10
$C_{\text{local}}_{\text{water}}$ ( $\mu\text{g/l}$ )	$1.6 \times 10^{-3}$	$2.7 \times 10^{-3}$	$1.5 \times 10^{-6}$
$\text{PEC}_{\text{local}(\text{water})}$ ( $\mu\text{g/l}$ )	$2.0 \times 10^{-3}$	$3.2 \times 10^{-3}$	$2.3 \times 10^{-6}$
$\text{PEC}_{\text{local}(\text{sediment})}$ (mg/kg wet wt.)	3.9	19	0.51

### Use in PVC

In Section 3.1.2, releases of LCCPs to water have been estimated from several stages of production of PVC. These release estimates have been used here, along with the behaviour in the generic waste water treatment plant to estimate the  $\text{PEC}_{\text{local}(\text{water})}$  and  $\text{PEC}_{\text{local}(\text{sediment})}$  for these stages. The calculations are summarised in Table 3.34 to Table 3.37.



**Table 3.34** PEC<sub>local</sub> for water and sediment for use in PVC (plastisol processes)

	Compounding site (formulation)	Conversion site (processing)	Combined compounding and conversion site
	C <sub>18-20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>18-20</sub> liquid
Local release to waste water (kg/day)	0.025	0.025	0.05
No of days of release/year	33	33	33
Size of WWTP (m <sup>3</sup> /day)	2,000	2,000	2,000
Influent concentration (µg/l)	13	13	25
% to water during WWTP	7	7	7
C <sub>local</sub> eff (µg/l)	0.88	0.88	1.8
Dilution factor	10	10	10
C <sub>local</sub> water (µg/l)	6.4×10 <sup>-4</sup>	6.4×10 <sup>-4</sup>	1.3×10 <sup>-3</sup>
PEC <sub>local</sub> (water) (µg/l)	1.0×10 <sup>-3</sup>	1.0×10 <sup>-3</sup>	1.7×10 <sup>-3</sup>
PEC <sub>local</sub> (sediment) (mg/kg wet wt.)	2.0	2.0	3.3

**Table 3.35** PEC<sub>local</sub> for water and sediment for use in PVC (extrusion/other – open systems)

	Compounding site (formulation)	Conversion site (processing)	Combined compounding and conversion site
	C <sub>18-20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>18-20</sub> liquid
Local release to waste water (kg/day)	0.0445	0.037	0.0815
No of days of release/year	33	33	33
Size of WWTP (m <sup>3</sup> /day)	2,000	2,000	2,000
Influent concentration (µg/l)	22	19	41
% to water during WWTP	7	7	7
C <sub>local</sub> eff (µg/l)	1.6	1.3	2.9
Dilution factor	10	10	10
C <sub>local</sub> water (µg/l)	1.1×10 <sup>-3</sup>	9.5×10 <sup>-4</sup>	2.1×10 <sup>-3</sup>
PEC <sub>local</sub> (water) (µg/l)	1.5×10 <sup>-3</sup>	1.3×10 <sup>-3</sup>	2.5×10 <sup>-3</sup>
PEC <sub>local</sub> (sediment) (mg/kg wet wt.)	3.0	2.6	4.9

**Table 3.36**  $PEC_{local}$  for water and sediment for use in PVC (extrusion/other – partially open systems)

	Compounding site (formulation)	Conversion site (processing)	Combined compounding and conversion site
	$C_{18-20}$ liquid	$C_{18-20}$ liquid	$C_{18-20}$ liquid
Local release to waste water (kg/day)	0.24	0.040	0.28
No of days of release/year	33	33	33
Size of WWTP ( $m^3/day$ )	2,000	2,000	2,000
Influent concentration ( $\mu g/l$ )	120	20	140
% to water during WWTP	7	7	7
$C_{local_{eff}}$ ( $\mu g/l$ )	8.4	1.4	9.8
Dilution factor	10	10	10
$C_{local_{water}}$ ( $\mu g/l$ )	$6.1 \times 10^{-3}$	$1.0 \times 10^{-3}$	$7.2 \times 10^{-3}$
$PEC_{local(water)}$ ( $\mu g/l$ )	$6.5 \times 10^{-3}$	$1.4 \times 10^{-3}$	$7.6 \times 10^{-3}$
$PEC_{local(sediment)}$ (mg/kg wet wt.)	13	2.8	15

**Table 3.37**  $PEC_{local}$  for water and sediment for use in PVC (extrusion/other – closed systems)

	Compounding site (formulation)	Conversion site (processing)	Combined compounding and conversion site
	$C_{18-20}$ liquid	$C_{18-20}$ liquid	$C_{18-20}$ liquid
Local release to waste water (kg/day)	0.0204	0.034	0.0544
No of days of release/year	33	33	33
Size of WWTP ( $m^3/day$ )	2,000	2,000	2,000
Influent concentration ( $\mu g/l$ )	10	17	27
% to water during WWTP	7	7	7
$C_{local_{eff}}$ ( $\mu g/l$ )	0.71	1.2	1.9
Dilution factor	10	10	10
$C_{local_{water}}$ ( $\mu g/l$ )	$5.2 \times 10^{-4}$	$8.7 \times 10^{-4}$	$1.4 \times 10^{-3}$
$PEC_{local(water)}$ ( $\mu g/l$ )	$9.1 \times 10^{-4}$	$1.3 \times 10^{-3}$	$1.8 \times 10^{-3}$
$PEC_{local(sediment)}$ (mg/kg wet wt.)	1.8	2.5	3.5

### ***Use in rubber***

In Section 3.1.3, releases of LCCPs to water have been estimated from the use in rubber. These release estimates have been used here, along with the behaviour in the generic waste water treatment plant to estimate the  $PEC_{local(water)}$  and  $PEC_{local(sediment)}$  for this use. The calculations are summarised in Table 3.38. The calculations are based on the releases expected from plastic processing. The releases, and hence PECs expected from the processing of rubber would be expected to be lower than these values due to the lower processing temperatures generally used.

**Table 3.38**  $PEC_{local}$  for water and sediment for use in rubber

	Combined conversion and processing site	
	$C_{>20}$ liquid	$C_{>20}$ solid
Local release to waste water (kg/day)	0.040	0.51
No of days of release/year	251	21
Size of WWTP (m <sup>3</sup> /day)	2,000	2,000
Influent concentration (µg/l)	20	255
% to water in WWTP	7	7
$C_{local,eff}$ (µg/l)	1.4	18
Dilution factor	10	10
$C_{local,water}$ (µg/l)	$3.4 \times 10^{-4}$	$1.2 \times 10^{-4}$
$PEC_{local(water)}$ (µg/l)	$8.2 \times 10^{-4}$	$1.2 \times 10^{-4}$
$PEC_{local(sediment)}$ (mg/kg wet wt.)	4.9	26

### ***Use in sealants/adhesives***

The releases of LCCPs to water from sites formulating or using sealants/adhesives are likely to be very low. No  $PEC_{local}$  is therefore calculated for this use.

### ***Use in paints and varnishes***

In Section 3.1.5, releases of LCCPs to water from the formulation and use of paints have been estimated using the default release estimates from the TGD, along with knowledge of the likely amounts of LCCPs formulated on a site. These default release estimates have been used here, along with the behaviour of LCCPs in the generic waste water treatment plant to estimate the  $PEC_{local(water)}$  and  $PEC_{local(sediment)}$  for these stages. The data available so far indicate that the releases of LCCPs to water from the formulation and use of paints should be very low. The default calculations are summarised in Table 3.39.

**Table 3.39**  $PEC_{local}$  for water and sediment for formulation and use in paints

	Paint formulation site (formulation)			Industrial application of paints (processing)		
	$C_{18-20}$ liquid	$C_{>20}$ liquid	$C_{>20}$ solid	$C_{18-20}$ liquid	$C_{>20}$ liquid	$C_{>20}$ solid
Local release to waste water (kg/day)	negligible	negligible	0.0023	0.06	0.06	0.11
No of days of release/year	300	300	300	300	300	300
Size of WWTP ( $m^3/day$ )	2,000	2,000	2,000	2,000	2,000	2,000
Influent concentration ( $\mu g/l$ )	-	-	1.2	30	30	55
% to water in WWTP	7	7	7	7	7	7
$C_{local,eff}$ ( $\mu g/l$ )	-	-	0.081	2.1	2.1	3.9
Dilution factor	10	10	10	10	10	10
$C_{local,water}$ ( $\mu g/l$ )	-	-	$5.4 \times 10^{-7}$	$1.5 \times 10^{-3}$	$5.0 \times 10^{-4}$	$2.6 \times 10^{-5}$
$PEC_{local(water)}$ ( $\mu g/l$ )	-	-	$1.4 \times 10^{-6}$	$1.9 \times 10^{-3}$	$9.8 \times 10^{-4}$	$2.7 \times 10^{-5}$
$PEC_{local(sediment)}$ (mg/kg wet wt.)	-	-	0.30	3.8	5.9	5.8

#### **Formulation and use in metal cutting/working fluids**

In Section 3.1.6, releases of LCCPs to water have been estimated from formulation and use in metal cutting/working fluids. These release estimates have been used here, along with the behaviour of LCCPs in the generic waste water treatment plant to estimate the  $PEC_{local}$  for water and sediment for these stages. The calculations are summarised in Table 3.40.

For the intermittent release scenario for metal cutting/working fluids, the Technical TGD does not provide any guidance on how this should be treated for sediment. The value reported in Table 3.40 assumes that the substance in water instantly equilibrates with the sediment. However, in reality, this is unlikely to occur as the release will be over a short period of time. An alternative approach would be to average the concentration over the year and add this to the concentration arising from the continuous use in the metalworking fluids (2.0 mg/kg wet weight for  $C_{18-20}$  liquid chlorinated paraffins and 4.2 mg/kg wet weight for  $C_{>20}$  liquid chlorinated paraffins). This method would give a  $PEC_{local(sediment)}$  of 8.9–23 mg/kg wet weight for  $C_{18-20}$  liquid chlorinated paraffins and 11–25 mg/kg wet weight for  $C_{>20}$  liquid chlorinated paraffins, assuming that the intermittent disposal occurs between two and six times per year.

#### **Formulation and use in leather fat liquors**

In Section 3.1.7, releases of LCCPs to water from the formulation and use of leather fat liquors have been estimated. These release estimates have been used here, along with the behaviour of LCCPs in the generic waste water treatment plant to estimate the  $PEC_{local}$  for water and sediment for these stages. The calculations are summarised in Table 3.41.

**Table 3.40 Type PEC<sub>local</sub> for water and sediment for use in metal cutting/working fluids**

	Formulation site		Use in oil-based fluids (processing)		Use in emulsifiable fluids (processing)				
	(formulation)		Large site	Small site	Continuous use		Intermittent discharge during solution renewal		
	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid
Local release to waste water (kg/day)	5×10 <sup>-4</sup>	3.4×10 <sup>-4</sup>	0.33 <sup>a</sup> –0.66 <sup>b</sup>	0.30 <sup>a</sup> –0.60 <sup>b</sup>	0.30 <sup>a</sup> –0.60 <sup>b</sup>	0.025	0.025	25	25
No of days of release/year	<10	25	300	300	300	300	300	2–6	2–6
Size of WWTP (m <sup>3</sup> /day)	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Influent concentration (µg/l)	0.25	0.17	165 <sup>a</sup> –330 <sup>b</sup>	150 <sup>a</sup> –300 <sup>b</sup>	150 <sup>a</sup> –300 <sup>b</sup>	13	13	12,500	12,500
% to water in WWTP	7	7	7	7	7	7	7	7	7
C <sub>local</sub> <sub>eff</sub> (µg/l)	0.018	0.012	12 <sup>a</sup> –23 <sup>b</sup>	11 <sup>a</sup> –21 <sup>b</sup>	11 <sup>a</sup> –21 <sup>b</sup>	0.88	0.88	875	875
Dilution factor	10	10	10	10	10	10	10	10	10
C <sub>local</sub> <sub>water</sub> (µg/l)	1.3×10 <sup>-5</sup>	2.9×10 <sup>-6</sup>	2.8×10 <sup>-3</sup> – 5.6×10 <sup>-3</sup>	7.7×10 <sup>-3</sup> – 0.015	2.5×10 <sup>-3</sup> – 5.0×10 <sup>-3</sup>	6.4×10 <sup>-4</sup>	2.10×10 <sup>-4</sup>	0.64	0.21
PEC <sub>local</sub> (water) (µg/l)	4.0×10 <sup>-4</sup>	4.8×10 <sup>-4</sup>	3.3×10 <sup>-3</sup> – 6.0×10 <sup>-3</sup>	8.1×10 <sup>-3</sup> – 0.016	3.0×10 <sup>-3</sup> – 5.5×10 <sup>-3</sup>	1.0×10 <sup>-3</sup>	6.9×10 <sup>-4</sup>	0.64	0.21
PEC <sub>local</sub> (sediment) (mg/kg wet wt.)	0.79	2.9	20–36	16–31	18–33	2.0	4.2	1,260	1,270

Notes: <sup>a</sup> Assumes five per cent chlorinated paraffin content in fluid.

<sup>b</sup> Assumes 10 per cent chlorinated paraffin in fluid.

**Table 3.41** PEC<sub>local</sub> for water and sediment for the formulation and use of leather fat liquors

	Formulation site (formulation)				Use site (processing)			
	Industry-specific information		Default generic calculation		Complete processing of raw hides (processing) <sup>b</sup>		Processing of “wet blue” (processing) <sup>b</sup>	
	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid
Local release to waste water (kg/day)	-	-	0.15	0.075	0.9	0.9	3.6	3.6
No of days of release/year	-	-	300	300	100	46	100	46
Size of WWTP (m <sup>3</sup> /day)	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Influent concentration (µg/l)	50 <sup>a</sup>	50 <sup>a</sup>	75	38	450	450	1,800	1,800
% to water in WWTP	7	7	7	7	7	7	7	7
C <sub>local</sub> <sub>eff</sub> (µg/l)	3.5	3.5	5.3	2.6	32	32	126	126
Dilution factor	10	10	10	10	10	10	10	10
C <sub>local</sub> <sub>water</sub> (µg/l)	2.6×10 <sup>-3</sup>	8.4×10 <sup>-4</sup>	3.8×10 <sup>-3</sup>	6.3×10 <sup>-4</sup>	0.023	7.6×10 <sup>-3</sup>	0.092	0.030
PEC <sub>local</sub> (water) (µg/l)	3.0×10 <sup>-3</sup>	1.3×10 <sup>-3</sup>	4.2×10 <sup>-3</sup>	1.1×10 <sup>-3</sup>	0.023	8.0×10 <sup>-3</sup>	0.092	0.031
PEC <sub>local</sub> (sediment) (mg/kg wet wt.)	5.8	8.0	8.3	6.7	46	48	182	185

Notes: <sup>a</sup> Industry-specific information indicates that the maximum total concentration of LCCPs in the waste water from a formulation site is likely to be <500 µg/l. In the absence of water flow rates from a typical site, it has been assumed that the waste water from a site is diluted by a factor of 10 in the influent to the waste water treatment plant. This value will be used in the risk assessment.

<sup>b</sup> The calculation for complete processing of raw hides is considered to be the most realistic and is taken forward to the risk characterisation.

### Formulation and use in textiles

In Section 3.1.8, releases of LCCPs to water have been estimated from use in textiles applications using default estimation methods. These release estimates have been used here, along with the behaviour of LCCPs in the generic waste water treatment plant to estimate the  $PEC_{local}$  for water and sediment for these stages. The calculations are summarised in Table 3.42.

**Table 3.42**  $PEC_{local}$  for water and sediment for use in textile applications

	Textile use
	$C_{18-20}$ liquid
Local release to waste water (kg/day)	4.3
No of days of release/year	300
Size of WWTP ( $m^3/day$ )	2,000
Influent concentration ( $\mu g/l$ )	1,800
% to water in WWTP	7
$C_{local,eff}$ ( $\mu g/l$ )	126
Dilution factor	10
$C_{local,water}$ ( $\mu g/l$ )	0.11
$PEC_{local(water)}$ ( $\mu g/l$ )	0.11
$PEC_{local(sediment)}$ (mg/kg wet wt.)	217

### 3.3.1.2 Calculation of $PEC_{regional}$ and $PEC_{continental}$

The predicted concentrations of LCCPs in the regional and continental scenarios have been estimated by EUSES 2.0.3, using the release data outlined in Table 3.11. The estimated  $PEC_{regional}$  and  $PEC_{continental}$  are shown in Table 3.43.

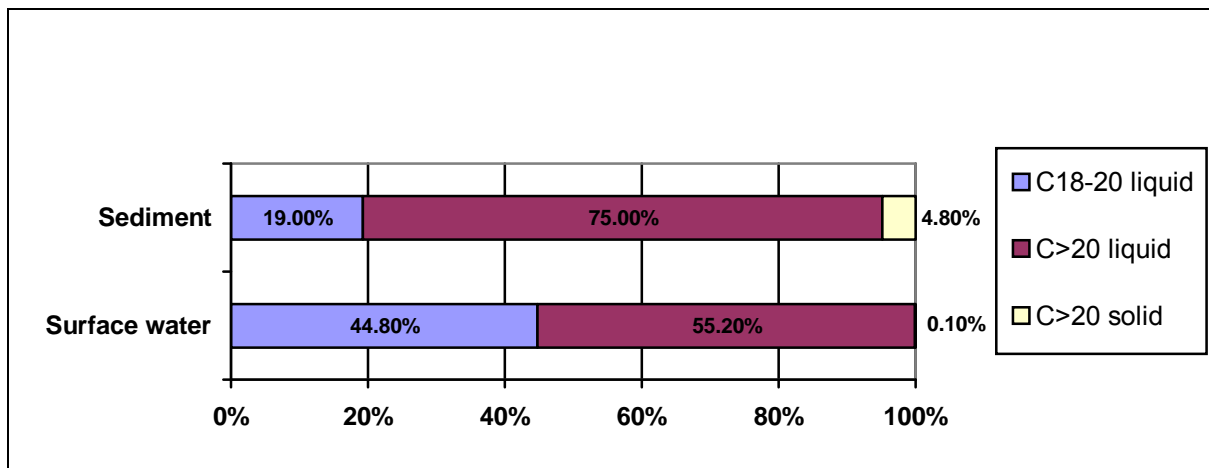
**Table 3.43** Estimated  $PEC_{regional}$  and  $PEC_{continental}$  for the aquatic compartment

Compartment	PEC	$C_{18-20}$ liquid	$C_{>20}$ liquid	$C_{>20}$ solid	Total LCCP <sup>a</sup>
Surface water	Regional	$3.2 \times 10^{-4}$ – $3.9 \times 10^{-4}$ $\mu g/l$	$4.5 \times 10^{-4}$ – $4.8 \times 10^{-4}$ $\mu g/l$	$8.2 \times 10^{-7}$ – $8.5 \times 10^{-7}$ $\mu g/l$	$7.7 \times 10^{-4}$ – $8.7 \times 10^{-4}$ $\mu g/l$
	Continental	$4.0 \times 10^{-5}$ – $5.0 \times 10^{-5}$ $\mu g/l$	$5.5 \times 10^{-5}$ – $5.9 \times 10^{-5}$ $\mu g/l$	$1.0 \times 10^{-7}$ $\mu g/l$	$9.5 \times 10^{-5}$ – $1.1 \times 10^{-4}$ $\mu g/l$
Sediment	Regional	1.3–1.5 mg/kg wet wt.	5.4–5.8 mg/kg wet wt.	0.36–0.37 mg/kg wet wt.	7.1–7.7 mg/kg wet wt.
	Continental	0.16–0.20 mg/kg wet wt.	0.66–0.71 mg/kg wet wt.	0.044–0.045 mg/kg wet wt.	0.86–0.96 mg/kg wet wt.

Note: <sup>a</sup> Total LCCPs is the sum of the three types of LCCPs.

The contribution of the various types of LCCPs to the total regional concentrations are shown in Figure 3.5

Appendix E considers the effects of the uncertainties and variability of some of the physico-chemical properties on the estimated concentrations.



**Figure 3.5** Relative contribution to the total regional concentration in surface water and sediment

### 3.3.1.3 Measured levels in water and sediment

The analysis of LCCPs in environmental media is complicated by the fact that there are a large number of possible chlorinated paraffins (of different carbon chain length, degrees of chlorination and position of chlorine atoms along the carbon chain) present in any given commercial product. Thus care has to be taken when comparing the results from one survey with another, since different reference compounds may have been used and hence different chemical species may have been measured. The main analytical methods used in the environmental analyses are discussed in Appendix D. Most of the reference compounds used in the analysis appear to have carbon chain lengths  $\geq C_{20}$ . Few studies appear to have been carried out using a  $C_{18-20}$  product as the reference substance.

#### **Water**

A study of the inputs of chlorinated paraffins to a sewage treatment plant in Germany has been published (Rieger and Ballschmiter, 1995). The sewage treatment plant processed 100,000 m<sup>3</sup>/day of municipal, industrial and mixed waste water. LCCPs ( $C_{18-20}$ ) were not detected (detection limit 0.1 mg/kg dry matter) in any of the sewage sludge samples taken at the plant (only short-chain chlorinated paraffins were found). Water samples taken from upstream and downstream of the plant also showed no detectable concentrations of LCCPs (detection limit 5 µg/l).

The levels of  $C_{10-20}$  and  $C_{20-30}$  chlorinated paraffins have been measured in marine and fresh waters remote from industry and in freshwaters from industrialised areas in the United Kingdom (Campbell and McConnell, 1980). These results are shown in Table 3.44 to Table 3.46. It should be noted that the  $C_{10-20}$  chlorinated paraffin levels are likely to be dominated by contributions from the short- and medium-chain chlorinated paraffins.



**Table 3.44 Concentration of chlorinated paraffins in marine waters in and around the UK (Campbell and McConnell, 1980)**

Location	Concentration of chlorinated paraffins (µg/l)	
	C <sub>10-20</sub>	C <sub>20-30</sub>
Irish Sea: Site a	1.0	ND
Irish Sea: Site b	0.5	ND
Irish Sea: Site c	0.5	ND
Irish Sea: Site d	0.5	ND
Irish Sea: Site e	ND	ND
Irish Sea: Site f	ND	ND
Barmouth Harbour	0.5	ND
Menai Straights, Caernarvon	0.5	0.5
Tremadoc Bay, Llandanwg	ND	ND
North Minch, Ardmair	0.5	1.0
North Minch, Port Bùn a' Ghlinne	ND	ND
North Minch, Port of Ness	0.5	ND
Goile Chròic, Lewis	0.5	0.5
Sound of Taransay, Harris	4.0	2.0
Sound of Arisaig	1.0	2.0
North Sea: N55° 5.7' W1° 9.3'	ND	ND
North Sea: N57° 26.2' W1° 17.0'	ND	ND
North Sea: N57° 56.5' W1° 22.0'	ND	ND

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

**Table 3.45 Concentration of chlorinated paraffins in fresh waters remote from industry in the UK (Campbell and McConnell, 1980)**

Location	Concentration of chlorinated paraffins ( $\mu\text{g/l}$ )	
	C <sub>10-20</sub>	C <sub>20-30</sub>
River Banwy, Llangadfan	0.5	ND
River Lea, Welwyn	ND*	NM
River Lea, Batford	ND*	NM
River Clwyd, Ruthin	ND	ND
Bala Lake	1.0	0.5
River Dee, Corwen	ND	ND
River Wnion, Merioneth	0.5	0.5
Firth of Lorne, Ganevan	0.5	ND
Loch Linnhe, Corran Narrows	ND	ND
Firth of Clyde, Ashcraig	ND	ND
Firth of Clyde, Girvan	0.5	2.0
An Garbh Allt	0.5	0.5
Five drinking water reservoirs, Manchester area	ND	ND

Notes: ND = not detected (detection limit = 0.5  $\mu\text{g/l}$ ).  
 ND\* = not detected (detection limit 1.0  $\mu\text{g/l}$ ).  
 NM = not measured.

**Table 3.46 Concentration of chlorinated paraffins in waters in industrialised areas in the UK (Campbell and McConnell, 1980)**

Location	Concentration of chlorinated paraffin ( $\mu\text{g/l}$ )	
	C <sub>10-20</sub>	C <sub>20-30</sub>
River Aire, Leeds	2.0	NM
River Aire, Woodlesford	2.0	NM
River Ouse, Boothberry edge	1-2	NM
River Trent, West Bromwich	1-2	NM
River Trent, Walton-upon-Trent	2-3	NM
River Trent, Swarkestone	1-2	NM
River Trent, Newark	4.0	NM
River Trent, Gainsborough	2.0	NM
River Trent, confluence with Humber	6.0	NM
Humber Estuary, Hull	1-2	NM
Humber Estuary, Grimsby	3.0	NM
Mersey Estuary, New Brighton	3.0	NM
Mersey Estuary, Liverpool Pier Head	4.0	NM
River Thames, Oxford	2.0	NM
River Thames, Sanford	1-2	NM
Wyre Estuary	ND-1.5	ND-0.5
River Tees, Low Dinsdale	ND	ND
River Tees, North Gare breakwater	0.5	ND
River Tees, Middlesbrough	ND	ND

Notes: ND = not detected (detection limit = 0.5  $\mu\text{g/l}$ ).

NM = not measured.

The levels of LCCPs in surface water have been measured near to a chlorinated paraffin manufacturing site in the United States (Murray *et al.*, 1988a and 1988b). The reference compound used in the study was a C<sub>20-30</sub>, 40-50% wt. Cl product. The effluent from the plant, after undergoing physical treatment, was discharged into Sugar Creek, via a surface impoundment lagoon and small ditch. The results of the analyses are shown in Table 3.47. Based on these measurements, Murray *et al.* (1988a) estimated a daily discharge to water of 1.46 g/day for LCCPs from the plant.

A similar study was also undertaken by Murray *et al.* (1988a and 1988b) near to a metalworking facility that was thought to be using lubricating oils containing chlorinated paraffins. Due to analytical interferences, it was not possible to detect chlorinated paraffins in surface water at the site, however, LCCPs were detected at 2.2  $\mu\text{g/l}$  in the process waste stream inside the plant that was collected near the end of the assembly process prior to discharge from the plant.

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

**Table 3.47 Measured levels of LCCPs near a production site in the United States (Murray et al., 1988a and 1988b)**

Location	Concentration ( $\mu\text{g/l}$ )	
	Particulates	Dissolved
Surface lagoon near to its effluent to drainage ditch	11	not detected (<0.15)
Surface lagoon near to influent from plant	3.6	not detected (<0.15)
Middle of surface lagoon	7.7	0.61
Drainage ditch, immediately above point of discharge into Sugar Creek	3.7	trace (0.15–0.5)
Sugar Creek, upstream of discharge	nd (<0.05)	nd (<0.05)
Sugar Creek, just upstream of discharge	trace (0.05–0.17)	nd (<0.05)
Sugar Creek, just downstream of discharge	0.62	nd (<0.05)
Sugar Creek, downstream of discharge	0.35	nd (<0.05)

Notes: Dissolved = concentration in dissolved phase.  
 Particulate = concentration in particulate phase (>0.45  $\mu\text{m}$ ).

### **Sediment**

The levels of total chlorinated paraffin (short-, medium- and long-chain) have been determined in estuarine sediments from Western Europe. In all, samples from 22 locations were analysed and the mean total level found in the <63  $\mu\text{m}$  sediment fraction was 10.5  $\mu\text{g/kg}$  dry weight in the Mersey and Seine estuaries, 5.5  $\mu\text{g/kg}$  dry weight in the Schelde estuary, 4.8  $\mu\text{g/kg}$  dry weight in the Liffey river estuary, 3.3  $\mu\text{g/kg}$  dry weight in the Forth estuary and 1.2  $\mu\text{g/kg}$  dry weight in the Humber estuary. Chlorinated paraffins were not detected (detection limit 0.5  $\mu\text{g/kg}$  dry weight) at the remaining 16 sites. LCCPs, with chlorine contents of around 42% wt., were thought to be the predominant type of chlorinated paraffin found in the samples, with only traces of medium-chain and short-chain chlorinated paraffins being seen in the samples (van Zeijl, 1997).

Greenpeace (1995) published the results of a survey of total chlorinated paraffin ( $\text{C}_{10-24}$ ) levels in mud samples from Rotterdam Harbour, Hamburg Harbour and from off-shore mud flats at Kaiser Wilhelm Koog and Den Helder. The total levels measured ranged between 25 and 125  $\mu\text{g/kg}$ . Long-chain (i.e.  $\text{C}_{18-24}$ ) chlorinated paraffins were thought to account for 10–60 per cent of the total chlorinated paraffins present. Using these percentages, the concentrations of medium-chain chlorinated paraffin can be estimated as 22–29.4  $\mu\text{g/kg}$  in Rotterdam Harbour samples, 25.2  $\mu\text{g/kg}$  in the Hamburg Harbour sample, 12.3  $\mu\text{g/kg}$  in the sample from Den Helder and 12.5  $\mu\text{g/kg}$  in the sample from Kaiser Wilhelm Koog. It is not clear from the paper if the levels are reported on a wet or dry weight basis.

The levels of  $\text{C}_{10-20}$  and  $\text{C}_{20-30}$  chlorinated paraffins have been measured in several types of sediment in the United Kingdom, often from the same areas where water concentrations were also measured (Campbell and McConnell, 1980; see above). The results of the analyses are shown in Table 3.48 to Table 3.50. It is not clear from the

paper if the levels found are expressed on a wet weight or dry weight sediment basis. Similar to the case with the water levels, the reported C<sub>10-20</sub> chlorinated paraffin concentrations are likely to be dominated by contributions from short- and medium-chain chlorinated paraffins.

**Table 3.48 Concentration of chlorinated paraffins in marine sediments around the UK (Campbell and McConnell, 1980)**

Location	Concentration of chlorinated paraffins (µg/kg)	
	C <sub>10-20</sub>	C <sub>20-30</sub>
Irish Sea: Site a	100	ND
Irish Sea: Site b	ND	ND
Irish Sea: Site c	NM	NM
Irish Sea: Site d	100	ND
Irish Sea: Site e	ND	ND
Irish Sea: Site f	ND	600
Irish Sea: Site g	NM	ND
Barmouth Harbour	500	ND
Menai Straights, Caernarvon	ND	ND
Tremadoc Bay, Llandanwg	ND	ND
North Minch, Ardmair	ND	ND
North Minch, Port Bùn á Ghlinne	ND	ND
North Minch, Port of Ness	ND	ND
Goile Chròic, Lewis	ND	ND
Sound of Taransay, Harris	ND	ND
Sound of Arisaig	ND	ND
North Sea: N55° 5.7' W1° 9.3'	ND	ND
North Sea: N57° 26.2' W1° 17.0'	ND	100
North Sea: N57° 56.5' W1° 22.0'	50	300

Notes: ND = not detected (detection limit = 50 µg/kg).  
 NM = not measured.

**Table 3.49 Concentration of chlorinated paraffins in fresh and other non-marine sediments remote from industry in the UK (Campbell and McConnell, 1980)**

Location	Concentration of chlorinated paraffins (µg/kg)	
	C <sub>10-20</sub>	C <sub>20-30</sub>
River Banwy, Llangadfan	ND	ND
River Lea, Batford	1,000	NM
River Clwyd, Ruthin	ND	ND
River Dee, Corwen	300	50
River Wnion, Merioneth	ND	ND
Five drinking water reservoirs, Manchester area	ND*	ND*

Notes: ND = not detected (detection limit = 50 µg/kg).  
 ND\* = not detected (detection limit 250 µg/kg).

**Table 3.50 Concentration of chlorinated paraffins in sediments in industrialised areas in the UK (Campbell and McConnell, 1980)**

Location	Concentration of chlorinated paraffin (µg/kg)	
	C <sub>10-20</sub>	C <sub>20-30</sub>
River Aire, Leeds	10,000	NM
River Ouse, Goole	2,000	NM
River Trent, West Bromwich	6,000	NM
River Trent, Walton-upon-Trent	1,000	NM
River Trent, Swarkestone	14,000	NM
River Trent, Newark	8,000	NM
River Trent, Gainsborough	3,000	NM
Humber Estuary, Hull	2,000	NM
Humber Estuary, Stone Creek	2,000	NM
Mersey Estuary, New Brighton	3,000	NM
Mersey Estuary, Liverpool Pier Head	8,000	NM
River Thames, Sanford	1,000	NM
Wyre Estuary	ND-1,600	ND-3,200
Mersey Estuary, 14 sediment samples	ND	ND
River Tees, Low Dinsdale	300	100
River Tees, North Gare breakwater	50	50
River Tees, Middlesbrough	15,000	3,000

Notes: ND = not detected (detection limit = 50 µg/kg).  
 NM = not measured.

Campbell and McConnell (1980) also reported levels of chlorinated paraffins in sewage sludge from the Liverpool area and the Manchester area. In sewage sludge from the Liverpool area, C<sub>10-20</sub> chlorinated paraffins were found to be present at concentrations

of 4–10 mg/kg but C<sub>20–30</sub> chlorinated paraffins were not detected (limit of detection was 0.05 mg/kg). No chlorinated paraffins were detected in the sewage sludge from the Manchester area (limit of detection was 0.05 mg/kg for both the C<sub>10–20</sub> and C<sub>20–30</sub> chlorinated paraffins).

Murray *et al.* (1988a and 1988b) reported the results of monitoring studies carried out near to a chlorinated paraffin manufacturing site and an industry using metalworking fluids in the United States. LCCPs (quantified using a C<sub>20–30</sub>, 40–50% wt. Cl product) were detected at 21, 84 and 170 mg/kg dry weight in sediment from an impoundment lagoon and 3.6 mg/kg dry weight in sediment from a drainage ditch at the production site. The levels in the stream sediments that received effluent from the lagoon via the drainage ditch were 8.1–11 µg/kg dry weight in sediments upstream of the discharge point and 9.8–21 µg/kg dry weight in sediments downstream of the discharge point. Due to analytical interferences, it was not possible to detect chlorinated paraffins at the site using metalworking fluids.

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

Kemmlin *et al.* (2002) reported the results of a study looking at the levels of chlorinated paraffins in marine sediments from an area close to a chlorinated paraffin manufacturer in Australia. The levels of total chlorinated paraffins found in four sediment samples were in the range 2,139–18,872 µg/kg dry weight. LCCPs were found to make up around 11–52 per cent of the total. The results for LCCPs are summarised in Table 3.51. The analysis was carried out by dechlorination of the chlorinated paraffins found, followed by analysis of the n-paraffins formed. The same results appear to be given in OSPAR (2000) referenced to an unpublished study by Rotard *et al.* (1998).

**Table 3.51 Concentration of chlorinated paraffins in marine sediment close to a chlorinated paraffin production site in Australia**

Chain length	Concentration of chlorinated paraffins (µg/kg dry weight) <sup>a</sup>			
	Sample I	Sample II	Sample III	Sample IV
C <sub>18</sub>	51	48	169	268
C <sub>19</sub>	21	47	69	82
C <sub>20</sub>	30	33	66	81
C <sub>21</sub>	24	20	102	48
C <sub>22</sub>	55	42	230	84
C <sub>23</sub>	74	43	342	124
C <sub>24</sub>	91	43	393	136
C <sub>25</sub>	111	59	417	154
C <sub>26</sub>	128	80	377	206
C <sub>27</sub>	159	89	348	222
C <sub>28</sub>	199	138	350	279
C <sub>29</sub>	308	254	329	337
Total LCCP	1,251	896	3,192	2,021

Note: <sup>a</sup> It is not clear from the paper if these are four independent samples or two samples that have been analysed in duplicate.

#### 3.3.1.4 Comparison of predicted and measured levels

The available monitoring data for LCCPs in surface water are limited. The most extensive dataset available is that of Campbell and McConnell (1980), which used a relatively crude thin layer chromatography analytical procedure. Here, levels up to around 1–2 µg/l of C<sub>>20</sub> chlorinated paraffins were measured at some sites in the United Kingdom. These levels are higher than those predicted in the assessment, and may reflect the fact that the available measured data probably refer to total water concentrations (i.e. dissolved and particulate phase), whereas the PECs are calculated for the dissolved phase only. In this respect, the results of Murray *et al.* (1988a and 1988b) are informative as they found the majority of the chlorinated paraffin was associated with the water-borne particulates, with only traces being generally found in the dissolved phase.

Therefore, in order to carry out a comparison of the predicted and measured concentrations, it may be more informative to consider the predicted concentrations before the adsorption onto suspended solids is taken into account. When this is done, the predicted local concentrations generally fall into the range of around 0.002–2 µg/l for the C<sub>18–20</sub> liquid chlorinated paraffins, 0.001–3 µg/l for the C<sub>>20</sub> liquid chlorinated paraffins and 0.01–2 µg/l for the C<sub>>20</sub> solid chlorinated paraffins. Given the limited scope of the available monitoring data, particularly for areas close to industry, these calculated values appear to be of the same order of magnitude as the measurements obtained.

The monitoring data available for sediment indicate that LCCPs are generally found at concentrations <100 µg/kg dry weight, with higher levels of up to around 10 mg/kg dry weight being found near to sources of release. On a wet weight basis, these concentrations are approximately <22 µg/kg wet weight and 2.2 mg/kg wet weight, using the default sediment water contents from the TGD. The higher measured levels are of a similar order of magnitude as the predicted local and regional concentrations.

As the coverage of the available monitoring data is fairly limited (in terms of areas close to sources of release), the predicted concentrations will be used in the risk characterisation.

The monitoring data also indicate that LCCPs are present at low levels in some estuaries and marine waters from around the United Kingdom and the rest of Europe.

### 3.3.2 Terrestrial compartment

#### 3.3.2.1 Predicted levels

The estimated concentrations of LCCPs in soil are shown in Table 3.52. These have been estimated using the EUSES 2.0.3 program (see Appendix A). The vast majority of the LCCP is likely to enter soil via adsorption onto and subsequent spreading of sewage sludge, but for uses where atmospheric emissions occur (e.g. PVC), then these releases can also contribute to the concentrations found in soil over time.

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



chlorinated paraffin. After this time period the fraction of the steady state concentration reached is estimated as  $2.5\text{--}2.6 \times 10^{-3}$  (0.3 per cent) for agricultural soil and grassland. This indicates that over prolonged periods of exposure (either through atmospheric deposition and/or sewage sludge application) higher concentrations than predicted here could theoretically build up in the soil compartment if there is no removal mechanism for LCCPs from soil.

**Table 3.52 Estimated concentrations in soil**

Scenario	Step	Predicted soil concentration (mg/kg wet wt.)							
		Agric. soil (30 days and 180 days average)				Grassland (180 days average)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>
Production		negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>
Use in PVC – plastisol applications	Compounding (O)	1.1	NA <sup>c</sup>	NA <sup>c</sup>	1.1	0.80	NA <sup>c</sup>	NA <sup>c</sup>	0.80
	Conversion (O)	1.1	NA <sup>c</sup>	NA <sup>c</sup>	1.1	0.80	NA <sup>c</sup>	NA <sup>c</sup>	0.80
	Compounding/conversion (O)	1.5	NA <sup>c</sup>	NA <sup>c</sup>	1.5	0.97	NA <sup>c</sup>	NA <sup>c</sup>	0.97
Use in PVC – extrusion/ other	Compounding (O)	1.4	NA <sup>c</sup>	NA <sup>c</sup>	1.4	0.93	NA <sup>c</sup>	NA <sup>c</sup>	0.93
	Compounding (PO)	4.8	NA <sup>c</sup>	NA <sup>c</sup>	4.8	2.3	NA <sup>c</sup>	NA <sup>c</sup>	2.3
	Compounding (C)	0.98	NA <sup>c</sup>	NA <sup>c</sup>	0.98	0.77	NA <sup>c</sup>	NA <sup>c</sup>	0.77
	Conversion (O)	1.3	NA <sup>c</sup>	NA <sup>c</sup>	1.3	0.88	NA <sup>c</sup>	NA <sup>c</sup>	0.88
	Conversion (PO)	1.3	NA <sup>c</sup>	NA <sup>c</sup>	1.3	0.90	NA <sup>c</sup>	NA <sup>c</sup>	0.90
	Conversion (C)	1.2	NA <sup>c</sup>	NA <sup>c</sup>	1.2	0.86	NA <sup>c</sup>	NA <sup>c</sup>	0.86
	Compounding/conversion (O)	2.0	NA <sup>c</sup>	NA <sup>c</sup>	2.0	1.2	NA <sup>c</sup>	NA <sup>c</sup>	1.2
	Compounding/conversion (PO)	5.5	NA <sup>c</sup>	NA <sup>c</sup>	5.5	2.6	NA <sup>c</sup>	NA <sup>c</sup>	2.6
	Compounding/conversion (C)	1.6	NA <sup>c</sup>	NA <sup>c</sup>	1.6	1.0	NA <sup>c</sup>	NA <sup>c</sup>	1.0
Use in rubber	Compounding/conversion	NA <sup>c</sup>	0.91	8.8	9.7	NA <sup>c</sup>	0.49	3.5	4.0
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>c</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>c</sup>	negligible
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	0.041	0.041	negligible <sup>b</sup>	negligible <sup>b</sup>	0.017	0.017
	Industrial application	1.7	1.3	1.9	4.9	1.0	0.63	0.76	2.4
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 3.52 continued overleaf

**Table 3.52 continued**

Scenario	Step	Predicted soil concentration (mg/kg wet wt.)							
		Agric. soil (30 days and 180 days average)				Grassland (180 days average)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>
Use in metal cutting/working fluids	Formulation	0.63	0.21	NA <sup>c</sup>	0.84	0.63	0.21	NA <sup>c</sup>	0.84
	Use in oil-based fluids (large)	NA <sup>c</sup>	5.9–12	NA <sup>c</sup>	5.9–12	NA <sup>c</sup>	2.5–4.8	NA <sup>c</sup>	2.5–4.8
	Use in oil-based fluids (small)	5.8–11	5.4–11	NA <sup>c</sup>	11–22	2.7–4.8	2.3–4.4	NA <sup>c</sup>	5.0–9.2
	Use in emulsifiable fluids	1.1	0.64	NA <sup>c</sup>	1.7	0.80	0.39	NA <sup>c</sup>	1.2
	Use in emulsifiable fluids – intermittent release	48	47	NA <sup>c</sup>	95	19	19	NA <sup>c</sup>	38
Use in leather fat liquors	Formulation	3.2	1.5	NA <sup>c</sup>	4.7	1.7	0.73	NA <sup>c</sup>	2.4
	Use – complete processing of raw hides <sup>e</sup>	16	16	NA <sup>c</sup>	32	6.9	6.4	NA <sup>c</sup>	13
	Use – processing of wet blue <sup>e</sup>	63	63	NA <sup>c</sup>	126	26	25	NA <sup>c</sup>	51
Use in textile applications	75	NA <sup>c</sup>	NA <sup>c</sup>	75	31	NA <sup>c</sup>	NA <sup>c</sup>	31	

Notes: <sup>a</sup> Sewage sludge from production sites is not thought to be applied to agricultural land.

<sup>b</sup> The process makes no significant contribution to the levels in soil.

<sup>c</sup> NA = not applicable; no significant use of the substance in this application.

<sup>d</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>e</sup> The calculation for complete processing of raw hides is considered to be the more realistic scenario, and is taken forward to the risk characterisation.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

For the intermittent release scenario in Table 3.52 the calculation of the concentration on sludge assumes that 93 per cent of the chemical released on that day is adsorbed onto the amount of sludge produced in the waste water treatment plant on that day. However, the retention time of sludge in the default waste water treatment plant is 9.2 days and so the calculation has assumed that this sludge is diluted by a factor of around 9.2 prior to being spread onto the land (the instantaneous estimated concentration on sludge is 29,400 mg/kg dry weight for both the C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins respectively, and so a value of 3,196 mg/kg dry weight is used in the subsequent calculations for both substances).

The regional and continental soil concentrations are shown in Table 3.53. In the regional model, agricultural soil received input from both sewage sludge and aerial deposition, whereas the natural soil received input from aerial deposition only. Higher concentrations have been estimated in the regional model than in some of the local scenarios given in Table 3.52. This occurs because the concentrations calculated in the regional model are "steady-state" concentrations, and reflect the possible build up in soil due to continuous application over many years (rather than 10 years as assumed in the local calculations). The model does not give any indication as to the time period that may be necessary for these concentrations to be reached.

A rough estimation of the time to steady state can be obtained from emission rate of the substance to the regional soil compartment and the volume of the regional soil compartment. For example the regional industrial/urban soil compartment covers an area of  $4 \times 10^3 \text{ km}^2$  ( $4 \times 10^9 \text{ m}^2$ ) and has a mixing depth of 0.05 m. Thus the volume of the regional industrial/urban soil compartment is  $2 \times 10^8 \text{ m}^3$ . The bulk density of soil in the regional model is  $1,700 \text{ kg/m}^3$ , thus the regional mass of soil is  $3.4 \times 10^{11} \text{ kg}$  wet weight. The estimated emission rates to industrial/urban soil are 7,791 kg/year for C<sub>18-20</sub> liquid chlorinated paraffins, 20,077 kg/year for C<sub>>20</sub> liquid chlorinated paraffins and 1,591 kg/year for C<sub>>20</sub> solid chlorinated paraffins. Considering that chlorinated paraffins have been in production for around 50 years, and taking a future look for the concentration in 100 years from now, the total amount of chlorinated paraffins released to industrial/urban soil over this 150 year time period would be around 1,170 tonnes of C<sub>18-20</sub> liquid chlorinated paraffins, 3,010 tonnes of C<sub>>20</sub> liquid chlorinated paraffins and 175 tonnes of C<sub>>20</sub> solid chlorinated paraffins.

Thus the resulting regional concentration in urban/industrial soil 100 years from now would be approximately 3 mg/kg wet weight for C<sub>18-20</sub> liquid chlorinated paraffins, 9 mg/kg wet weight for C<sub>>20</sub> liquid chlorinated paraffins and 0.5 mg/kg wet weight for C<sub>>20</sub> solid chlorinated paraffins. These are approximately 9–25 per cent of the predicted regional steady state concentrations, and would imply a time to steady state of >400 to >1,000 years.

The calculations in the model, particularly at the regional level, are very sensitive to the degradation rate (the default degradation rate constant is  $6.93 \times 10^{-7} \text{ days}^{-1}$  for an LCCP, corresponding to a half-life of 2,740 years). The effects of varying the degradation rate in the regional model are shown in Appendix E. Information on the actual degradation rates of LCCPs in soil would be useful to indicate whether or not the substance is likely to build up in the soil as indicated by the current model.

The concentrations predicted in urban/industrial soil result mainly from the contribution from particulate waste ("waste remaining in the environment") containing the chlorinated paraffins. The actual availability of the chlorinated paraffin in this form is unknown.

**Table 3.53 Predicted regional and continental soil concentrations**

Scale	Soil type	PEC (mg/kg wet wt.)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total LCCPs
Regional	Agricultural	0.42–0.55	2.8	0.016–0.017	3.2–3.4
	Natural	0.46–0.63	0.17–0.21	4.0×10 <sup>-4</sup>	0.63–0.84
	Urban/industrial	11–12	62–65	5.3–5.5	78–83
Continental	Agricultural	0.052–0.068	0.28–0.29	1.7×10 <sup>-3</sup>	0.33–0.36
	Natural	0.059–0.080	0.019–0.023	5.6×10 <sup>-5</sup>	0.078–0.11
	Urban/industrial	1.1–1.3	6.3–6.7	0.55–0.56	8.0–8.6

Note: Measured levels

No measured levels of LCCPs in soil were located in the literature.

### 3.3.2.2 Comparison of predicted and measured levels

No comparison of predicted and measured levels can be made at present. The predicted concentrations will therefore be considered in the risk characterisation.

## 3.3.3 Atmospheric compartment

### 3.3.3.1 Predicted levels

The concentrations of LCCPs in the atmosphere have been predicted using EUSES 2.0.3 (see Appendix A). The local concentrations arise from direct emissions of LCCPs from the various industrial processes involved (emissions to air from waste water treatment plants are considered to be negligible due to the physico-chemical properties of the substance). At the regional and continental level, diffuse source releases have also been considered in the model. The predicted atmospheric concentrations are shown in Table 3.54.

**Table 3.54 Estimated air concentrations of LCCPs**

Scenario	Step	Air concentrations (C <sub>local</sub> – Emission episode) (mg/m <sup>3</sup> )				Air concentrations (C <sub>local</sub> – annual average) (mg/m <sup>3</sup> )			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
		Production		negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>
Use in PVC – plastisol coating	Compounding (O)	negligible <sup>a</sup>	NA <sup>b</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
	Conversion (O)	7.0×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	7.0×10 <sup>-6</sup>	6.3×10 <sup>-7</sup>	NA <sup>b</sup>	NA <sup>b</sup>	6.3×10 <sup>-7</sup>
Use in PVC – extrusion/ other	Compounding/conversion (O)	7.0×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	7.0×10 <sup>-6</sup>	6.3×10 <sup>-7</sup>	NA <sup>b</sup>	NA <sup>b</sup>	6.3×10 <sup>-7</sup>
	Compounding (O)	2.1×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	2.1×10 <sup>-6</sup>	1.9×10 <sup>-7</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.9×10 <sup>-7</sup>
	Compounding (PO)	1.1×10 <sup>-5</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.1×10 <sup>-5</sup>	1.1×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.1×10 <sup>-6</sup>
	Compounding (C)	9.5×10 <sup>-7</sup>	NA <sup>b</sup>	NA <sup>b</sup>	9.5×10 <sup>-7</sup>	8.6×10 <sup>-8</sup>	NA <sup>b</sup>	NA <sup>b</sup>	8.6×10 <sup>-8</sup>
	Conversion (O)	1.0×10 <sup>-5</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.0×10 <sup>-5</sup>	9.3×10 <sup>-7</sup>	NA <sup>b</sup>	NA <sup>b</sup>	9.3×10 <sup>-7</sup>
	Conversion (PO)	1.1×10 <sup>-5</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.1×10 <sup>-5</sup>	1.1×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.1×10 <sup>-6</sup>
	Conversion (C)	9.5×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	9.5×10 <sup>-6</sup>	8.6×10 <sup>-7</sup>	NA <sup>b</sup>	NA <sup>b</sup>	8.6×10 <sup>-7</sup>
	Compounding/conversion (O)	1.2×10 <sup>-5</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.2×10 <sup>-5</sup>	1.1×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.1×10 <sup>-6</sup>
Use in rubber	Compounding/conversion (PO)	2.2×10 <sup>-5</sup>	NA <sup>b</sup>	NA <sup>b</sup>	2.2×10 <sup>-5</sup>	2.0×10 <sup>-6</sup>	NA <sup>b</sup>	NA <sup>b</sup>	2.0×10 <sup>-6</sup>
	Compounding/conversion (C)	1.0×10 <sup>-5</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.0×10 <sup>-5</sup>	9.4×10 <sup>-7</sup>	NA <sup>b</sup>	NA <sup>b</sup>	9.4×10 <sup>-7</sup>
Use in sealants	Compounding/conversion	NA <sup>b</sup>	4.2×10 <sup>-6</sup>	4.2×10 <sup>-6</sup>	8.4×10 <sup>-6</sup>	NA <sup>b</sup>	2.9×10 <sup>-6</sup>	2.4×10 <sup>-7</sup>	3.1×10 <sup>-6</sup>
Use in paints	Formulation and use	negligible <sup>b</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	negligible <sup>b</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
Use in paints	Formulation	negligible <sup>a</sup>	negligible <sup>a</sup>	1.1×10 <sup>-6</sup>	1.1×10 <sup>-6</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	8.9×10 <sup>-7</sup>	8.9×10 <sup>-7</sup>
	Industrial application	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>
	Domestic application	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>

Table 3.54 continued overleaf.

**Table 3.54 continued**

Scenario	Step	Air concentrations (C <sub>local</sub> – Emission episode) (mg/m <sup>3</sup> )				Air concentrations (C <sub>local</sub> – annual average) (mg/m <sup>3</sup> )			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
		Use in metal cutting/working fluids	Formulation	1.1×10 <sup>-7</sup>	1.1×10 <sup>-8</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	6.1×10 <sup>-10</sup>	7.6×10 <sup>-10</sup>
	Use in oil-based fluids (large)	NA <sup>b</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
	Use in oil-based fluids (small)	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
	Use in emulsifiable fluids	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
	Use in emulsifiable fluids – intermittent release	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
Use in leather fat liquors	Formulation	1.5×10 <sup>-5</sup>	7.0×10 <sup>-6</sup>	NA <sup>b</sup>	2.2×10 <sup>-5</sup>	1.3×10 <sup>-5</sup>	5.7×10 <sup>-6</sup>	NA <sup>b</sup>	1.9×10 <sup>-5</sup>
	Use – complete processing of raw hides	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
	Use – processing of wet blue	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	negligible <sup>a</sup>	NA <sup>b</sup>	negligible <sup>a</sup>
Use in textile applications		2.3×10 <sup>-3</sup>	NA <sup>b</sup>	NA <sup>b</sup>	2.3×10 <sup>-3</sup>	1.9×10 <sup>-3</sup>	NA <sup>b</sup>	NA <sup>b</sup>	1.9×10 <sup>-3</sup>
Regional sources						7.6×10 <sup>-7</sup> – 1.0×10 <sup>-6</sup>	8.5×10 <sup>-8</sup> – 1.0×10 <sup>-7</sup>	1.7×10 <sup>-10</sup>	8.5×10 <sup>-7</sup> – 1.1×10 <sup>-6</sup>

Notes: <sup>a</sup> The process makes no significant contribution to the local levels in air.

<sup>b</sup> NA = not applicable; no significant use of the substance in this application.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

### 3.3.3.2 Measured levels

No measured levels for LCCPs in air have been found in the literature.

### 3.3.3.3 Comparison of predicted and measured levels

No comparison of predicted and measured levels can be made at present. The predicted concentrations will therefore be considered in the risk characterisation.

## 3.3.4 Food chain exposure

### 3.3.4.1 Predicted levels

The levels of LCCPs in fish and earthworms for the secondary poisoning assessment have been calculated by EUSES 2.0.3 using the methods given in the TGD. For fish, no reliable measured BCF value is available for LCCPs and so estimated values have to be used. The values used are 1,096 l/kg for C<sub>18-20</sub> liquid chlorinated paraffins, 192 l/kg for C<sub>>20</sub> liquid chlorinated paraffins and <1 for C<sub>>20</sub> solid chlorinated paraffins (see Section 3.2.9).

The TGD indicates that as well as the bioconcentration factor, the biomagnification factor (BMF) for fish should also be considered in determination of the PEC for secondary poisoning i.e.:

$$PEC_{\text{oral}} = PEC_{\text{water}} \times BCF \times BMF$$

A default BMF of 1 was used in the calculations for all LCCPs (see Section 3.2.9.4). This was supported by experimentally determined BMFs of the same order for C<sub>18-20</sub> liquid chlorinated paraffins in laboratory feeding studies. The predicted concentrations are shown in Table 3.55.

It should be noted, however, that the above equation given in the TGD may not be appropriate when considering actual BMF data from laboratory feeding studies. The intention in the TGD is to model the concentration in fish resulting from simultaneous exposure via both water and food, and this is represented by the scheme below (Figure 3.6). The term food accumulation factor (FAF) is used in this scheme to distinguish it from the BMF given in the equation from the TGD.

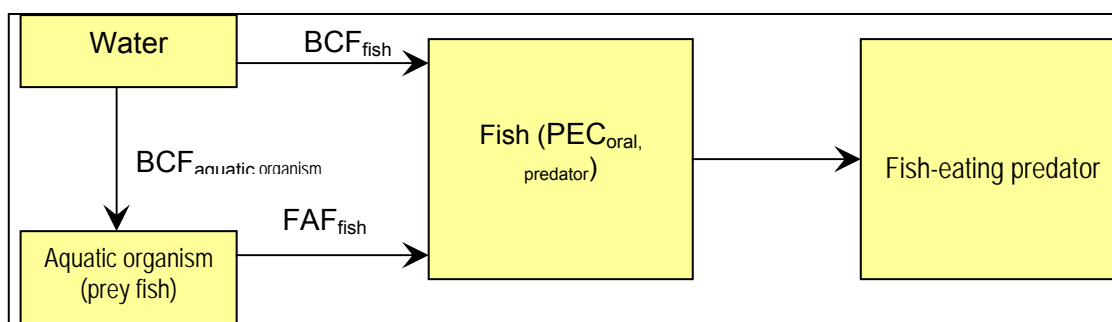


Figure 3.6 Model of fish exposure to LCCPs



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

Assuming that the “aquatic organism” in the food chain is also a fish (as assumed in the TGD), then this equation simplifies to the following:

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

Using a FAF (BMF) of 1 for C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins, and a FAF <<1 for C<sub>>20</sub> solid chlorinated paraffins, the resulting PECs in predatory fish are shown in Table 3.55 (marked as “alternate method”). These values are derived using equation 2, assuming that 50 per cent of the exposure comes from local sources and 50 per cent comes from regional sources (as stated in the TGD).

For earthworms, no measured accumulation data are available for LCCPs and so predicted values are used in the assessment. As discussed in Section 3.2.9.2), a number of approaches have been considered for predicting the accumulation in earthworms and the following BAF values based on a correction to the TGD methodology (relating the concentration in earthworms to the concentration in soil) are thought to be most representative of the actual accumulation potential. The estimated concentrations in earthworms for secondary poisoning obtained using these values are summarised in Table 3.56.

	BAF <sub>earthworm_corrected</sub>
C <sub>18-20</sub> liquid	0.29 kg/kg
C <sub>&gt;20</sub> liquid	0.22 kg/kg
C <sub>&gt;20</sub> solid	0.010 kg/kg

The concentrations of LCCPs in food and other media for human consumption have been estimated using EUSES 2.0.3 (see Appendix A) and are shown in Table 3.57. The resulting estimated daily human intake figures, using the default consumption and bioavailability figures from the TGD, are summarised in Table 3.58. As is the case with earthworms, there are no experimental data available on the actual uptake of LCCPs through the food chain.

For uptake into plants from soil, the following plant-water partition coefficient values are used (see Section 3.2.9.2).

	K <sub>plant-water</sub> (m <sup>3</sup> /m <sup>3</sup> )
C <sub>18-20</sub> liquid	1.1 × 10 <sup>3</sup>
C <sub>&gt;20</sub> liquid	2.0 × 10 <sup>3</sup>
C <sub>&gt;20</sub> solid	200

For the other parts of the food-chain the default values from the TGD are used. The resulting concentrations in the food chain are therefore uncertain as the default methods rely mainly on the log Kow value and the reliability of these estimation methods at very high log Kow values is unclear.

**Table 3.55 Estimated concentrations in fish for secondary poisoning**

Scenario	Step	Predicted concentration in fish (mg/kg wet wt.) <sup>a</sup> – TGD method				Predicted concentration in fish (mg/kg wet wt.) <sup>a</sup> – alternate Method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>
Production		1.2×10 <sup>-3</sup>	3.0×10 <sup>-4</sup>	1.5×10 <sup>-9</sup>	1.5×10 <sup>-3</sup>	2.4×10 <sup>-3</sup>	6.0×10 <sup>-3</sup>	1.5×10 <sup>-9</sup>	8.4×10 <sup>-3</sup>
Use in PVC – plastisol applications	Compounding (O)	4.6×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.6×10 <sup>-4</sup>	9.2×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.2×10 <sup>-4</sup>
	Conversion (O)	4.6×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.6×10 <sup>-4</sup>	9.2×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.2×10 <sup>-4</sup>
	Compounding/conversion (O)	4.9×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.9×10 <sup>-4</sup>	9.8×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.8×10 <sup>-4</sup>
Use in PVC – extrusion/ other	Compounding (O)	4.8×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.8×10 <sup>-4</sup>	9.6×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.6×10 <sup>-4</sup>
	Compounding (PO)	7.3×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	7.3×10 <sup>-4</sup>	1.5×10 <sup>-3</sup>	NA <sup>c</sup>	NA <sup>c</sup>	1.5×10 <sup>-3</sup>
	Compounding (C)	4.5×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.5×10 <sup>-4</sup>	9.0×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.0×10 <sup>-4</sup>
	Conversion (O)	4.7×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.7×10 <sup>-4</sup>	9.4×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.4×10 <sup>-4</sup>
	Conversion (PO)	4.8×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.8×10 <sup>-4</sup>	9.6×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.6×10 <sup>-4</sup>
	Conversion (C)	4.7×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	4.7×10 <sup>-4</sup>	9.4×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	9.4×10 <sup>-4</sup>
	Compounding/conversion (O)	5.3×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	5.3×10 <sup>-4</sup>	1.1×10 <sup>-3</sup>	NA <sup>c</sup>	NA <sup>c</sup>	1.1×10 <sup>-3</sup>
Compounding/conversion (PO)	7.8×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	7.8×10 <sup>-4</sup>	1.6×10 <sup>-3</sup>	NA <sup>c</sup>	NA <sup>c</sup>	1.6×10 <sup>-3</sup>	
Compounding/conversion (C)	5.0×10 <sup>-4</sup>	NA <sup>c</sup>	NA <sup>c</sup>	5.0×10 <sup>-4</sup>	1.0×10 <sup>-3</sup>	NA <sup>c</sup>	NA <sup>c</sup>	1.0×10 <sup>-3</sup>	
Use in rubber	Compounding/conversion	NA <sup>c</sup>	1.1×10 <sup>-4</sup>	4.3×10 <sup>-9</sup>	1.1×10 <sup>-4</sup>	NA <sup>c</sup>	2.2×10 <sup>-4</sup>	4.3×10 <sup>-9</sup>	2.2×10 <sup>-4</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>c</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>c</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	1.1×10 <sup>-9</sup>	1.1×10 <sup>-9</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	1.1×10 <sup>-9</sup>	1.1×10 <sup>-9</sup>
	Industrial application	1.1×10 <sup>-3</sup>	1.3×10 <sup>-4</sup>	1.1×10 <sup>-8</sup>	1.2×10 <sup>-3</sup>	2.2×10 <sup>-3</sup>	2.6×10 <sup>-4</sup>	1.1×10 <sup>-8</sup>	2.5×10 <sup>-3</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 3.55 continued overleaf

**Table 3.55 continued**

Scenario	Step	Predicted concentration in fish (mg/kg wet wt.) <sup>*</sup> – TGD method				Predicted concentration in fish (mg/kg wet wt.) <sup>*</sup> – alternate Method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>
Use in metal cutting/working fluids	Formulation	4.3×10 <sup>-4</sup>	9.2×10 <sup>-5</sup>	NA <sup>c</sup>	5.2×10 <sup>-4</sup>	8.6×10 <sup>-4</sup>	1.8×10 <sup>-4</sup>	NA <sup>c</sup>	1.0×10 <sup>-3</sup>
	Use in oil-based fluids (large)	NA <sup>c</sup>	3.1×10 <sup>-4</sup>	NA <sup>c</sup>	3.1×10 <sup>-4</sup>	NA <sup>c</sup>	6.2×10 <sup>-4</sup>	NA <sup>c</sup>	6.2×10 <sup>-4</sup>
				5.3×10 <sup>-4</sup>		5.3×10 <sup>-4</sup>		1.1×10 <sup>-3</sup>	
	Use in oil-based fluids (small)	3.9×10 <sup>-3</sup>	2.9×10 <sup>-4</sup>	NA <sup>c</sup>	4.2×10 <sup>-3</sup>	7.8×10 <sup>-3</sup>	5.8×10 <sup>-4</sup>	NA <sup>c</sup>	8.4×10 <sup>-3</sup>
		7.3×10 <sup>-3</sup>	4.9×10 <sup>-4</sup>		7.8×10 <sup>-3</sup>	0.015	9.8×10 <sup>-4</sup>		0.016
Use in emulsifiable fluids	7.2×10 <sup>-4</sup>	1.1×10 <sup>-4</sup>	NA <sup>c</sup>	8.3×10 <sup>-4</sup>	1.4×10 <sup>-3</sup>	2.2×10 <sup>-4</sup>	NA <sup>c</sup>	1.6×10 <sup>-3</sup>	
Use in emulsifiable fluids – intermittent release	2.4×10 <sup>-3</sup>	2.0×10 <sup>-4</sup>	NA <sup>c</sup>	2.6×10 <sup>-3</sup>	4.8×10 <sup>-3</sup>	4.0×10 <sup>-4</sup>	NA <sup>c</sup>	5.2×10 <sup>-3</sup>	
Use in leather fat liquors	Formulation	8.1×10 <sup>-4</sup>	1.0×10 <sup>-4</sup>	NA <sup>c</sup>	9.1×10 <sup>-4</sup>	1.6×10 <sup>-3</sup>	2.0×10 <sup>-4</sup>	NA <sup>c</sup>	1.8×10 <sup>-3</sup>
	Use – complete processing of raw hides <sup>e</sup>	3.9×10 <sup>-3</sup>	1.8×10 <sup>-4</sup>	NA <sup>c</sup>	4.1×10 <sup>-3</sup>	7.8×10 <sup>-3</sup>	3.6×10 <sup>-4</sup>	NA <sup>c</sup>	8.2×10 <sup>-3</sup>
	Use – processing of wet blue <sup>e</sup>	0.014	4.6×10 <sup>-4</sup>	NA <sup>c</sup>	0.014	0.028	9.2×10 <sup>-4</sup>	NA <sup>c</sup>	0.029
Use in textile applications	0.050	NA <sup>c</sup>	NA <sup>c</sup>	0.050	0.10	NA <sup>c</sup>	NA <sup>c</sup>	0.10	

Notes: <sup>\*</sup> 50 per cent from local and 50 per cent from regional concentrations.

<sup>a</sup> Assumes dilution of sewage sludge at wwtp before application to soil.

<sup>b</sup> The process makes no significant contribution to the levels in fish.

<sup>c</sup> NA = not applicable; no significant use of the substance in this application.

<sup>d</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>e</sup> The calculation for complete processing of raw hides is thought to be the more realistic scenario, and will be taken forward to the risk characterisation.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

**Table 3.56 Estimated concentrations in earthworms for secondary poisoning**

Scenario	Step	Predicted concentration in earthworms (mg/kg wet wt.) <sup>*</sup> – corrected TGD method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>
Production		negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in PVC – plastisol applications	Compounding (O)	0.24	NA <sup>c</sup>	NA <sup>c</sup>	0.24
	Conversion (O)	0.24	NA <sup>c</sup>	NA <sup>c</sup>	0.24
	Compounding/conversion (O)	0.30	NA <sup>c</sup>	NA <sup>c</sup>	0.30
Use in PVC – extrusion/ other	Compounding (O)	0.28	NA <sup>c</sup>	NA <sup>c</sup>	0.28
	Compounding (PO)	0.78	NA <sup>c</sup>	NA <sup>c</sup>	0.78
	Compounding (C)	0.22	NA <sup>c</sup>	NA <sup>c</sup>	0.22
	Conversion (O)	0.27	NA <sup>c</sup>	NA <sup>c</sup>	0.27
	Conversion (PO)	0.27	NA <sup>c</sup>	NA <sup>c</sup>	0.27
	Conversion (C)	0.25	NA <sup>c</sup>	NA <sup>c</sup>	0.25
	Compounding/conversion (O)	0.37	NA <sup>c</sup>	NA <sup>c</sup>	0.37
	Compounding/conversion (PO)	0.88	NA <sup>c</sup>	NA <sup>c</sup>	0.88
	Compounding/conversion (C)	0.31	NA <sup>c</sup>	NA <sup>c</sup>	0.31
Use in rubber	Compounding/conversion	NA <sup>c</sup>	0.41	0.044	0.45
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>c</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	2.9×10 <sup>-4</sup>	2.9×10 <sup>-4</sup>
	Industrial application	0.33	0.45	9.6×10 <sup>-3</sup>	0.79
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 3.56 continued overleaf

**Table 3.56 continued**

Scenario	Step	Predicted concentration in earthworms (mg/kg wet wt.) <sup>a</sup> – corrected TGD method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>d</sup>
Use in metal cutting/working fluids	Formulation	0.17	0.33	NA <sup>c</sup>	0.50
	Use in oil-based fluids (large)	NA <sup>c</sup>	0.96–1.6	NA <sup>c</sup>	0.96–1.6
	Use in oil-based fluids (small)	0.92–1.7	0.90–1.5	NA <sup>c</sup>	1.8–3.2
	Use in emulsifiable fluids	0.24	0.38	NA <sup>c</sup>	0.62
	Use in emulsifiable fluids – intermittent release	7.0	5.5	NA <sup>c</sup>	12.5
Use in leather fat liquors	Formulation	0.54	0.47	NA <sup>c</sup>	1.0
	Use – complete processing of raw hides <sup>e</sup>	2.4	2.1	NA <sup>c</sup>	4.5
	Use – processing of wet blue <sup>e</sup>	0.99	7.2	NA <sup>c</sup>	8.2
Use in textile applications		11	NA <sup>c</sup>	NA <sup>c</sup>	11

Notes: <sup>a</sup>50 per cent from local and 50 per cent from regional concentrations.

<sup>a</sup> Assumes dilution of sewage sludge at wwtp before application to soil.

<sup>b</sup> The process makes no significant contribution to the levels in earthworms.

<sup>c</sup> NA = not applicable; no significant use of the substance in this application.

<sup>d</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>e</sup> The calculation for complete processing of raw hides is thought to be the more realistic scenario, and will be taken forward to the risk characterisation.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

**Table 3.57 Estimated concentrations in food for human consumption**

Scenario	Step	Concentration						
		Fish (mg/kg) <sup>e</sup>	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m <sup>3</sup> ) <sup>f</sup>
<b>C<sub>18-20</sub> liquids</b>								
Production	Generic	1.9×10 <sup>-3</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in PVC – plastisol applications	Compounding (O)	4.9×10 <sup>-4</sup>	1.0×10 <sup>-3</sup>	1.7×10 <sup>-4</sup>	6.6×10 <sup>-7</sup>	0.030	9.6×10 <sup>-3</sup>	negligible <sup>b</sup>
	Conversion (O)	4.9×10 <sup>-4</sup>	1.0×10 <sup>-3</sup>	2.7×10 <sup>-4</sup>	6.6×10 <sup>-7</sup>	0.031	9.8×10 <sup>-3</sup>	6.3×10 <sup>-7</sup>
Use in PVC – extrusion/ other	Compounding/conversion (O)	5.5×10 <sup>-4</sup>	1.5×10 <sup>-3</sup>	2.7×10 <sup>-4</sup>	9.3×10 <sup>-7</sup>	0.037	0.012	6.3×10 <sup>-7</sup>
	Compounding (O)	5.4×10 <sup>-4</sup>	1.4×10 <sup>-3</sup>	2.0×10 <sup>-4</sup>	8.7×10 <sup>-7</sup>	0.036	0.011	1.9×10 <sup>-7</sup>
	Compounding (PO)	1.0×10 <sup>-3</sup>	4.7×10 <sup>-3</sup>	3.3×10 <sup>-4</sup>	3.0×10 <sup>-6</sup>	0.086	0.027	1.1×10 <sup>-7</sup>
	Compounding (C)	4.8×10 <sup>-4</sup>	9.6×10 <sup>-4</sup>	1.8×10 <sup>-4</sup>	6.1×10 <sup>-7</sup>	0.029	9.3×10 <sup>-3</sup>	8.6×10 <sup>-8</sup>
	Conversion (O)	5.2×10 <sup>-4</sup>	1.2×10 <sup>-3</sup>	3.2×10 <sup>-4</sup>	7.9×10 <sup>-7</sup>	0.034	0.011	9.3×10 <sup>-7</sup>
	Conversion (PO)	5.3×10 <sup>-4</sup>	1.3×10 <sup>-3</sup>	3.3×10 <sup>-4</sup>	8.2×10 <sup>-7</sup>	0.035	0.011	1.1×10 <sup>-6</sup>
	Conversion (C)	5.1×10 <sup>-4</sup>	1.2×10 <sup>-3</sup>	3.1×10 <sup>-4</sup>	7.6×10 <sup>-7</sup>	0.033	0.011	8.6×10 <sup>-7</sup>
	Compounding/conversion (O)	6.3×10 <sup>-4</sup>	2.0×10 <sup>-3</sup>	3.5×10 <sup>-4</sup>	1.3×10 <sup>-6</sup>	0.046	0.015	1.1×10 <sup>-6</sup>
	Compounding/conversion (PO)	1.1×10 <sup>-3</sup>	5.4×10 <sup>-3</sup>	4.9×10 <sup>-4</sup>	3.4×10 <sup>-6</sup>	0.097	0.031	2.0×10 <sup>-6</sup>
	Compounding/conversion (C)	5.7×10 <sup>-4</sup>	1.5×10 <sup>-3</sup>	3.2×10 <sup>-4</sup>	9.8×10 <sup>-7</sup>	0.039	0.012	9.4×10 <sup>-7</sup>
Use in rubber	Compounding/conversion	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
	Industrial application	1.8×10 <sup>-3</sup>	1.6×10 <sup>-3</sup>	1.7×10 <sup>-4</sup>	1.0×10 <sup>-6</sup>	0.039	0.012	negligible <sup>b</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 3.57 continued overleaf

**Table 3.57 continued**

Scenario	Step	Concentration						
		Fish (mg/kg) <sup>e</sup>	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m <sup>3</sup> ) <sup>f</sup>
Use in metal cutting/ working fluids	Formulation	4.3×10 <sup>-4</sup>	6.2×10 <sup>-4</sup>	1.7×10 <sup>-4</sup>	4.0×10 <sup>-7</sup>	0.024	7.6×10 <sup>-3</sup>	6.1×10 <sup>-10</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Use in oil-based fluids (small)	7.3×10 <sup>-3</sup> – 0.014	5.7×10 <sup>-3</sup> – 0.011	1.7×10 <sup>-4</sup>	3.6×10 <sup>-6</sup> – 6.9×10 <sup>-6</sup>	0.10–0.18	0.032– 0.056	negligible <sup>b</sup>
	Use in emulsifiable fluids	1.0×10 <sup>-3</sup>	1.0×10 <sup>-4</sup>	1.7×10 <sup>-4</sup>	6.6×10 <sup>-7</sup>	0.030	9.6×10 <sup>-3</sup>	negligible <sup>b</sup>
	Use in emulsifiable fluids – intermittent release	4.3×10 <sup>-3</sup>	0.047	1.7×10 <sup>-4</sup>	3.0×10 <sup>-5</sup>	0.72	0.23	negligible <sup>b</sup>
Use in leather fat liquors	Formulation	3.9×10 <sup>-3</sup>	3.2×10 <sup>-3</sup>	2.2×10 <sup>-3</sup>	2.0×10 <sup>-6</sup>	0.073	0.023	1.3×10 <sup>-5</sup>
	Use – complete processing of raw hides <sup>e</sup>	7.3×10 <sup>-3</sup>	0.016	1.7×10 <sup>-4</sup>	1.0×10 <sup>-5</sup>	0.25	0.080	negligible <sup>b</sup>
	Use – processing of wet blue <sup>e</sup>	0.028	0.062	1.7×10 <sup>-4</sup>	3.9×10 <sup>-5</sup>	0.94	0.30	negligible <sup>b</sup>
Use in textile applications		0.10	0.074	0.31	4.7×10 <sup>-5</sup>	2.8	0.89	1.9×10 <sup>-3</sup>
Regional sources		4.3×10 <sup>-4</sup>	5.4×10 <sup>-4</sup>	1.7×10 <sup>-4</sup>	3.4×10 <sup>-7</sup>	0.021	6.7×10 <sup>-3</sup>	7.6×10 <sup>-7</sup> – 1.0×10 <sup>-6</sup>

Table 3.57 continued overleaf

**Table 3.57 continued**

Scenario	Step	Concentration						
		Fish (mg/kg) <sup>e</sup>	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m <sup>3</sup> ) <sup>f</sup>
<b>C<sub>&gt;20</sub> liquids</b>								
Production	Generic	5.2×10 <sup>-4</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in PVC – plastisol applications	Compounding (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Use in PVC – extrusion/ other	Compounding/conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding (PO)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding (C)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (PO)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (C)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding/conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding/conversion (PO)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Compounding/conversion (C)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	
Use in rubber	Compounding/conversion	1.4×10 <sup>-4</sup>	5.3×10 <sup>-4</sup>	2.6×10 <sup>-4</sup>	1.9×10 <sup>-7</sup>	0.020	6.2×10 <sup>-3</sup>	2.9×10 <sup>-6</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
	Industrial application	1.7×10 <sup>-4</sup>	7.3×10 <sup>-4</sup>	8.9×10 <sup>-6</sup>	2.6×10 <sup>-7</sup>	0.023	7.3×10 <sup>-3</sup>	negligible <sup>b</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 3.57 continued overleaf



**Table 3.57 continued**

Scenario	Step	Concentration						
		Fish (mg/kg) <sup>e</sup>	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m <sup>3</sup> ) <sup>f</sup>
Use in metal cutting/working fluids	Formulation	9.2×10 <sup>-5</sup>	1.3×10 <sup>-4</sup>	8.9×10 <sup>-6</sup>	1.2×10 <sup>-7</sup>	8.0×10 <sup>-3</sup>	2.5×10 <sup>-3</sup>	7.6×10 <sup>-10</sup>
	Use in oil-based fluids (large)	5.3×10 <sup>-4</sup> –	3.5×10 <sup>-3</sup> –	8.9×10 <sup>-6</sup> –	1.2×10 <sup>-6</sup> –	0.092–	0.029–	negligible <sup>b</sup>
		9.7×10 <sup>-4</sup>	6.8×10 <sup>-3</sup>	9.0×10 <sup>-6</sup>	2.4×10 <sup>-6</sup>	0.18	0.056	
	Use in oil-based fluids (small)	4.9×10 <sup>-4</sup> –	3.2×10 <sup>-3</sup> –	8.9×10 <sup>-6</sup>	1.1×10 <sup>-6</sup> –	0.085–	0.027–	negligible <sup>b</sup>
		8.9×10 <sup>-4</sup>	6.2×10 <sup>-3</sup>		2.2×10 <sup>-6</sup>	0.16	0.051	
Use in emulsifiable fluids	1.3×10 <sup>-4</sup>	3.8×10 <sup>-4</sup>	8.9×10 <sup>-6</sup>	1.6×10 <sup>-7</sup>	0.014	4.5×10 <sup>-3</sup>	negligible <sup>b</sup>	
Use in emulsifiable fluids – intermittent release	3.1×10 <sup>-4</sup>	0.028	9.2×10 <sup>-6</sup>	9.7×10 <sup>-6</sup>	0.70	0.22	negligible <sup>b</sup>	
Use in leather fat liquors	Formulation	1.9×10 <sup>-4</sup>	8.8×10 <sup>-4</sup>	5.0×10 <sup>-4</sup>	3.1×10 <sup>-7</sup>	0.030	9.4×10 <sup>-3</sup>	5.7×10 <sup>-6</sup>
	Use – complete processing of raw hides <sup>e</sup>	2.8×10 <sup>-4</sup>	9.2×10 <sup>-3</sup>	9.0×10 <sup>-6</sup>	3.2×10 <sup>-6</sup>	0.24	0.075	negligible <sup>b</sup>
	Use – processing of wet blue <sup>e</sup>	8.2×10 <sup>-4</sup>	0.037	9.3×10 <sup>-6</sup>	1.3×10 <sup>-5</sup>	0.93	0.29	negligible <sup>b</sup>
Use in textile applications		NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Regional sources		9.2×10 <sup>-5</sup>	1.6×10 <sup>-3</sup>	8.9×10 <sup>-6</sup>	5.7×10 <sup>-7</sup>	0.10	0.032	8.5×10 <sup>-8</sup> – 1.0×10 <sup>-7</sup>

Table 3.57 continued overleaf

**Table 3.57 continued**

Scenario	Step	Concentration						
		Fish (mg/kg) <sup>e</sup>	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m <sup>3</sup> ) <sup>f</sup>
<b>C<sub>&gt;20</sub> solids</b>								
Production	Generic	2.1×10 <sup>-9</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in PVC – plastisol applications	Compounding (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Use in PVC – extrusion/ other	Compounding/conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding (PO)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding (C)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (PO)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Conversion (C)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding/conversion (O)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding/conversion (PO)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Use in rubber	Compounding/conversion (C)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Compounding/conversion	7.7×10 <sup>-9</sup>	1.4×10 <sup>-5</sup>	3.9×10 <sup>-8</sup>	5.0×10 <sup>-8</sup>	0.13	0.041	2.4×10 <sup>-7</sup>
Use in sealants	Formulation and use	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Use in paints	Formulation	1.3×10 <sup>-9</sup>	6.6×10 <sup>-8</sup>	1.9×10 <sup>-10</sup>	3.2×10 <sup>-10</sup>	6.4×10 <sup>-4</sup>	2.0×10 <sup>-4</sup>	8.9×10 <sup>-7</sup>
	Industrial application	2.2×10 <sup>-8</sup>	3.1×10 <sup>-6</sup>	8.3×10 <sup>-9</sup>	1.1×10 <sup>-8</sup>	0.028	8.9×10 <sup>-3</sup>	negligible <sup>b</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 3.57 continued overleaf

**Table 3.57 continued**

Scenario	Step	Concentration						
		Fish (mg/kg) <sup>e</sup>	Root crops (mg/kg)	Leaf crops (mg/kg)	Drinking water (mg/l)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m <sup>3</sup> ) <sup>f</sup>
Use in metal cutting/working fluids	Formulation	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Use in oil-based fluids (small)	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Use in emulsifiable fluids	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Use in emulsifiable fluids – intermittent release	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Use in leather fat liquors	Formulation	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Use – complete processing of raw hides <sup>e</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
	Use – processing of wet blue <sup>e</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
Use in textile applications	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	
Regional sources		8.5×10 <sup>-10</sup>	2.7×10 <sup>-8</sup>	7.2×10 <sup>-11</sup>	2.1×10 <sup>-10</sup>	6.1×10 <sup>-4</sup>	1.9×10 <sup>-4</sup>	1.7×10 <sup>-10</sup>

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in food.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

<sup>e</sup> No BMF or FAF has been assumed in the calculation here. This is in line with the methodology outlined in the TGD.

<sup>f</sup> For the local scenario, the concentrations in air are the annual average air concentration for a site (C<sub>local\_ann\_average</sub>) taken from Table 3.54 and do not include the regional contribution. The contribution of the inhalation route to the total daily intake is very small.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

**Table 3.58 Estimated total human food intake of LCCPs**

Scenario	Step	Estimated daily intake (mg/kg bw/day)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Production	Generic	3.1×10 <sup>-6</sup>	8.5×10 <sup>-7</sup>	3.4×10 <sup>-12</sup>	4.0×10 <sup>-6</sup>
Use in PVC – plastisol applications	Compounding (O)	2.2×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.2×10 <sup>-4</sup>
	Conversion (O)	2.2×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.2×10 <sup>-4</sup>
	Compounding/conversion (O)	2.7×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.7×10 <sup>-4</sup>
Use in PVC – extrusion/ other	Compounding (O)	2.6×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-4</sup>
	Compounding (PO)	6.2×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	6.2×10 <sup>-4</sup>
	Compounding (C)	2.1×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.1×10 <sup>-4</sup>
	Conversion (O)	2.5×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.5×10 <sup>-4</sup>
	Conversion (PO)	2.5×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.5×10 <sup>-4</sup>
	Conversion (C)	2.4×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.4×10 <sup>-4</sup>
	Compounding/conversion (O)	3.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.3×10 <sup>-4</sup>
	Compounding/conversion (PO)	7.1×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	7.1×10 <sup>-4</sup>
	Compounding/conversion (C)	2.8×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.8×10 <sup>-4</sup>
Use in rubber	Compounding/conversion	NA <sup>a</sup>	1.4×10 <sup>-4</sup>	8.9×10 <sup>-4</sup>	1.0×10 <sup>-3</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	4.6×10 <sup>-6</sup>	4.6×10 <sup>-6</sup>
	Industrial application	2.8×10 <sup>-4</sup>	1.6×10 <sup>-4</sup>	1.9×10 <sup>-4</sup>	6.3×10 <sup>-4</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 3.58 continued overleaf

**Table 3.58 continued**

Scenario	Step	Estimated daily intake (mg/kg bw/day)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in metal cutting/working fluids	Formulation	1.7×10 <sup>-4</sup>	5.6×10 <sup>-5</sup>	NA <sup>a</sup>	2.3×10 <sup>-4</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	6.5×10 <sup>-4</sup> –1.2×10 <sup>-3</sup>	NA <sup>a</sup>	6.5×10 <sup>-4</sup> –1.2×10 <sup>-3</sup>
	Use in oil-based fluids (small)	7.3×10 <sup>-4</sup> –1.3×10 <sup>-3</sup>	6.0×10 <sup>-4</sup> –1.1×10 <sup>-3</sup>	NA <sup>a</sup>	1.3×10 <sup>-3</sup> –2.4×10 <sup>-3</sup>
	Use in emulsifiable fluids	2.2×10 <sup>-4</sup>	1.0×10 <sup>-5</sup>	NA <sup>a</sup>	2.3×10 <sup>-4</sup>
	Use in emulsifiable fluids – intermittent release	5.2×10 <sup>-3</sup>	4.9×10 <sup>-3</sup>	NA <sup>a</sup>	0.010
Use in leather fat liquors	Formulation	5.7×10 <sup>-4</sup>	2.2×10 <sup>-4</sup>	NA <sup>a</sup>	7.9×10 <sup>-4</sup>
	Use – complete processing of raw hides <sup>d</sup>	1.8×10 <sup>-3</sup>	1.7×10 <sup>-3</sup>	NA <sup>a</sup>	3.5×10 <sup>-3</sup>
	Use – processing of wet blue <sup>d</sup>	6.8×10 <sup>-3</sup>	6.5×10 <sup>-3</sup>	NA <sup>a</sup>	0.013
Use in textile applications		0.026	NA <sup>a</sup>	NA <sup>a</sup>	0.026
Regional sources		1.5×10 <sup>-4</sup>	7.1×10 <sup>-4</sup>	4.2×10 <sup>-6</sup>	8.6×10 <sup>-4</sup>

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in food.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

### 3.3.4.2 Measured data

Murray *et al.* (1988a) reported the results of monitoring of chlorinated paraffins in mussels (*Unionidae* sp.) collected in a stream receiving effluent from a chlorinated paraffin production site in the United States. The levels of LCCPs found (using a C<sub>20-30</sub>, 40–50% wt. Cl product as a reference) were 180 µg/kg in mussels from downstream of the discharge. LCCPs were not detected (<7 µg/kg) in mussels from upstream of the discharge.

Kemmlin *et al.* (2002) reported the results of a study looking at the levels of chlorinated paraffins in marine mussels and crabs from an area close to a chlorinated paraffin manufacturer in Australia. The levels of total chlorinated paraffins found were 25 mg/kg lipid in mussel and 109.5 mg/kg lipid in crabs. LCCPs were found to make up around 27 per cent of the total in mussel and 13 per cent of the total in crabs. The results for LCCPs are summarised in Table 3.59. The analysis was carried out by dechlorination of the chlorinated paraffins found, followed by analysis of the n-paraffins formed. The same results appear to be given in OSPAR (2000) referenced to an unpublished study by Rotard *et al.* (1998).

**Table 3.59 Concentration of chlorinated paraffins in marine mussels and crab close to a chlorinated paraffin production site in Australia**

Chain length	Concentration of chlorinated paraffins (mg/kg lipid)	
	Mussel	Crab
C <sub>18</sub>	1.4	4.0
C <sub>19</sub>	0.5	1.3
C <sub>20</sub>	0.9	1.6
C <sub>21</sub>	0.4	0.7
C <sub>22</sub>	0.7	1.0
C <sub>23</sub>	0.4	0.9
C <sub>24</sub>	0.6	0.9
C <sub>25</sub>	0.6	1.3
C <sub>26</sub>	1.2	1.1
C <sub>27</sub>	1.1	0.7
C <sub>28</sub>	0.9	0.5
C <sub>29</sub>	0.6	0.3
Total LCCP	9.3	14.3

Details of an unpublished study (Froescheis, 1997) were also reported by OSPAR (2000). This study detected chlorinated paraffins of all chain lengths in the deep sea fish *Sebastes altivelis*, but it was not possible to quantify the levels found.

The levels of C<sub>10-20</sub> and C<sub>20-30</sub> chlorinated paraffins have been measured in seal, marine shellfish and salt and freshwater fish from around the United Kingdom (Campbell and McConnell, 1980). The results of the analyses are shown in Table 3.60. The same authors also determined the levels in several other parts of the (human) food chain. These data are shown in Table 3.61 to Table 3.64. The C<sub>10-20</sub> levels are likely to be dominated by contributions from the short- and medium-chain chlorinated paraffins.

**Table 3.60 Concentrations of chlorinated paraffins in aquatic organisms (Campbell and McConnell, 1980)**

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

Note: ND = not detected (detection limit = 50 µg/kg wet weight).

**Table 3.61 Concentration of chlorinated paraffins in birds (Campbell and McConnell, 1980)**

Species	Organ	Concentration of chlorinated paraffins (µg/kg wet weight)	
		C <sub>10-20</sub>	C <sub>20-30</sub>
		Heron ( <i>Ardea cinerea</i> )	Liver
Guillemot ( <i>Uria aalge</i> )	Liver	100-1,100	ND
Herring gull ( <i>Larus argentatus</i> )	Liver	200-900	100-500

Note: ND = not detected (detection limit = 100 µg/kg wet weight).

**Table 3.62 Concentration of chlorinated paraffins in seabirds' eggs<sup>a</sup> (Campbell and McConnell, 1980)**

Concentration (µg/kg)	No of eggs containing chlorinated paraffins	
	C <sub>10-20</sub>	C <sub>20-30</sub>
Not detected (<50 µg/kg)	7	17
50	3	3
100	3	3
200	5	0
300	1	0
400	2	0
600	1	0
>600 (=2,000 µg/kg)	1	0

Note: <sup>a</sup> Species included were: Cormorant (*Phalacrocoracidae carbo*); Gannet (*Morus bassanus*); Great skua (*Catharacta skua*); Guillemot (*Uria aalge*); Kittiwake (*Rissa tridactyla*); Puffin (*Frateruela arctica*); Manx shearwater (*Puffinus puffinus*); Razorbill (*Alca torda*) and Shag (*Phalacrocorax aristotelis*).

**Table 3.63 Concentration of chlorinated paraffins in human foodstuffs (Campbell and McConnell, 1980)**

Foodstuff class	No of samples analysed	Concentration of chlorinated paraffin µg/kg wet weight)	
		C <sub>10-20</sub> <sup>a</sup>	C <sub>20-30</sub> <sup>b</sup>
Dairy products	13	300	190
Vegetable oils and derivatives	6	150	ND
Fruit and vegetables	16	5	25
Beverages	6	ND	ND

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

<sup>a</sup> C<sub>10-20</sub> chlorinated paraffins detected in approximately 70 per cent of samples; average concentration given.

<sup>b</sup> C<sub>20-30</sub> chlorinated paraffins found in only one sample of cheese (190 µg/kg wet wt.), one sample of potato crisps (25 µg/kg wet wt.) and one sample of peach fruit (25 µg/kg wet wt.).



**Table 3.64 Concentration of chlorinated paraffins 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 chlorinated paraffin ( $\mu\text{g}/\text{kg}$ )	
		C <sub>10-20</sub>	C <sub>20-30</sub>
Remote from industry	Liver, brain, kidney, mesenteric fat	ND	ND
Close to a chlorinated paraffin production plant	Heart	ND	ND
	Liver	200	ND
	Lung	ND	ND
	Mesenteric fat	50	ND
	Kidney	50	ND
	Perinephritic fat	ND	ND

Note: ND = not detected (detection limit = 50  $\mu\text{g}/\text{kg}$ ).

Campbell and McConnell (1980) also analysed some post-mortem human tissues for the presence of chlorinated paraffins. Of the 24 subjects analysed, C<sub>20-30</sub> chlorinated paraffins were detected in fat tissues of three subjects (100  $\mu\text{g}/\text{kg}$  wet wt.), the liver of one subject (80  $\mu\text{g}/\text{kg}$  wet wt.) and the fat (3,500  $\mu\text{g}/\text{kg}$  wet wt.) and liver (200  $\mu\text{g}/\text{kg}$  wet wt.) of one further subject. The concentration of C<sub>20-30</sub> chlorinated paraffins in the remaining samples analysed was less than the limit of detection of the method used (<50  $\mu\text{g}/\text{kg}$  wet wt.). In contrast to this, the C<sub>10-20</sub> chlorinated paraffins were frequently detected in liver tissues (up to 1,500  $\mu\text{g}/\text{kg}$  wet wt.), adipose tissues (up to ~500–600  $\mu\text{g}/\text{kg}$  wet wt.) and kidney tissues (up to ~400–500  $\mu\text{g}/\text{kg}$  wet wt.). No C<sub>10-20</sub> chlorinated paraffins were detected in brain tissues (detection limit for these samples was 90  $\mu\text{g}/\text{kg}$  wet wt.).

The results of an unpublished survey of levels of LCCPs (average carbon chain length C<sub>24</sub>) in biota carried out by Baldwin and Bennett (1974) have been reported by Zitko (1980). In all, 52 samples were analysed, covering eggs from four species of aquatic bird, six species of fish and two species of shell fish and the LCCPs were detected only once, at 0.06 mg/kg, which was close to the detection limit of the method used. Few other details (for example location, analytical methods used) of this study are available.

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  $\mu\text{g}/\text{kg}$  lipid in fish and 130–280  $\mu\text{g}/\text{kg}$  lipid in seal from in and around Sweden. In addition they also reported levels of chlorinated paraffins of 2,900  $\mu\text{g}/\text{kg}$  lipid in rabbit muscle, 4,400  $\mu\text{g}/\text{kg}$  lipid in moose muscle, 140  $\mu\text{g}/\text{kg}$  in reindeer suet and 530  $\mu\text{g}/\text{kg}$  in osprey muscle in pooled samples from the same area. The results are shown in Table 3.65. These levels will also include contributions from chlorinated paraffins other than LCCPs.

**Table 3.65 Concentrations of chlorinated paraffins (unspecified chain length) in pooled samples from in and around Sweden (Jansson *et al.*, 1993)**

Sample	Number of samples	Location/date	Lipid content	Concentration* ( $\mu\text{g}/\text{kg}$ lipid)
Whitefish muscle	35	Lake Storvindeln, Lapland, 1986	0.66%	1,000
Arctic char muscle	15	Lake Vättern, Central Sweden, 1987	5.3%	570
Herring muscle	100	Bothnian Sea, 1986	5.4%	1,400
Herring muscle	60	Baltic proper, 1987	4.4%	1,500
Herring muscle	100	Skagerrak, 1987	3.2%	1,600
Ringed seal blubber	7	Kongsfjorden, Svalbard, 1981	88%	130
Grey seal blubber	8	Baltic Sea, 1979–85	74%	280
Rabbit muscle	15	Revingehed, Skåne, 1986	1.1%	2,900
Moose muscle	13	Grimsö, Västmanland, 1985–86	2.0%	4,400
Reindeer suet	31	Ottsjö, Jämtland, 1986	56%	140
Osprey muscle	35	Sweden, 1982–1986	4.0%	530

Note: \* Refers to chlorinated paraffins with 6–16 chlorine atoms and so may contain chlorinated paraffins other than LCCPs.

Levels of total ( $\text{C}_{10-24}$ ) chlorinated paraffins in food, fish and marine animals have been reported by Greenpeace (1995). The total levels measured (on a fat weight basis) were 271  $\mu\text{g}/\text{kg}$  in mackerel, 62  $\mu\text{g}/\text{kg}$  in fish oil (herring), 98  $\mu\text{g}/\text{kg}$  in margarine containing fish oil, 16–114  $\mu\text{g}/\text{kg}$  in common porpoise, 963  $\mu\text{g}/\text{kg}$  in fin whale, 69  $\mu\text{g}/\text{kg}$  in pork, 74  $\mu\text{g}/\text{kg}$  in cows milk and 45  $\mu\text{g}/\text{kg}$  in human breast milk. The average chlorine content of the chlorinated paraffins detected was around 33 per cent. LCCPs were thought to make up between 53.5 and 94 per cent of the total chlorinated paraffins found. The concentrations of LCCPs present can be estimated from the data as 225  $\mu\text{g}/\text{kg}$  in mackerel, 50  $\mu\text{g}/\text{kg}$  in fish oil, 58  $\mu\text{g}/\text{kg}$  in margarine, 13–107  $\mu\text{g}/\text{kg}$  in porpoise, 819  $\mu\text{g}/\text{kg}$  in fin whale, 37  $\mu\text{g}/\text{kg}$  in pork, 43  $\mu\text{g}/\text{kg}$  in cows' milk and 35  $\mu\text{g}/\text{kg}$  in mothers' milk.

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

### 3.3.4.3 Comparison of predicted and measured levels

The comparison of the predicted and measured concentrations in biota is complicated by the fact that some of the analyses carried out so far have not tested specifically for LCCPs, and are generally not related to specific sources of release. From the available studies where LCCPs have been specifically identified, concentrations up to around 100–200  $\mu\text{g}/\text{kg}$  lipid in fish have been measured, but higher levels (up to around 800  $\mu\text{g}/\text{kg}$  lipid) have been measured in a whale sample, and up to 14.3 mg/kg lipid have been reported in crabs.

These few measured levels in fish agree reasonably well with the predicted concentrations. For example, most predicted concentrations in fish for the secondary poisoning scenario are in the range of around 0.5–10 µg/kg wet weight, with a maximum of 50 µg/kg wet weight. Using a typical lipid content of fish as 8 per cent, these concentrations are equivalent to 6–125 µg/kg lipid, with a maximum of 625 µg/kg lipid.

The predicted concentrations in fish are calculated using estimated fish bioconcentration factors, which are themselves uncertain. These indicate that the types of LCCPs present are likely to be dominated by the C<sub>18–20</sub> liquid and to a lesser extent the C<sub>>20</sub> liquid products. The estimates of total LCCP concentrations in fish obtained using this approach appear to agree reasonably well with the available monitoring data. However, the available monitoring data are not always able to distinguish between the C<sub>18–20</sub> liquid, C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins, so it is not possible to determine if the relative contribution of the three types is as predicted here.

The analytical methods currently available for LCCPs all have potential drawbacks that result mainly from the lack of any analytical reference material that would allow unambiguous identification of the chlorinated paraffins either by chlorine content or carbon chain length (see Appendix D). Currently, the analytical data can only give an approximation to the actual concentrations present, and provide little information on the types of chlorinated paraffin present (either in terms of the chlorine content and in some cases the chain length distribution). Therefore it is not possible to confirm the expected pattern of uptake of the various types of LCCPs from the currently available monitoring data.

The predicted data will be considered in the risk characterisation for secondary poisoning.

The available monitoring data for levels in food indicate that levels up to about 200 µg/kg wet weight have been determined in some dairy products and up to around 25 µg/kg in fruit and vegetables.

### **3.3.5 Marine compartment**

#### *3.3.5.1 Predicted environmental concentrations*

The predicted concentrations of LCCPs in the marine environment (resulting from the production and use of LCCPs) have been estimated using the methodology outlined in the TGD. The method essentially assumes that the adsorption/desorption, degradation and accumulation behaviour of a substance in the marine environment can, in the absence of specific information for the marine environment, be adequately described by the properties of same substance in the freshwater environment.

The starting point for the local marine assessment is the concentration of LCCP in effluent from the site of discharge. This effluent from industrial sites is assumed to enter into the marine environment without further waste water treatment. The one exception to this situation is when the substance is found in products used by the general population, where discharge via a waste water treatment plant can be assumed (in these circumstances the effluent concentration from the waste water treatment plant is used as a starting point for the assessment). For LCCPs the disposal of LCCPs via waste water treatment applies only in the case of DIY paints.

The predicted concentrations are summarised in Table 3.66 (marine water), Table 3.67 (marine sediment), Table 3.68 (predators) and Table 3.69 (top predators).

For the intermittent release scenario for metal cutting/working fluids, the TGD does not provide any guidance on how releases should be treated for sediment. The value reported in Table 3.66 assumes that the substance in water instantly equilibrates with the sediment. However, in reality, this is unlikely to occur as the release will be over a short period of time.

An alternative approach would be to average the concentration of the released LCCP over the year and add this value to the concentration arising from the continuous use of LCCPs in the metalworking fluids (2.0 mg/kg wet weight for C<sub>18-20</sub> liquid chlorinated paraffins and 2.5 mg/kg wet weight for C<sub>>20</sub> liquid chlorinated paraffins). This approach gives a PEC<sub>local(sediment)</sub> of 12–32 mg/kg wet weight for C<sub>18-20</sub> liquid chlorinated paraffins and 12–32 mg/kg wet weight for C<sub>>20</sub> liquid chlorinated paraffins, assuming that the intermittent disposal occurs 2–6 times/year.

**Table 3.66 Predicted concentrations in marine water**

Scenario	Step	PEC <sub>local(seawater)</sub> (µg/l)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Production	Generic <sup>e</sup>	2.4×10 <sup>-3</sup>	4.0×10 <sup>-3</sup>	2.3×10 <sup>-6</sup>	6.4×10 <sup>-3</sup>
Use in PVC – plastisol applications	Compounding – O	1.0×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.0×10 <sup>-3</sup>
	Conversion – O	1.0×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.0×10 <sup>-3</sup>
	Compounding/ conversion – O	1.9×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.9×10 <sup>-3</sup>
Use in PVC – extrusion/ other	Compounding – O	1.7×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.7×10 <sup>-3</sup>
	Compounding – PO	8.9×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	8.9×10 <sup>-3</sup>
	Compounding – C	8.5×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	8.5×10 <sup>-4</sup>
	Conversion – O	1.5×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.5×10 <sup>-3</sup>
	Conversion – PO	1.6×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.6×10 <sup>-3</sup>
	Conversion – C	1.4×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.4×10 <sup>-3</sup>
	Compounding/ conversion – O	3.1×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.1×10 <sup>-3</sup>
	Compounding/ conversion – PO	0.010	NA <sup>a</sup>	NA <sup>a</sup>	0.010
	Compounding/ conversion – C	2.1×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.1×10 <sup>-3</sup>
	Use in rubber	Compounding/ conversion	NA <sup>a</sup>	6.0×10 <sup>-4</sup>	1.7×10 <sup>-4</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	9.8×10 <sup>-7</sup>	9.8×10 <sup>-7</sup>
	Industrial application	2.3×10 <sup>-3</sup>	8.4×10 <sup>-4</sup>	3.7×10 <sup>-5</sup>	3.2×10 <sup>-3</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in metal cutting/ working fluids	Formulation	1.2×10 <sup>-4</sup>	1.2×10 <sup>-4</sup>	NA <sup>a</sup>	2.4×10 <sup>-4</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	4.1×10 <sup>-3</sup> – 8.0×10 <sup>-3</sup>	NA <sup>a</sup>	4.1×10 <sup>-3</sup> – 8.0×10 <sup>-3</sup>
	Use in oil-based fluids (small)	0.011– 0.022	3.7×10 <sup>-3</sup> – 7.3×10 <sup>-3</sup>	NA <sup>a</sup>	0.015– 0.029
	Use in emulsifiable fluids	1.0×10 <sup>-3</sup>	4.2×10 <sup>-4</sup>	NA <sup>a</sup>	1.2×10 <sup>-3</sup>
	Use in emulsifiable fluids – intermittent release	0.91	0.30	NA <sup>a</sup>	1.2

continued overleaf

**Table 3.66 continued**

Scenario	Step	PEC <sub>local(seawater)</sub> (µg/l)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in leather fat liquors	Formulation	3.8×10 <sup>-3</sup>	1.3×10 <sup>-3</sup>	NA <sup>a</sup>	5.1×10 <sup>-3</sup>
	Use – complete processing of raw hides <sup>d</sup>	0.033	0.011	NA <sup>a</sup>	0.044
Use in textile applications		0.16	NA <sup>a</sup>	NA <sup>a</sup>	0.16
Regional sources		1.1×10 <sup>-4</sup>	1.2×10 <sup>-4</sup>	2.2×10 <sup>-7</sup>	2.3×10 <sup>-4</sup>

Notes: a NA = not applicable; no significant use of the substance in this application.  
 b The process makes no significant contribution to the levels in marine water.  
 c Total = total concentration, assuming all types of chlorinated paraffin are released from a site.  
 d The calculation for complete processing of raw hides is considered to be the most realistic scenario.  
 e Calculation for a generic site. It is known that there is only one chlorinated paraffin production site that discharges into the sea after on-site treatment of the effluent. A confidential calculation for this site indicates that the maximum concentration in seawater would be <<4×10<sup>-4</sup> µg/l.  
 O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

**Table 3.67 Predicted concentrations in marine sediment**

Scenario	Step	PEC <sub>local(marine sediment)</sub> (mg/kg wet wt.)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Production	Generic <sup>e</sup>	4.7	24	0.50	29
Use in PVC – plastisol applications	Compounding (O)	2.0	NA <sup>a</sup>	NA <sup>a</sup>	2.0
	Conversion (O)	2.0	NA <sup>a</sup>	NA <sup>a</sup>	2.0
	Compounding/ conversion (O)	3.8	NA <sup>a</sup>	NA <sup>a</sup>	3.8
Use in PVC – extrusion/ other	Compounding (O)	3.4	NA <sup>a</sup>	NA <sup>a</sup>	3.4
	Compounding (PO)	18	NA <sup>a</sup>	NA <sup>a</sup>	18
	Compounding (C)	1.7	NA <sup>a</sup>	NA <sup>a</sup>	1.7
	Conversion (O)	2.9	NA <sup>a</sup>	NA <sup>a</sup>	2.9
	Conversion (PO)	3.1	NA <sup>a</sup>	NA <sup>a</sup>	3.1
	Conversion (C)	2.7	NA <sup>a</sup>	NA <sup>a</sup>	2.7
	Compounding/ conversion (O)	6.1	NA <sup>a</sup>	NA <sup>a</sup>	6.1
	Compounding/ conversion (PO)	20	NA <sup>a</sup>	NA <sup>a</sup>	20
	Compounding/ conversion (C)	4.1	NA <sup>a</sup>	NA <sup>a</sup>	4.1
	Use in rubber	Compounding/ conversion	NA <sup>a</sup>	3.6	37
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	0.21	0.21
	Industrial application	4.5	5.1	8.0	18
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in metal cutting/ working fluids	Formulation	0.24	0.75	NA <sup>a</sup>	1.0
	Use in oil-based fluids (large)	NA <sup>a</sup>	25–48	NA <sup>a</sup>	25–48
	Use in oil-based fluids (small)	22–43	22–44	NA <sup>a</sup>	44–87
	Use in emulsifiable fluids	2.0	2.5	NA <sup>a</sup>	4.5
	Use in emulsifiable fluids – intermittent release	1,800	1,810	NA <sup>a</sup>	3,610

Table 3.67 continued overleaf

**Table 3.67 continued**

Scenario	Step	PEC <sub>local(marine sediment)</sub> (mg/kg wet wt.)			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in leather fat liquors	Formulation	7.4	8.0	NA <sup>a</sup>	15
	Use – complete processing of raw hides <sup>d</sup>	65	66	NA <sup>a</sup>	131
Use in textile applications		310	NA <sup>a</sup>	NA <sup>a</sup>	310
Regional sources		0.42	1.4	0.092	1.9

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in sediment.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

<sup>e</sup> Calculation for a generic site. It is known that there is only one chlorinated paraffin production site that discharges into the sea after on-site treatment of the effluent. A confidential calculation for this site indicates that the maximum concentration in sediment would be >>10 times smaller than for the generic site.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

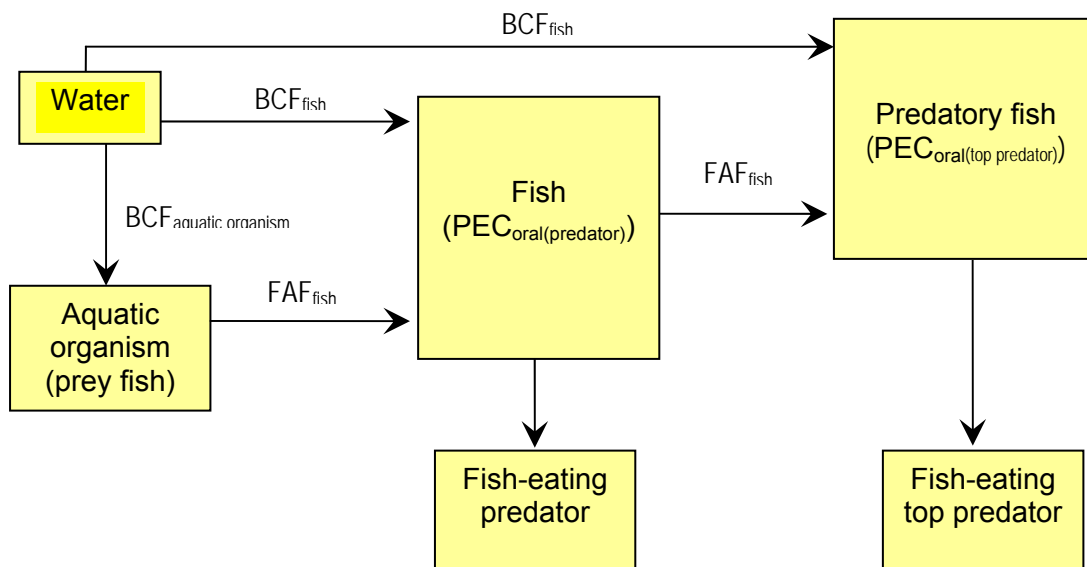
For secondary poisoning, the concentrations in predators and top predators have been estimated using the following equations given in the TGD.

$$PEC_{\text{oral(predator)}} = 0.5 \times (PEC_{\text{local(seawater, ann)}} + PEC_{\text{regional(seawater, ann)}}) \times BCF_{\text{fish}} \times BMF_1$$

$$PEC_{\text{oral(top predator)}} = (0.1 \times PEC_{\text{local(seawater, ann)}} + 0.9 \times PEC_{\text{regional(seawater, ann)}}) \times BCF_{\text{fish}} \times BMF_1 \times BMF_2$$

Similar to the situation for secondary poisoning discussed in Section 3.3.4.1, the above equations given in the TGD may not be appropriate when considering actual BMF data from feeding studies. The intention in the TGD is to model the concentration in fish resulting from simultaneous exposure via both water and food in a simplified food chain. An example scheme which uses this available food uptake data for LCCPs is presented in Figure 3.7. The term food accumulation factor (FAF) is used in this scheme to distinguish it from the BMF given in the equation from the TGD. It should be noted that this scheme differs from the one used in the TGD, where the top predator could be a predatory mammal or bird that feeds on other marine mammals or birds (a different equation would be needed for such food chains). However, the scheme presented does allow the available food uptake data for LCCPs by fish to be used in an extended food chain.





**Figure 3.7 Feeding scheme with simultaneous exposure via both water and food**

Assuming that the “aquatic organism” in the food chain is also a fish, then the appropriate equations for this scheme are as follows.

$$PEC_{oral(predator)} = PEC_{water} \times BCF_{fish} \times (1 + FAF_{fish}) \quad \text{- equation 3.}$$

$$PEC_{oral(top\ predator)} = (1 + FAF_{fish})^2 \times BCF_{fish} \times PEC_{water} \quad \text{- equation 4.}$$

Using a FAF (BMF) of 1 for both  $C_{18-20}$  liquid and  $C_{>20}$  liquid chlorinated paraffins, and a value  $\ll 1$  for  $C_{>20}$  solid chlorinated paraffins as before, the resulting PECs for predators and top predators using equations 3 and 4 would be around two times higher using this alternate method than using the TGD method for predators, and around four times higher for top predators for both the  $C_{18-20}$  liquid and  $C_{>20}$  liquid chlorinated paraffins, but would lead to essentially the same PECs as the TGD method for the  $C_{>20}$  solid chlorinated paraffins.

**Table 3.68 Predicted concentrations for marine predators**

Scenario	Step	PEC <sub>local(marine predators)</sub> (mg/kg wet wt.)			
		C <sub>18-20 liquid</sub> <sup>e</sup>	C <sub>&gt;20 liquid</sub> <sup>e</sup>	C <sub>&gt;20 solid</sub>	Total <sup>c</sup>
Production	Generic	1.2×10 <sup>-3</sup>	3.3×10 <sup>-4</sup>	1.1×10 <sup>-9</sup>	1.5×10 <sup>-3</sup>
Use in PVC – plastisol applications	Compounding (O)	1.6×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.6×10 <sup>-4</sup>
	Conversion (O)	1.6×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.6×10 <sup>-4</sup>
	Compounding/ conversion (O)	2.1×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.1×10 <sup>-4</sup>
Use in PVC – extrusion/ other	Compounding (O)	2.0×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.0×10 <sup>-4</sup>
	Compounding (PO)	5.5×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	5.5×10 <sup>-4</sup>
	Compounding (C)	1.5×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.5×10 <sup>-4</sup>
	Conversion (O)	1.8×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.8×10 <sup>-4</sup>
	Conversion (PO)	1.9×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.9×10 <sup>-4</sup>
	Conversion (C)	1.8×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.8×10 <sup>-4</sup>
	Compounding/ conversion (O)	2.6×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-4</sup>
	Compounding/ conversion (PO)	6.2×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	6.2×10 <sup>-4</sup>
Use in rubber	Compounding/ conversion	2.1×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.1×10 <sup>-4</sup>
	Compounding/ conversion (C)	NA <sup>a</sup>	5.5×10 <sup>-5</sup>	5.1×10 <sup>-9</sup>	5.5×10 <sup>-5</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	5.3×10 <sup>-10</sup>	5.3×10 <sup>-10</sup>
	Industrial application	1.1×10 <sup>-3</sup>	8.0×10 <sup>-5</sup>	1.5×10 <sup>-8</sup>	1.2×10 <sup>-3</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in metal cutting/ working fluids	Formulation	1.2×10 <sup>-4</sup>	2.3×10 <sup>-5</sup>	NA <sup>a</sup>	1.4×10 <sup>-4</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	3.4×10 <sup>-4</sup> –	NA <sup>a</sup>	3.4×10 <sup>-4</sup> –
		6.5×10 <sup>-4</sup>	6.5×10 <sup>-4</sup>		
	Use in oil-based fluids (small)	5.1×10 <sup>-3</sup> –	3.1×10 <sup>-4</sup> –	NA <sup>a</sup>	5.4×10 <sup>-3</sup> –
		0.010	5.9×10 <sup>-4</sup>		0.011
Use in emulsifiable fluids	5.3×10 <sup>-4</sup>	4.7×10 <sup>-5</sup>	NA <sup>a</sup>	5.8×10 <sup>-4</sup>	
Use in emulsifiable fluids – intermittent release	2.9×10 <sup>-3</sup>	1.8×10 <sup>-4</sup>	NA <sup>a</sup>	3.1×10 <sup>-3</sup>	

Table 3.68 continued overleaf

**Table 3.68 continued**

Scenario	Step	PEC <sub>local(marine predators)</sub> (mg/kg wet wt.)			
		C <sub>18-20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in leather fat liquors	Formulation	6.6×10 <sup>-4</sup>	3.8×10 <sup>-5</sup>	NA <sup>a</sup>	7.0×10 <sup>-4</sup>
	Use – complete processing of raw hides <sup>d</sup>	5.1×10 <sup>-3</sup>	1.5×10 <sup>-4</sup>	NA <sup>a</sup>	5.3×10 <sup>-3</sup>
Use in textile applications		0.071	NA <sup>a</sup>	NA <sup>a</sup>	0.071

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in fish.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

<sup>e</sup> The PECs for C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins would be around two times higher using the alternate method of calculation.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

**Table 3.69 Predicted concentrations for marine top predators**

Scenario	Step	PEC <sub>local(marine top predators)</sub> (mg/kg wet wt.)			
		C <sub>18-20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Production	Generic	3.2×10 <sup>-4</sup>	8.4×10 <sup>-5</sup>	3.9×10 <sup>-10</sup>	4.0×10 <sup>-4</sup>
Use in PVC – plastisol applications	Compounding (O)	1.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
	Conversion (O)	1.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
	Compounding/ conversion (O)	1.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
Use in PVC – extrusion/ other	Compounding (O)	1.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
	Compounding (PO)	2.0×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.0×10 <sup>-4</sup>
	Compounding (C)	1.2×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.2×10 <sup>-4</sup>
	Conversion (O)	1.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
	Conversion (PO)	1.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
	Conversion (C)	1.3×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
	Compounding/ conversion (O)	1.5×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.5×10 <sup>-4</sup>
	Compounding/ conversion (PO)	2.2×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.2×10 <sup>-4</sup>
	Compounding/ conversion (C)	1.4×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.4×10 <sup>-4</sup>
Use in rubber	Compounding/ conversion	NA <sup>a</sup>	2.9×10 <sup>-5</sup>	1.2×10 <sup>-9</sup>	2.9×10 <sup>-5</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	2.8×10 <sup>-10</sup>	2.8×10 <sup>-10</sup>
	Industrial application	3.1×10 <sup>-4</sup>	3.4×10 <sup>-5</sup>	3.2×10 <sup>-9</sup>	3.4×10 <sup>-4</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>
Use in metal cutting/ working fluids	Formulation	1.2×10 <sup>-4</sup>	2.3×10 <sup>-5</sup>	NA <sup>a</sup>	1.4×10 <sup>-4</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	8.6×10 <sup>-5</sup> – 1.5×10 <sup>-4</sup>	NA <sup>a</sup>	8.6×10 <sup>-5</sup> – 1.5×10 <sup>-4</sup>
	Use in oil-based fluids (small)	1.1×10 <sup>-3</sup> – 2.1×10 <sup>-3</sup>	8.0×10 <sup>-5</sup> – 1.4×10 <sup>-4</sup>	NA <sup>a</sup>	1.2×10 <sup>-3</sup> – 2.2×10 <sup>-3</sup>
	Use in emulsifiable fluids	2.0×10 <sup>-4</sup>	2.8×10 <sup>-5</sup>	NA <sup>a</sup>	2.3×10 <sup>-4</sup>
	Use in emulsifiable fluids – intermittent release	6.6×10 <sup>-4</sup>	5.5×10 <sup>-5</sup>	NA <sup>a</sup>	7.2×10 <sup>-4</sup>

Table 3.69 continued overleaf

**Table 3.69 continued**

Scenario	Step	PEC <sub>local(marine top predators)</sub> (mg/kg wet wt.)			
		C <sub>18-20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in leather fat liquors	Formulation	2.3×10 <sup>-4</sup>	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	2.6×10 <sup>-4</sup>
	Use – complete processing of raw hides <sup>d</sup>	1.1×10 <sup>-3</sup>	4.9×10 <sup>-5</sup>	NA <sup>a</sup>	1.1×10 <sup>-3</sup>
Use in textile applications		0.014	NA <sup>a</sup>	NA <sup>a</sup>	0.014

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in fish.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

<sup>e</sup> The PECs for C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins would be around two times higher using the alternate method of calculation.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

### 3.3.5.2 Measured data

The available measured data for LCCPs are summarised in Section 3.3.1.3 (water and sediment) and Section 3.3.4.2 (biota).

For marine water, LCCPs have been found at concentrations up to 2 µg/l in samples from around the United Kingdom (Campbell and McConnell, 1980). LCCPs have also been found to be present in marine sediments. A range of concentrations have been measured, for example:

- around 12.3–12.5 µg/kg were measured in off-shore mudflats at Kaiser Wilhelm Koog and Den Helder (Greenpeace (1995) estimation from the total chlorinated paraffin concentration, assuming that the LCCPs accounted for 10–60 per cent of the total);
- up to 10.5 µg/kg dry weight in estuarine samples from Western Europe (van Zeijl (1997) measured the total chlorinated paraffin concentration, but LCCPs with chlorine contents around 42% wt. were thought to be the predominant type of chlorinated paraffin found in the samples);
- up to 600 µg/kg in marine sediments from around the UK (Campbell and McConnell, 1980);
- up to 3.2 mg/kg dry weight in marine sediments close to a chlorinated paraffin manufacturing site in Australia (Kemmlin *et al.*, 2002).

For marine biota, LCCPs have been detected in marine fish (up to 200 µg/kg wet wt.) and mussels (up to 100 µg/kg wet wt.) from around the UK (Campbell and McConnell, 1980); mussels (9.3 mg/kg lipid) and crab (14.3 mg/kg lipid) from close to a chlorinated paraffin production site in Australia (Kemmlin *et al.*, 2002). They have also been detected in mackerel (at 225 µg/kg lipid), fish (herring) oil (at 50 µg/kg lipid), porpoise (at 13–107 µg/kg lipid) and fin whale (at 819 µg/kg lipid) samples (Greenpeace (1995),

estimated from the total chlorinated paraffin concentration, assuming that the LCCPs accounted for 53.4–94 per cent of the total).

### 3.3.5.3 *Comparison of predicted and measured levels*

The comparison of the predicted and measured levels is complicated by the fact that some of the analyses carried out so far have not analysed specifically for LCCPs, and the data are often not related to specific sources of release. From the available studies where LCCPs have been specifically identified, concentrations up to around 225 µg/kg lipid have been measured in marine fish, with higher concentrations of up to 14.3 µg/kg lipid and 819 µg/kg lipid being reported in crabs and whales respectively.

The limited data available for fish agree reasonably well with the predicted concentrations. For example the PECs for marine predators are in the general range 0.1–10 µg/kg wet weight, with a maximum of 71 µg/kg wet weight, and those for marine top predators are in the general range 0.1–2 µg/kg wet weight, with a maximum of 14 µg/kg wet weight. Taking 8 per cent as a typical lipid content for fish, these concentrations are equivalent to 1–125 µg/kg lipid (predators) and 1–25 µg/kg lipid (top predators), with a maximum of 890 µg/kg lipid (predators) and 175 µg/kg lipid (top predators).

For surface water and sediment, few data are available and it is not possible to carry out a meaningful comparison of the predicted and measured concentrations. For sediment it is, however, worth noting that the predicted concentrations of LCCPs are generally of a similar order to the concentration measured in marine sediment close to a known potential emission source in Australia (a chlorinated paraffin manufacturing site).

# 4. Effects assessment: Hazard identification and dose (concentration) – response (effect) assessment

## 4.1 Aquatic compartment (including sediment)

The following sections review the available toxicity data for aquatic organisms. Where possible, a validity marking is given for each study (this appears in the summary tables within each section).

The following validity markings have been used:

- 1 Valid without restriction**  
The test is carried out to internationally recognised protocols (or equivalent protocols) and all or most of the important experimental details are available.
- 2 Use with care**  
The test is carried out to internationally recognised protocols (or equivalent protocols), but either some important experimental details are missing, or the method used or the endpoint studied in the test means that interpretation of the results is not straightforward.
- 3 Not valid**  
There is a clear deficiency in the test that means that the results cannot be considered as valid.
- 4 Not assignable**  
Insufficient detail is available on the method used to allow a decision to be made on the validity of the study.

In terms of the risk assessment, toxicity data assigned a validity marking of 1 or 2 will be considered suitable for deriving the PNEC.

Several of the tests are unpublished studies carried out by industry or other organisations. It has not been possible to validate all of these tests within the scope of this report and these are assigned a validity marking of 4 unless it is clear that there are some aspects of the test that invalidate the results (for these, a validity marking of 3 is given). The studies given a validity marking of 4 have also been considered along with the studies assigned a validity marking of 1 and 2 when deriving the PNEC.

### 4.1.1 Toxicity to fish

The toxicity of LCCPs to fish is summarised in Table 4.1.

Madeley and Birtley (1980) summarised the results of acute toxicity tests using a C<sub>20-30</sub>, 42% wt. Cl product with rainbow trout (*Oncorhynchus mykiss*). A concentrated emulsion of the chlorinated paraffin was prepared and dilutions of this emulsion were used in the test. No further information is available on the media preparation technique. A semi-static test system was used, with the test solution being renewed every 24 hours. The tests were carried out at a temperature of 15±1°C for 96 hours with 10 fish at each exposure concentration. The emulsion concentration was verified by measurement (using infrared spectrophotometry after solvent extraction of the chlorinated paraffin). Some loss of chlorinated paraffin from the test emulsions was seen, particularly at the higher concentrations tested, so the results are based on the mean measured level found in the emulsions. No toxicity or unusual behaviour was seen at the highest concentration tested (the mean measured emulsion concentration was 770 mg/l).

Johnson and Finley (1980) summarised the results of acute toxicity tests carried out by the Columbia National Fisheries Research Laboratory over the years 1965–1978. Few details of the test methods are available, and so it is not possible to validate these data. The 96-hour LC<sub>50</sub> values reported for LCCPs with both rainbow trout (*Oncorhynchus mykiss*) and bluegill sunfish (*Lepomis macrochirus*) were >300 mg/l for a C<sub>>20</sub>, 40–42% wt. Cl product, >300 mg/l for a C<sub>>20</sub>, 48–54% wt. Cl product and >300 mg/l for a C<sub>>20</sub>, 70% wt. Cl product. The paper also reports similar results for a commercial product (Chlorowax LV) with rainbow trout and bluegill sunfish. The IUCLID (2000a) datasheet indicates that this substance is a C<sub>>17</sub>, 39% wt. Cl product.

Hoechst AG (1976 and 1977) reported the results of acute toxicity tests using several LCCPs with golden orfe (*Leuciscus idus*). Few details of the test methodology are available and so it is not possible to validate these data. The results are reported in Table 4.1 as supporting information.

The IUCLID (2000a) datasheet contains a further 96h LC<sub>50</sub> value of >300 mg/l for channel catfish (*Ictalurus punctatus*), but the substance tested was not identified. It has not been possible to trace the origin of this result, although it is possible that it is part of the Johnson and Finley (1980) dataset. If this is the case, then the result most probably refers to a short-chain chlorinated paraffin (C<sub>10-13</sub>, 60–65% wt. Cl), and so the result is not considered further in this assessment.

Lindén *et al.* (1979) studied the toxicity of a C<sub>22-26</sub>, 42% wt. Cl product over 96 hours with bleak (*Alburnus alburnus*) in brackish water. The tests were carried out under static conditions with no aeration (the dissolved oxygen level was measured at the end of the test and was considered to be acceptable if the concentration was ≥5 mg/l). The water used in the test had a salinity of 7‰, a temperature of 10°C and a pH of around 7.8. Six test concentrations and one control were used in the test, with groups of 10 fish exposed at each concentration. The test substance was firstly dissolved in acetone prior to addition to the test chamber; the concentration of acetone in the final solution was ≤0.5 mg/l. No monitoring of the actual concentration of the test substance was carried out during the test, and the 96h LC<sub>50</sub> was determined as >5,000 mg/l based on the nominal concentration added at the start of the test.

Bengtsson *et al.* (1979) also studied the toxicity of an LCCP in bleak (*Alburnus alburnus*) as part of a bioaccumulation study. The chlorinated paraffin tested was a C<sub>18-26</sub>, 49% wt. Cl substance. The tests were performed at 10°C using a semi-static procedure in which the test solutions containing 125 µg/l of the substance were



renewed every two to three days over the 14-day exposure period. The water used in the experiment was Baltic Sea water with a salinity of 7‰, and acetone was present in all aquaria, including controls at a concentration of 0.1 ml/l. The fish used in the experiment had an average weight of 4.5 g and were not fed during the exposure period. Six groups of 15 fish were used for both the exposure and control solutions. No mortality or effect on behaviour was seen in fish exposed to the LCCP during the test.

The toxicity of two LCCPs in rainbow trout (*Oncorhynchus mykiss*) has been studied over 60 days in a GLP study (Madeley and Maddock, 1983a and 1983b). The substances tested were a C<sub>22-26</sub>, 43% wt. Cl commercial product and a C<sub>>20</sub>, 70% wt. Cl product. Both products were mixed with an n-pentacosane-13-<sup>14</sup>C that had been chlorinated to a similar degree. Neither of the commercial products tested contained a stabiliser. A flow-through system was used for each test and the concentrations of chlorinated paraffin were determined by both radioactivity measurements and parent compound analysis (using a TLC technique). The tests were carried out at 12±1°C. For the tests with the 43% wt. Cl product the water quality parameters were: dissolved oxygen 9.3–11.4 mg/l; pH 7.4–8.55; hardness 42–71 mg/l as CaCO<sub>3</sub>. Similarly for the tests with the 70% wt. Cl product the water quality parameters were: dissolved oxygen 10.4–12.5 mg/l; pH 7.5–8.1; hardness 36–46 mg/l as CaCO<sub>3</sub>. The fish were fed a diet of proprietary trout food throughout the test at a rate of two per cent of body weight per day. The major endpoint determined at the end of the studies was mortality.

Qualitative observations were also made in these studies on behaviour (the control fish were assumed to show "normal" behaviour) in terms of:

- swimming behaviour;
- general behaviour of individuals (e.g. intense activity, sluggishness, quiescence, position in test vessel);
- response to presence of food;
- skin pigmentation.

These observations were made because certain tests using another type of chlorinated paraffin (e.g. short-chain chlorinated paraffins) had shown effects on behaviour in similar tests.

In both tests, fish were introduced into the exposure vessels one week prior to addition of the test substance. At the start of the test, the chlorinated paraffin (as an acetone solution) was added to the in-flowing water. The flow-through system had a 95 per cent replacement time of around seven hours, so the actual exposure concentration would have reached the steady state level within a relatively short space of time. The fish used in the study weighed 1.4–3.2 g (for the experiments with 43% wt. Cl substances) and 0.53–2.77 g (for the experiments with the 70% wt. Cl substance) at the start of the study; groups of 30 fish were used at each exposure concentration.

For the C<sub>22-26</sub>, 43% wt. Cl substance (Madeley and Maddock, 1983a), two nominal exposure concentrations of 1.0 and 3.2 mg/l were used. Acetone at a concentration of 500 ppm (0.5 ml/l) was also present in the test solutions and so acetone controls were also run in the test. The actual mean measured exposure concentrations during the test were 0.97 mg/l and 4.0 mg/l at the two exposure concentrations respectively. These values were based on <sup>14</sup>C measurements (parent compound analysis was in general agreement with these values).

No fish died during the study. One fish was lost from the acetone control (assumed to have escaped), and no significant effects were seen on behaviour of the exposed fish compared with controls. The NOEC from this study was therefore reported as 4.0 mg/l, the highest concentration tested. The test report gives details of the fish weights and lengths at the end of the study. These were 9.46 g and 84.2 mm in the freshwater controls; 9.23 g and 81.2 mm in the acetone controls, 8.59 g and 81.5 mm in the 0.97 mg/l exposure group and 8.38 g (this is incorrectly given as 7.38 g in the original report) and 80.7 mm in the 4.0 mg/l exposure group. These weight data are not commented on in the report but have subsequently been analysed statistically to show that there were no significant ( $p=0.05$ ) differences in mean fish weights between the exposed populations or the control or solvent control populations (Thompson, 2001). The mean length of the fish was similar in all exposed and control populations.

For the C<sub>>20</sub>, 70% wt. Cl substance (Madeley and Maddock, 1983b), three nominal exposure concentrations of 1.0 mg/l, 2.1 mg/l and 4.2 mg/l were used. Acetone at a concentration of 500 ppm (0.5 ml/l) for the two lower exposure concentrations or 1,000 ppm (1 ml/l) for the higher exposure concentration was also present (two acetone controls were also run). The mean measured exposure concentrations by <sup>14</sup>C analysis were 0.84 mg/l, 1.9 mg/l and 3.8 mg/l in the three test solutions respectively (parent compound analysis gave similar values).

No significant mortalities occurred as a result of the exposures. A small number of deaths or losses did occur in all exposure vessels, but this was not considered unusual in a 60-day study. Abnormal behaviour (a few individuals were slow to respond to the presence of food and showed a darkening of skin pigmentation) was observed in all populations, including controls. These symptoms became apparent on day 3 and had disappeared by day 7. A similar behaviour re-occurred in the acetone control populations between days 12–16. Subsequently, all populations behaved normally except for isolated occurrences. In the early part of the study, the fish in the 3.8 mg/l group, and to a lesser extent the 1.9 mg/l group, found it difficult to locate their food due to the cloudy nature of the suspensions tested, however they later appeared to become acclimatised to the test conditions. It was concluded that no chemical-related effects on the behaviour of the fish was seen in the study. Although the test report provides no comment, mean fish weights and lengths were also reported. These were 3.87 g and 59.2 mm in the freshwater controls, 4.14 g and 60.9 mm in the 500 ppm acetone controls, 3.70 g and 59.5 mm in the 1,000 ppm acetone controls, 4.74 g and 65.3 mm in the 0.84 mg/l exposure group, 5.05 g and 66.0 mm in the 1.9 mg/l exposure group and 4.11 g and 62.4 mm in the 3.8 mg/l exposure group. Although it is not possible to analyse these data statistically, it is clear that no effects on growth were seen as a result of the chlorinated paraffin treatments in this test. The NOEC from this study is therefore 3.8 mg/l.

Zitko (1974) determined LT<sub>50</sub> values (time for 50 per cent of the fish to die) for juvenile Atlantic salmon (*Salmo salar*) in a long-term feeding study. Two LCCPs were used in the study; a C<sub>>20</sub>, 42% wt. Cl product and a C<sub>>20</sub>, 70% wt. Cl product. In the study, 20 juvenile fish were kept in 20 litre tanks with a continuous flow of fresh water (500 ml/minute). The chlorinated paraffins were administered in the diet (trout chow) for 181 days. The concentrations of the chlorinated paraffins used were either 10 or 100 mg/kg food, and around 8 g of the food was added to the tanks during the course of a week.

During the experiment mortalities occurred in all fish populations, including the control groups. The authors suggested that the mortalities seen in the control group were a result of the use of nutritionally deficient food in the test. In particular, the lipid content of the fish food used was later found to have decreased from the normal value of 5–8

per cent to ~2.5 per cent towards the end of the study; it was thought that this decrease may have been caused by auto-oxidation of the lipids present in the food, possibly forming toxic products. The  $LT_{50}$  value for the control population was determined as 138 days. The  $LT_{50}$  values for the exposed populations were lower than this at 47 and 80 days for the  $C_{>20}$ , 42% wt. Cl substance and 71 and 39 days for the  $C_{>20}$ , 70% wt. Cl substance for doses of 10 and 100 mg/l respectively. The authors interpreted these results as providing an indication that the LCCPs are toxic to salmon via the diet. However, given the deficiencies of the study, particularly the response of the control population, the validity of these findings is questionable.

**Table 4.1 Toxicity to fish**

Species	Substance tested	Comments	Results	Reference	Val. <sup>a</sup>
Bleak ( <i>Alburnus alburnus</i> )	C <sub>22-26</sub> , 42% wt. Cl	Static test; acetone as cosolvent; 10°C, brackish water (7‰), nominal concentrations. No effects seen at solubility.	96h LC <sub>50</sub> >5,000 mg/l	Lindén <i>et al.</i> , 1979.	2
	C <sub>18-26</sub> , 49% wt. Cl	Semi-static bioaccumulation test, 10°C, brackish water (7‰), nominal concentrations. No effects seen at solubility.	14-day NOEC ≥0.125 mg/l	Bengtsson <i>et al.</i> , 1979	2
	C <sub>18-26</sub> , 49% wt. Cl	Observations as part of an accumulation study. No mortalities seen during 91 days exposure in food. No effects seen.	91-day LC <sub>0</sub> >3,400 mg/kg food	Bengtsson and Baumann Ofstad, 1982	2
Bluegill sunfish ( <i>Lepomis macrochirus</i> )	Chlorowax LV	Static test, 20°C, nominal concentrations. Test substance tentatively identified as C <sub>&gt;17</sub> , 39% wt. Cl. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	3
	C <sub>&gt;20</sub> , 40–42% wt. Cl	Static test, 20°C, nominal concentrations. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	2
	C <sub>&gt;20</sub> , 48–54% wt. Cl	Static test, 20°C, nominal concentrations. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	2
	C <sub>&gt;20</sub> , 70% wt. Cl	Static test, 20°C, nominal concentrations. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	2

Table 4.1 continued overleaf

**Table 4.1 continued**

Species	Substance tested	Comments	Results	Reference	Val. <sup>a</sup>
Golden orfe ( <i>Leuciscus idus</i> )	C <sub>18-20</sub> , 35% wt. CI	Static test, substance added directly to test vessel. Effects seen at concentrations above solubility.	48h toxic threshold = 400 mg/l	Hoechst AG, 1976	3
	C <sub>18-20</sub> , 44% wt. CI	Static test, substance added directly to test vessel. Effects seen at concentrations above solubility.	48h toxic threshold = 500 mg/l	Hoechst AG, 1976	3
	C <sub>18-20</sub> , 49% wt. CI	Static test, substance added directly to test vessel. No effects seen at solubility.	48h toxic threshold >500 mg/l	Hoechst AG, 1976	2
	C <sub>18-20</sub> , 52% wt. CI	Static test. No effects seen at solubility.	48h toxic threshold >500 mg/l	Hoechst AG, 1977	2
Rainbow trout ( <i>Oncorhynchus mykiss</i> )	Chlorowax LV	Static test; 10°C, nominal concentration. Test substance tentatively identified as C <sub>&gt;17</sub> , 39% wt. CI. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	3
	C <sub>&gt;20</sub> , 40–42% wt. CI	Static test; 10°C, nominal concentration. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	2
	C <sub>20-30</sub> , 42% wt. CI	Substance tested as an emulsion. Semi-static test; 15°C, measured emulsion concentrations. No effects seen at solubility.	96h LC <sub>50</sub> >770 mg/l	Madeley and Birtley, 1980	2
	C <sub>&gt;20</sub> , 48–54% wt. CI	Static test; 10°C, nominal concentrations. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	2
	C <sub>&gt;20</sub> , 70% wt. CI	Static test; 10°C, nominal concentrations. No effects seen at solubility.	96h LC <sub>50</sub> >300 mg/l	Johnson and Finley, 1980	2

Table 4.1 continued overleaf

**Table 4.1 continued**

Species	Substance tested	Comments	Results	Reference	Val. <sup>a</sup>
Rainbow trout ( <i>Oncorhynchus mykiss</i> )	C <sub>22-26</sub> , 43% wt. CI	Flow-through test; acetone as cosolvent; measured concentrations. No effects seen at solubility.	60-day NOEC ≥4 mg/l	Madeley and Maddock, 1983a	2
	C <sub>&gt;20</sub> , 70% wt. CI	Flow-through test; acetone as cosolvent; measured concentrations. No effects seen at solubility.	60-day NOEC ≥3.8 mg/l	Madeley and Maddock, 1983b	2
Atlantic salmon ( <i>Salmo salar</i> )	C <sub>&gt;20</sub> , 42% wt. CI	Feeding study. A high level of mortality was seen in the control population. The results are not considered valid.	LT <sub>50</sub> = 47 days at 10 mg/kg food LT <sub>50</sub> = 80 days at 100 mg/kg food	Zitko, 1974	3
	C <sub>&gt;20</sub> , 70% wt. CI	Feeding study. A high level of mortality was seen in the control population. The results are not considered valid.	LT <sub>50</sub> = 71 days at 10 mg/kg food LT <sub>50</sub> = 39 days at 100 mg/kg food	Zitko, 1974	3

Note: <sup>a</sup> Validity markings: 1 – Valid without restriction; 2 – Use with care; 3 – Not valid; 4 – Not assignable.

In contrast to these results, Bengtsson and Baumann Ofstad (1982) found no mortality occurred in bleak (*Alburnus alburnus*) fed on a diet containing a C<sub>18-26</sub>, 49% wt. Cl product at concentrations up to 3,400 mg/kg food for 91 days. Although this study was designed to investigate bioaccumulation rather than toxicity, it does provide further evidence that the results from the Zitko (1974) are uncertain.

#### 4.1.2 Toxicity to aquatic invertebrates

The results of the available toxicity tests with aquatic invertebrates are summarised in Table 4.2.

Frank (1993) carried out a series of acute and longer-term studies with *Daphnia magna* using a commercial C<sub>18-20</sub>, 52% wt. Cl product. The tests were carried out using dilutions of the water-soluble fraction of the chlorinated paraffin. Stock solutions of the chlorinated paraffin were made up in water to give nominal concentrations of either 100 mg/l or 10 g/l. The 100 mg/l solution was sonicated for one hour and then left to stand in the dark for 48 hours before use. The 10 g/l solution also stood for 48 hours in the dark before use, but this time without sonication. After this period, both solutions were filtered firstly with glass filters and then with membrane filters to remove undissolved test material (microscopic and spectroscopic investigation of the filtered solutions gave no indication of the presence of droplets) to give the respective water-soluble fractions. The concentration of the chlorinated paraffin in the water-soluble fractions was determined by AOX (adsorbable organic halogen) analysis. The detection limit of the method used was around 10 µg Cl/l, which is equivalent to around 20 µg/l of the chlorinated paraffin. This analysis showed that the concentration of chlorinated paraffin present in the water-soluble fraction was around 462–519 µg/l for the 10 g/l nominal solution but was not detectable in the 100 mg/l solution (i.e. <20 µg/l).

Experiments were carried out to show that in the test vessels, although the concentration of chlorinated paraffin present fell over time, it remained within 80 per cent of the initial concentration over 2–3 days. This time period was used in the long-term tests as the renewal period for the solution (semi-static method).

Acute (48-hour) toxicity tests were carried out using dilutions of the two prepared water-soluble fractions (the actual dilutions used are not explicitly stated in the paper but there was a factor of 2 between each dilution step used). The method used was DIN 38 412, Teil 11, which is equivalent to the OECD 202 method. In the test using the water-soluble fraction from the 100 mg/l nominal solutions, no toxicity was seen at concentrations up to the undiluted stock solution. In the experiment using the 10 g/l nominal stock solution an EC<sub>0</sub> of 360 µg/l and an EC<sub>15</sub> of 500 µg/l was determined (maximum mortality seen was 15 per cent).

**Table 4.2 Toxicity to invertebrates**

Species	Substance tested	Comments	Results	Reference	Val. <sup>a</sup>
Water flea ( <i>Daphnia magna</i> )	C <sub>18-20</sub> , 52% wt. Cl	Tested as water-soluble fraction; measured results; variable results.	48h EC <sub>0</sub> = 0.36 mg/l 48h EC <sub>15</sub> = 0.4–0.5 mg/l	Frank, 1983; Frank and Steinhäuser, 1994	2
	C <sub>18-20</sub> , 52% wt. Cl	Tested as water-soluble fraction from a 10 g/l nominal solution; semi-static test; measured dissolved concentrations	21-day NOEC = 0.029–0.032 mg/l	Frank, 1983; Frank and Steinhäuser, 1994	2
		Tested as water-soluble fraction from a 100 mg/l nominal solution; semi-static test; dissolved concentrations based on detection limit of analytical method	Result unreliable due to inappropriate statistical analysis.		
		Tested as water-soluble fraction from a 1 mg/l nominal solution; semi-static test; actual dissolved concentrations unknown	No effects seen in 21-day study.		
	C <sub>18-20</sub> , 52% wt. Cl	Saturated test solution was generated using a column method. Substance tested contained a stabiliser. The mean number of young per adult was reduced compared to the control groups, but it is not clear if this was statistically significant or not.	Effects on reproduction may have occurred at around 2 µg/l	TNO, 1993	2
	C <sub>18-27</sub> , 60% wt. Cl	Static test; unstabilised product; emulsifier. Effects seen at concentrations above solubility.	24h NOEC = 23 mg/l 24h EC <sub>50</sub> = 102 mg/l	BUA, 1992	3
C <sub>18-27</sub> , 60% wt. Cl	Static test; stabilised product; emulsifier. Effects seen at concentrations above solubility.	24h NOEC = 45 mg/l 24h EC <sub>50</sub> = 149 mg/l	BUA, 1992	3	

Table 4.2 continued overleaf



**Table 4.2 continued**

Species	Substance tested	Comments	Results	Reference	Val. <sup>a</sup>
Water flea ( <i>Daphnia magna</i> ) – continued	C <sub>18-27</sub> , 60% wt. Cl	Static test; unstabilised product; acetone as cosolvent. Effects seen at concentrations above solubility.	24h NOEC = 100 mg/l 24h EC <sub>50</sub> = 553 mg/l	BUA, 1992	3
	C <sub>18-27</sub> , 60% wt. Cl	Static test; stabilised product; acetone as cosolvent. Effects seen at concentrations above solubility.	24h NOEC = 100 mg/l 24h EC <sub>50</sub> = 1,024 mg/l	BUA, 1992	3
	C <sub>18-27</sub> , 60% wt. Cl	Emulsifier. Effects seen at concentrations above solubility.	21-day NOEC = 4.2 mg/l 21-day EC <sub>50</sub> = 40.8 mg/l	BUA, 1992	3
	C <sub>&gt;20</sub> , 43% wt. Cl	Water accommodated fraction tested. No effects seen at initial loadings of 0.21, 1.0 and 5.1 mg/l. It is not clear if the equilibration time was sufficient to allow a saturated solution to be prepared.	No adverse effects seen over 48 hours.	Thompson, 2005	2
	C <sub>&gt;20</sub> , 43% wt. Cl	No effects were seen on reproduction. The adult survival in some of the exposures was lower than the control and solvent control populations but this was not statistically significant.	21-day NOEC for reproduction ≥55 µg/l	Sharpe and Penwell, 2007	2
Mussel ( <i>Mytilus edulis</i> )	C <sub>22-26</sub> , 43% wt. Cl	No mortality seen. Endpoint = decreased filtration activity. No effects seen at solubility.	60-day NOEC/LOEC = 2.18 mg/l	Madeley and Thompson, 1983a	2
	C <sub>&gt;20</sub> , 70% wt. Cl	No mortality seen. Endpoint = decreased filtration activity. No effects seen at solubility.	60-day NOEC/LOEC = 1.33 mg/l	Madeley and Thompson, 1983b	2
Marine crustacean ( <i>Nitocra spinipes</i> )	C <sub>22-26</sub> , 42% wt. Cl	No details available.	96h LC <sub>50</sub> >1,000 mg/l	Tarkpea <i>et al.</i> , 1981	4
	C <sub>18-26</sub> , 49% wt. Cl	No details available.	96h LC <sub>50</sub> >10,000 mg/l	Tarkpea <i>et al.</i> , 1981	4

Note: <sup>a</sup> Validity markings: 1 – Valid without restriction; 2 – Use with care; 3 – Not valid; 4 – Not assignable.

These same results (recalculated as EC<sub>0</sub> of 357 µg/l and EC<sub>15</sub> of 400 µg/l for the 10 g/l nominal stock solution), along with the results of another acute test using the same methodology, are reported in Frank and Steinhäuser (1994). In this case, the mean concentration of the chlorinated paraffin in the 10 g/l nominal and 100 mg/l nominal stock solutions was given as 578 µg/l and 35 µg/l respectively. No effects were seen in the repeat acute toxicity tests with the 100 mg/l nominal stock solution (EC<sub>0</sub> ≥26 µg/l) or the 10 g/l nominal stock solution (EC<sub>0</sub> ≥877 µg/l). The authors noted that the effects seen in the acute tests showed poor reproducibility, probably because effects were seen only around the solubility limit in the test system used. However, the authors thought that the possibility of undissolved droplets affecting the results could be ruled out as floating *Daphnia* were only sporadically observed in the test. Nevertheless, the results of this test should be treated with caution, as the effects were mainly seen in the saturated solutions only.

Long-term (21-day) reproduction studies were also performed using dilutions of the water-soluble fractions of the two stock solutions. The dilutions used were 1:2, 1:4, 1:8 and 1:16 for the 100 mg/l loading and 1:4, 1:8, 1:16, 1:32 and 1:64 for the 10 g/l loading. In these experiments, the test medium was changed three times per week and 10 animals were used per concentration. The tests were carried out at 20°C and a pH of 7.79–8.44.

Two endpoints were determined in the study: effects on parent mortality and effects on reproduction (number of offspring per adult). Parent mortality in the controls was 0 per cent in the test carried out with the 10 g/l nominal stock solution and 10 per cent in the test carried out with the 100 mg/l nominal stock solution.

Elevated mortality was seen in the exposed populations. For the 10 g/l stock solution the LOEC was determined as the 1:8 dilution (approximately 58–65 µg/l) and the NOEC was determined as the 1:16 dilution (approximately 29–32 µg/l). For the 100 mg/l nominal stock solution the LOEC was determined as the 1:4 dilution and the NOEC was determined as the 1:8 dilution. These dilutions are based on the detection limit for the analysis of the 100 mg/l stock solution, and equate to LOEC and NOEC of <5 and <2.5 µg/l respectively). From the dose response curves it appears that 100 per cent parent mortality occurred at a concentrations of around <10 µg/l in the 100 mg/l nominal stock solution experiments and around 125 µg/l in the 10 g/l nominal stock solution experiments.

For the reproduction endpoint, the average number of young per adult in controls was 72.3 (variability 17.8 per cent) in the 100 mg/l nominal stock solution series of experiments and 73.5 (variability 6.2 per cent) in the 10 g/l nominal stock solution experiments. A significant reduction in the number of young per adult was seen in some of the exposed organisms. For the 100 mg/l nominal stock solution, this effect on reproduction was significantly different from the control groups at the lowest concentration tested (a 1:16 dilution which is equivalent to a chlorinated paraffin concentration of <1.2 µg/l, based on the detection limit of the analytical method used). Thus the NOEC/LOEC for this series of experiments was <1.2 µg/l. Similarly, for the 10 g/l nominal stock solution effects were again seen at the lowest concentration tested (a 1:64 dilution, which is equivalent to a chlorinated paraffin concentration of 7.3–8.1 µg/l). This value is treated as the LOEC for this series of experiments. The report also indicates that the NOEC is very close to this value, since using a different statistical method (Dunnett's Test rather than Williams' Test), the effects seen at this concentration were not statistically significantly different from controls.

The same 21-day results were reported by Frank and Steinhäuser (1994). In addition, this paper also reports the results of a similar test carried out using the water-soluble

fraction from a 1 mg/l nominal stock solution. This stock solution appears to have been prepared in a different manner from those previously. A solution of the chlorinated paraffin in pentane was prepared and a portion of this was added to the water, followed by stirring for one hour at 40°C to evaporate the solvent, prior to filtration. This showed no effects on parent mortality or reproduction in the test. However, it was not possible to determine the concentration of AOX (and hence chlorinated paraffins) present in these solutions, and so the actual exposure concentration is unknown.

The raw data from the 10 g/l loading used in the 21-day Frank (1993) and the Frank and Steinhäuser (1994) studies have been obtained and reanalysed (Thompson, 2001; Environment Agency, 2001). These reanalyses revealed a number of issues that were not apparent from the published reports. Firstly, on day 8 of the study, the temperature appeared to have reached 37°C, although this must have occurred only for a short period otherwise the animals would have all died at this temperature and invalidated the study.

The second point was that parent mortality at the 1:8 dilution was 20 per cent. As groups of 10 animals per treatment were used, the statistical significance of this effect compared with controls is debatable. This was considered as the LOEC in the original paper, but this is a marginal effect at best. The NOEC for parent mortality could be considered to be the 1:8 dilution (equivalent to 58–65 µg/l).

Thirdly, a serious error was found in the statistical method (Williams' Test) used to analyse the reproduction data. This error appears to have arisen in the way the data were entered into the statistical software, leading to the software mis-interpreting increasing dilutions as increasing concentrations. The software associated the apparent lowest concentration with the highest effect and hence, in accordance with the Williams procedure, compared the control with the mean reproduction rate across all the dilutions.

Re-analysis of the data by both Dunnett's test, Williams' test and the Steel test showed that effects were statistically significant ( $p=0.05$ ) compared with controls only at the 1:8 dilution. Therefore the NOEC from the study is the 1:16 dilution (equivalent to a concentration of 29–32 µg/l). The mean number of offspring per parent at this dilution was 95 per cent of the control value and the mean number of offspring per parent at the 1:8 dilution was 74 per cent of the control value. The mean number of offspring per parent at the 1:64 dilution, which is treated as the LOEC in the original publication, was 98 per cent of the control value.

This problem with the statistical analysis may also explain why the NOEC/LOEC from the 100 mg/l stock appeared to be below the lowest concentration tested. The NOEC/LOEC reported of <1.2 µg/l is therefore questionable.

The method for administering the test substance in the original studies also makes interpretation of the results difficult for a number of reasons, as discussed below.

It is not clear if the method of preparation of the test solutions would have achieved the maximum possible concentration of the test substance. For example, substances with very low solubility may take many days or weeks to dissolve. This phenomenon may not be so much of a concern for the 100 mg/l and 10 g/l loadings, as effects were seen in these tests (indicating that sufficient test substance was present in the test solution even if it may not be the maximum theoretically possible). However, this may not be true for the 1 mg/l loading; only a very short (one hour at 40°C) equilibration period was allowed, which may explain the lack of effects seen in tests at this loading rate.

The interpretation of the results is further complicated by the relatively crude analytical method used. The AOX method would detect chlorinated substances present in the solution, but provides no information on their identity. Further, the method would provide no indication of whether or not non-chlorinated substances were present in the test solutions. Therefore, although effects were seen in some of the tests, it is not at all clear what caused these effects.

For example, as these tests were carried out using water-soluble fractions (also known as water-accommodated fractions or WAFs), toxic impurities or additives present in the commercial product may be preferentially extracted into the water phase, thus complicating the interpretation of the results. The C<sub>18-20</sub> chlorinated paraffins are known to contain relatively large amounts of C<sub>17</sub> and, to a lesser extent, C<sub>16</sub> chlorinated paraffins (although these themselves would be of limited water solubility (up to approximately 27 µg/l)). Medium-chain (C<sub>14-17</sub>) chlorinated paraffins are known to be toxic to *Daphnia*, and a 21-day NOEC of around 10 µg/l has been determined for these substances. Therefore, it is possible that at least some of the effects seen in these tests could be due to the presence of other chlorinated paraffin impurities (or other more soluble unidentified chlorinated impurities) in the commercial product.

Similarly, the method of preparation of the test solution (dilution of a WAF) would enhance the more water-soluble C<sub>18-20</sub> chlorinated paraffins over the less soluble components; the composition of the C<sub>18-20</sub> chlorinated paraffin in solution may not have been the same as that in the commercial product, and may even be different at different loading rates. Dilution of WAFs is not generally recommended because it is likely that the more soluble components will be over-represented relative to the composition of the bulk material tested. In this case, the shorter chain-length components of the material (which are likely to be more soluble) – or any more soluble impurity – would be present at greater concentrations relative to the proportions of chain-length found in the commercial material.

With regard to the effect of different WAF loading rates, Frank (1993) reported higher concentrations of measured AOX from the 10 g/l loading rate compared to the 100 mg/l loading rate, but the measured AOX may represent more soluble lower chain-length components of the test material (or indeed more soluble impurities) simply because a far greater quantity of these preferentially dissolved components was available<sup>10</sup>. In the end, the material tested in solution may not be entirely representative of the commercial substance.

Whilst these factors make the studies far from ideal, they may be considered to represent a worst case because:

- the bioavailability of chlorinated paraffins as a group appears to decrease with increasing carbon chain length and chlorine content;
- the BCF values of the group as a whole appear to generally decrease with increasing carbon chain length and chlorine content;
- the water solubility of the group as a whole appears to decrease with increasing carbon chain length (and also probably increasing chlorine content).

These points therefore indicate that using the water-soluble fraction should enhance the relative contribution of the more accumulative and bioavailable chlorinated paraffin components (or impurities) of the product (i.e. those components most likely to be toxic).

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<sup>10</sup>. Assuming that the water solubility of the components is not exceeded in the solution.

It is not clear from the test report whether the chlorinated paraffin used in the tests contained a stabiliser. If one was present and had a higher water solubility than the chlorinated paraffin itself, this may have preferentially dissolved during the preparation of the saturated solutions and would also not be detectable by the AOX analytical method used. A common stabiliser in this type of product is epoxidised soybean oil. This is reported to be of very low water solubility, and also shows low toxicity in acute toxicity tests (24h EC<sub>0</sub> >100 mg/l) with *Daphnia* (IUCRID, 2000b). This information is insufficient to rule out the possibility of at least a contribution from any stabiliser present to the effects seen in the 21-day tests.

There are many uncertainties in the actual values obtained in the Frank (1993) study, not least because the actual exposure concentration in the 100 mg/l nominal stock solution is uncertain, and the significance of the effects seen at the low concentrations is unclear. It is also worth noting that the actual measured chlorinated paraffin concentration in the 10 g/l nominal stock solution of around 500 µg/l is well in excess of the expected water solubility for this type of substance. Further, the analytical method used provides no real indication of what actual substances were present in the test solutions.

If the toxicity seen in the Frank (1983) and Frank and Steinhäuser (1994) study was due to impurities or additives present in the chlorinated paraffin tested, then it is possible that the concentration of these additives or impurities – and hence their effect – would have been heightened as the amount added to the nominal stock solution increased. However, the LOEC was reported in the original paper to be lower in the test using the 100 mg/l stock solution than seen in the 10 g/l stock solution. This may again reflect the uncertainty in the actual exposure concentration in the 100 mg/l stock solution, but is more likely a reflection of the inappropriate statistical analysis carried out on the data.

Overall, the results of the Frank (1983) and Frank and Steinhäuser (1994) studies are extremely difficult to interpret in terms of the effects of the C<sub>18-20</sub> liquid chlorinated paraffins. However, given that effects were seen in the test, and the known toxicity of other chlorinated paraffins to *Daphnia*, it is difficult to dismiss the results at this stage. These results from these studies are considered further in the PNEC determination (Section 4.1.9.1).

Another long-term toxicity test has come to light, using a similar (possibly the same) C<sub>18-20</sub> 52% wt. Cl product to the one used by Frank (1983) and by Frank and Steinhäuser (1994). This study was carried out by TNO (1993). The substance tested was a commercial product containing 1.5 per cent epoxidised soybean oil. The test was carried out according to the OECD 202 methodology using a semi-static test procedure (test solution renewal was carried out every 48–72 hours). The dilution water used was a synthetic medium (DSWL) prepared by the addition of various salts to ground water. The hardness of the medium was 214 mg/l as CaCO<sub>3</sub>.

The test was carried out using saturated solutions of the chlorinated paraffin. These were prepared using a column technique. The column was prepared by firstly dissolving/suspending 0.1 g of the test substance in 25 ml of acetone. This solution was then added to 10 g of the packing material for the column (chromosorb 60/80 mesh) and the acetone removed by rotation evaporation. The coated packing material was stored at room temperature in the dark until needed. The columns were stainless steel (25 cm long with an internal diameter of 4.3 mm) filled with 1 g of the coated packing material. The column was conditioned by pumping dilution water through at a flow rate of 6.2 ml every three minutes; the first 500 ml was collected and discarded. Around 18 litres of dilution water was then collected in a bottle and continually

recirculated through the column at a flow rate of 3.4 ml per minute throughout the test. The required amount of the saturated solution needed for the start of the test, and at each renewal period, was then taken from the bottle.

The test was carried out using the saturated solution, a blank control (DSWL medium only) and a column control (DSWL medium pumped through a column containing unspiked chromosorb 60/80 mesh). Four replicates (10 daphnids in 400 ml of test solution) were carried out for each treatment. The tests were performed in 600 ml beakers and these were conditioned to the test solutions for two days prior to the start of the test. The solutions were renewed every Monday, Wednesday and Friday during the test. From day 10 the test solutions were gently aerated.

The concentration of test substance was determined at each renewal time in both the “fresh” solution and the “spent” solution. The analytical method used was based on extractable organic halogen (EOX; similar in principle to AOX) analysis. The mean EOX measured in the test solution over the course of the test was around 1 µg/l (the range found in the “fresh” solutions was 1.0–1.5 µg/l and the range in the “spent” solutions was 0.5–1.5 µg/l). The EOX concentrations in the control solutions were generally <0.5 µg/l in the “fresh” solution but the range found in the spent solutions was <0.5–1.0 µg/l for the blank control and 0.5–2.0 µg/l for the column control. These levels of EOX in the “spent” column control solution throw some uncertainty over the actual level of EOX that can be attributed to the chlorinated paraffin tested in the saturated solution. Assuming that the EOX present in the saturated test solution was related to the chlorinated paraffin, then an EOX level of around 1 µg/l is equivalent to a chlorinated paraffin concentration of around 2 µg/l (the chlorinated paraffin tested had a halogen content of 52% by weight).

The temperature, dissolved oxygen concentration and pH during the test were between 19.2 and 20.3,  $\geq 7.1$  mg/l and between 7.6 and 8.5 mg/l, respectively, throughout the test. The mortality and reproduction data determined in the study are summarised in Table 4.3. Also shown in this table are data obtained using a saturated solution of a medium-chain chlorinated paraffin (C<sub>14–17</sub>, 52% wt. Cl) using the same test system (these data are relevant to the statistical analysis of the data for the C<sub>18–20</sub>, 52% wt. Cl substance).

**Table 4.3 Summary of survival and reproduction in the 21-day study with *Daphnia magna* (TNO, 1993)**

Treatment group	Number of surviving adults at day 21	Cumulative number of living young per living female (mean±standard deviation)
Blank control	97.5%	113.6±11.8
Column control	97.5%	127.3±14.3
C <sub>18–20</sub> , 52% wt.	92.5%	100.8±11.4
Medium-chain chlorinated paraffin	37.5%	99.8±22.1

The parent survival in both of the control groups was 97.5 per cent. In the C<sub>18–20</sub>, 52% wt. Cl treatment group the parent survival was 92.5 per cent. This survival was not significantly different (at the p=0.05 level) from the control group. Therefore it was concluded that no treatment-related effects on parent mortality were seen in the study.

The reproduction rate (expressed as the cumulative number of young per living female) in the study was 113.6 in the blank control and 127.3 in the column control. The response of the two controls was not significantly different (at the  $p=0.05$  level). The reproduction rate in the C<sub>18-20</sub>, 52% wt. Cl treatment group was 100.8. This was 88.7 per cent of the blank control response and 79.1 per cent of the column control response. These responses were analysed statistically in TNO (1993) using the two-tailed Dunnett-test with a 95 per cent significance level. No statistically significant differences were found between the C<sub>18-20</sub>, 52% wt. Cl treatment group and the blank control, but it is not entirely clear from the report whether the reduction in the reproduction rate in the treatment group compared to the column control was statistically significant or not. In various parts of the report (including the overall summary) it is stated that this difference was statistically significant, but in other places there are statements that no statistically significant differences were found.

In order to investigate these results further, Thompson (2007) carried out a re-analysis of the data from this study. The statistical analysis was carried out on the same dataset as summarised in the TNO (1993) study and incorporated the dataset for a medium-chain chlorinated paraffin that was also tested at the same time as the C<sub>18-20</sub>, 52% wt. Cl substance. The data were found to be normally distributed and the variances were homogenous, satisfying the requirements for the use of ANOVA (with Dunnett's procedure to maintain a family error rate of 0.05) to determine significant differences from the column control. Using this procedure, no significant difference was seen between the reproduction rate in the C<sub>18-20</sub>, 52% wt. Cl treatment group (or the medium-chain chlorinated paraffin treatment group) and the column control. In addition, a further analysis was carried out comparing the treatment groups with the pooled control group (the combined blank control and column control); no statistically significant differences for the C<sub>18-20</sub>, 52% wt. Cl treatment group were found.

As part of this assessment, the Thompson (2007) re-analysis has been carefully checked; it appears to have been carried out appropriately. These data have been re-analysed using ANOVA with Dunnett's procedure in the same way as in Thompson (2007), confirming that the response from the C<sub>18-20</sub>, 52% wt. Cl treatment group was not significantly different (at the  $p=0.05$  level) from the column control group, the blank control group or the pooled control. However when the medium-chain chlorinated paraffins dataset was omitted from the same ANOVA procedure, a statistically significant difference was found between the C<sub>18-20</sub>, 52% wt. Cl treatment group and the column control and pool control, but not the blank control.<sup>11</sup>

The dependence of the statistical analysis on inclusion of the medium-chain chlorinated paraffin dataset may explain the apparent discrepancies found in the TNO (1993) compared with the Thompson (2007) re-analysis (it is not clear if the analysis in the TNO (1993) report included the medium-chain chlorinated paraffin dataset or not).

Another consideration to take into account when considering the results of the TNO (1993) study is that the tests were carried out using a saturated solution. In this case

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<sup>11</sup>In the TNO (1993) dataset the number of young per adult were estimated based on the mean number of adults surviving over the 2–3 day observation period (in line with the test guideline). In order to investigate the sensitivity of the data to this method of calculation, an analysis of the dataset was also performed using the number of adults present at the end of the observation period to estimate the mean number of young per adult (for example, if there were 10 live adults at the start of the 2–3 day observation period, and nine at the end, the mean number of young per adult were estimated by dividing the total number of young over the period by nine rather than 9.5. This lead to essentially the same findings as for the original dataset.

the saturated solution was prepared using a column technique, whereby an excess of the chlorinated paraffin was adsorbed onto column material and allowed to equilibrate with the water phase. There are some similarities between this method of preparation and the method used in the Frank (1993) and Frank and Steinhäuser (1994) series of studies. In particular, the composition tested in solution may not be representative of the composition in the bulk material. In the TNO (1993) the effective "loading rate" used was around 0.1 g in 18 litres of water (~6 mg/l) which is much lower than those used in the Frank (1993) and Frank and Steinhäuser (1994) studies (loading rates of 10 g/l and 100 mg/l). This difference in loading would suggest that the test solutions prepared in the TNO (1993) may have resulted in a lower preferential extraction of the more soluble components (or impurities) than in the Frank (1993) and Frank and Steinhäuser (1994) studies.

However, it also should be considered that the test solution in the TNO (1993) study was continually circulated through the column during the test and so had a much longer time to equilibrate with the chlorinated paraffin than was the case in the Frank (1993) and Frank and Steinhäuser (1994) studies (which had a 48 hour equilibration period with, in one case, sonication for one hour). Furthermore, in the TNO (1993) study the volume of water circulating through the column would have reduced during the test as samples of water were taken for renewal of the test solution and so the effective "loading rate" would have increased as the test progressed. Based on the renewal rates given in the test report, the amount of solution circulating through the column at the end of the test would have been around two litres, which would give an effective "loading rate" of around 50 mg/l.

These differences in the method of preparation of the test solution mean it is very difficult to make a direct comparison over the likelihood of the enhanced extraction of the more water-soluble components (or impurities) between the TNO (1993) study and the Frank (1993) and Frank and Steinhäuser (1994) studies. However it is likely that all of these studies suffer from the same problem, to a greater or lesser extent: the components present in solution may not be entirely representative of the commercial substance.

Overall, the results of the TNO (1993) study indicate that although a reduction in reproduction rate occurred in the study compared with the control group, the statistical significance of this reduction is marginal, and depends on the exact method used to analyse the data. Either way, the study can be interpreted as showing a NOEC (or a response close to a NOEC) at a concentration of 2 µg/l. It should also be noted that there are other uncertainties associated with this study, notably the presence of EOX in the "spent" column control solutions at concentrations similar to or higher than those in the C<sub>18-20</sub>, 52% wt. treatment groups. The identity of the EOX in the column control group is unknown. These results and uncertainties will be considered in Section 4.1.9.1 in relation to the PNEC derivation.

BUA (1992) reports the results of unpublished studies carried out by Hüls. The substance tested was a C<sub>18-27</sub>, 60% wt. Cl substance and was tested in both a stabilised and non-stabilised form (the stabiliser was not stated). The tests were carried out over 24 hours using either an emulsifier or acetone as cosolvent. The method used was DIN 38412 Teil 11, which is reportedly equivalent to OECD 202, Part I. The results are shown in Table 4.2. In addition, the same chlorinated paraffin (stabilised) was tested in a 21-day *Daphnia* reproduction study (OECD 202, Part II). The test was carried out with an emulsifier. The toxicity values obtained in the study were: NOEC = 4.2 mg/l, EC<sub>50</sub> = 40.8 mg/l and EC<sub>100</sub> = 395 mg/l. There are few other experimental details available about this study.



The concentrations tested in this study are clearly well above the water solubility of the substance and so the results need to be treated with caution. Two possibilities exist:

- i. The effects seen were indirect physical effects caused by the high test concentrations used, for example entrapment in a surface film.
- ii. The effects were direct toxicity of the substance in the dissolved phase.

In this study the results do not provide any information on the actual NOEC and EC<sub>50</sub> in terms of the dissolved substance. It is not possible from the available data to distinguish between these two possibilities, but given the high concentrations tested and the physical nature of the test substance it is most likely that the effects seen in this test were physical effects rather than direct toxicity.

A further acute toxicity test with *Daphnia magna* has recently been carried out for a C<sub>>20</sub>, 43% wt. Cl chlorinated paraffin (Thompson, 2005). The test was carried out using the OECD Guideline 202 methodology using water accommodated fractions. The water accommodated fractions were prepared by placing a small amount of the test substance onto a pre-weighed glass microscope slide (the substance was distributed across an area of approximately 1–3 cm<sup>2</sup>) and then each slide was placed in a support frame within a glass vessel containing 1.8 litres of dilution water which was stirred for 24 hours. After stirring, the vessels were allowed to settle for 50 minutes (no visible signs of undissolved test substance were present), and 200 ml aliquots of each water accommodated fraction were drawn off for use in the test. Three different water accommodated fractions were prepared using initial chlorinated paraffin loading rates of 0.21, 1.0 and 5.1 mg/l.

The tests were carried out using a static system with a total of 20 animals per treatment (four replicates of five animals were used) along with a control. No mortalities were seen in the control over the 48 hour experiment. Around 10-15 per cent of the animals in the 0.21 and 1.0 mg/l water accommodated fractions were found to be floating on the surface after 24 hours exposure, but these were found to be re-submerged by 48 hours and no further floatation was observed. No immobilised animals were seen in any treatment group. The 48h EC<sub>50</sub> was therefore taken to be >5.1 mg/l, expressed as a water accommodated fraction loading rate. It was therefore concluded that the substance was not toxic at the water solubility limit.

It should be noted, however, that there are some possible limitations with this study. For example, only 24 hours was allowed for preparation of the water accommodated fraction, and no analytical verification of the actual amount of test substance dissolved was carried out in the toxicity test. Overall, it is therefore difficult to judge how much chlorinated paraffin was dissolved in the toxicity test.

Another 21-day reproduction test with *Daphnia magna* has recently been completed (Sharpe and Penwell, 2007). The substance tested in this study was prepared by mixing a <sup>14</sup>C-labelled, C<sub>25</sub> paraffin (~1 g) with unlabelled C<sub>>20</sub> paraffin feedstock (~3.7 per cent) and chlorinating the mixture to a final chlorine content of 43% by weight. The test was carried out according to the OECD 211 method using a semi-static test procedure. A stock solution of the test substance was firstly prepared in dimethylformamide and aliquots of this were added to Elendt's M4 medium for use in the test (the amount of dimethylformamide in the test solution was 0.1 ml/l). The test medium had a hardness of 234 mg/l as CaCO<sub>3</sub>. Test solutions were renewed every 48 hours during the test.

The exposures were carried out using borosilicate glass beakers each containing one organism and 80 ml of test solution. A total of 10 replicates per treatment group were

carried out. The nominal concentrations tested were 2.0, 4.0, 8.0, 16, 32 and 64 µg/l and a dilution water control and solvent control group were also run. The actual concentration of chlorinated paraffin present was determined in “fresh” and “spent” solution at days 0–2, 4–6, 10–12 and 18–20. The analytical method used was radiochemical analysis (direct scintillation counting of the test solution). The measured concentrations in “fresh” solutions ranged from 85 per cent to 105 per cent of the nominal values and the measured concentrations in the “spent” solutions ranged from 39 per cent to 84 per cent of the nominal values. The mean measured concentrations found in the six treatment groups were 1.6, 3.0, 5.4, 13, 27 and 55 µg/l respectively. It should be noted that this analytical method would not necessarily distinguish between truly dissolved chlorinated paraffin and non-dissolved chlorinated paraffin, as discussed further below.

During the test the temperature, pH and dissolved oxygen concentration were in the ranges 19.9–20.9°C, 7.33–8.12 and 8.2 to 9.2 mg/l respectively. The endpoints determined in the study were adult length, reproduction (number of live offspring produced per parent animal surviving to the end of the study) and adult mortality. The results are summarised in Table 4.4. No statistically significant differences (at the p=0.05 level) were seen between the treatment groups and the control groups for either adult length or reproduction.

**Table 4.4 Summary of survival, adult length and reproduction data from in the 21-day study with *Daphnia magna* using a C<sub>>20</sub>, 43% wt. Cl chlorinated paraffin (Sharpe and Penwell, 2007)**

Treatment group	Percentage of surviving adults at day 21	Adult length (mean±standard deviation)	Number of live offspring per surviving adult (mean±standard deviation)
Dilution water control	90%	4.5±0.2 mm	108±31
Solvent control	80%	4.4±0.1 mm	123±27
1.6 µg/l	100%	4.6±0.1 mm	123±22
3.0 µg/l	60%	4.5±0.2 mm	114±19
5.4 µg/l	70%	4.3±0.5 mm	97±44
13 µg/l	80%	4.5±0.1 mm	113±11
27 µg/l	60%	4.7±0.1 mm	152±15
55 µg/l	80%	4.5±0.2 mm	130±32

For the parent survival, the mortality seen in the control groups was 10 per cent in the dilution water control group and 20 per cent in the solvent control group; this level of mortality falls within the guidelines for a valid test. Higher mortalities were evident in some of the chlorinated paraffin treatment groups. The test report indicates that the mortality seen in the treatment groups was not dose-related and not statistically significant compared with the solvent control group when tested using the Fisher’s exact test.

Whilst it is evident that no clear dose response was obtained, the mortality seen in some of the treatment groups was substantial (up to 40 per cent) and, although this difference from the solvent control response was not statistically significant, this

observation warrants further consideration.<sup>12</sup> The concentrations of the chlorinated paraffin used in this study were up to 55 µg/l. Based on the limited information available on the water solubility of LCCPs, at least some of the test concentrations used are likely to have exceeded the water solubility of the test substance. It is worth noting here that, although the concentrations present during the test were confirmed by measurement, the analytical method used would not necessarily distinguish between dissolved and undissolved test substance. Therefore it is possible that a lack of a clear dose response could relate to the fact that the actual “dissolved” concentration of the test substance was similar in most of the treatment groups once the solubility limit had been reached, and that concentrations at or close to this solubility limit (i.e. from 3.0 µg/l and above) resulted in 20–40 per cent parent mortality. Alternatively, it is possible that the mortality seen was a result of undissolved test substance or a chance occurrence.

Overall, it can be concluded from this test that the NOEC for parent mortality is at least 1.6 µg/l, and is probably higher than this value. These results will be considered in relation to the PNEC derivation in Section 4.1.9.1.

The results of tests with the brackish water harpacticoid *Nitocra spinipes* have been reported (Tarkpea *et al.*, 1981; as quoted in WHO, 1996). The results reported were a 96h LC<sub>50</sub> of >1,000 mg/l for a C<sub>22–26</sub>, 42% wt. Cl compound and a 96h LC<sub>50</sub> of >10,000 mg/l for a C<sub>18–26</sub>, 49% wt. Cl compound. No other details of the test were reported by WHO (1996), but the test method was probably the same as reported by Tarkpea *et al.* (1986), where a static method was employed using water of salinity 7‰ at a temperature of 20–22°C without aeration, probably using acetone as cosolvent.

The toxicity of two LCCPs to common mussel (*Mytilus edulis*) has been determined over 60 days (Madeley and Thompson, 1983a and 1983b). The compounds tested were the same C<sub>22–26</sub>, 43% wt. Cl and C<sub>>20</sub>, 70% wt. Cl products (mixed with a small amount of radiolabelled n-pentacosane that had been chlorinated to a similar degree) as used in the 60-day rainbow trout study (see Section 4.1.1). The test used a flow-through system with filtered natural seawater (salinity 35‰, pH 8.0–8.3, dissolved oxygen 6.1–8.25 mg/l) at 15°C. Acetone was present in the test solutions at a concentration of 0.5 ml/l (500 ppm), and acetone controls were also run using this concentration. Groups of 30 mussels were used for each exposure concentration and controls and they were constantly fed during the test (algal cells were added to the in-flowing water at a rate of 1.0–1.1×10<sup>9</sup> cells/day).

For the C<sub>22–26</sub>, 43% wt. Cl substance, two nominal concentrations of 0.32 mg/l and 3.2 mg/l were tested. The mean measured concentrations for these two exposures over the duration of the test were determined as 0.12 mg/l and 2.18 mg/l respectively by <sup>14</sup>C-analysis. Measurements by parent compound analysis (using a TLC method) at various times during the test were in general agreement with these values. The 2.18 mg/l exposure solution was reported to be cloudy in appearance, with a fine white deposit being observed, indicating that the solubility of the substance in the test system

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<sup>12</sup> The test design used on the OECD 211 methodology (particularly the use of 10 replicates of one organism each per treatment group) does not appear to be particularly sensitive for identifying statistically significant effects on mortality. For example, hypothetical calculations using Fischer’s exact test for this test design indicate that a mortality rate of around 70% may be required in a treatment group before it is significantly different from a solvent control group of 10 organisms with 20 per cent mortality. A mortality rate of around 60 per cent would be needed in a treatment group before it is significantly different from a pooled control group of 20 organisms with 15–20 per cent mortality.

had been exceeded. No significant mortality occurred in the test. Reduced filter feeding activity compared to control populations was consistently observed in the 2.18 mg/l exposure group from the seventh day onwards, but this effect was thought to stem from the "particulate" nature of the test solution.

For the C<sub>>20</sub>, 70% wt. Cl substance, the two nominal concentrations tested were 0.56 mg/l and 1.8 mg/l. The mean measured concentrations at these two exposures were determined as 0.46 mg/l and 1.33 mg/l by <sup>14</sup>C-measurements. Occasional parent compound analyses were in general agreement with these values. Some deposition of the test substance was noted at the highest concentration, indicating that the solubility of the substance in the test system had been exceeded. No mortality as a result of exposure to the chlorinated paraffin was seen in the test. Again, reduced filtration activity was seen in the 1.33 mg/l exposure group when compared with the control populations, particularly during the second half of the exposure period. However, this observation was variable, and on a number of occasions the filter feeding activity was comparable to controls; this reduction in activity was considered to be minimal and tentative.

#### 4.1.3 Toxicity to algae and plants

No data appear to be available on the toxicity of LCCPs to freshwater algae or plants.

Craigie and Hutzinger (1975) determined the toxicity of a C<sub>>20</sub>, 50% wt. Cl product to three species of marine algae (*Dunaliella tertiolecta*, *Olisthodiscus* sp. and *Thalassiosira fluviatilis*). The tests were carried out for six days at 20°C. The chlorinated paraffin was dissolved in acetone and an appropriate volume of this solution was added to the flask and evaporated to dryness under a jet of air. Natural sea water (30 ml) was then added to the flasks and the flasks were stoppered with a cotton wool bung and autoclaved. The nominal chlorinated paraffin concentrations tested were 1 mg/l and 100 mg/l but no measurements were carried out to verify the actual exposure concentration. The test was started by adding a 1 ml inoculum of 3–4 day old algal culture to the flask and each flask was shaken by hand twice daily. Each concentration was tested in duplicate. The algal biomass was determined by turbidity measurements after a six day exposure. No effects on biomass was seen in any of the exposed populations (the turbidity of the solutions was within 96–105 per cent of the control values).

The validity of this test is highly questionable as the method of administration of the test substance may not have been appropriate. It appears that an acetone solution of the substance was added directly to the test vessel and evaporated to dryness before the test water was added, and then the vessel was autoclaved (the temperature was not stated). As this substance is likely to be highly adsorptive onto the glass vessel used, and twice daily shaking of the vessel was the only method used to effect mixing, it is highly uncertain that all the chlorinated paraffin added would be in solution, or even in suspension and it is possible that most of it remained adsorbed onto the test vessel. As no monitoring was carried out during the test it is not possible to determine if any substance was lost during the autoclaving procedure.

#### 4.1.4 Quantitative structure-activity relationships (QSARs)

The log Kow values of LCCPs are well outside the validity range of most of the available QSAR methods for estimating toxicity to aquatic organisms (for example the methods given in the TGD are valid only for log Kow values up to 6). Therefore no QSAR estimates of toxicity have been carried out.

Another approach that can be considered here is that of the critical body burden. This approach is being developed in the Reference TGD in relation to the assessment of substances with persistent, bioaccumulative and toxic (PBT) properties under REACH<sup>13</sup>. The approach is still in the draft stage but the current approach is outlined below.

The approach is based on the assumption that, for substances acting by a common mechanism such as narcosis, the toxicity is expressed only when a critical internal body burden of the chemical is reached, and that this critical body burden, when expressed on a molar basis, is similar for all chemicals acting by that mechanism. Critical body burdens have been defined by several groups for substances acting by narcotic (and other) modes of action. These are summarised in Table 4.5 below. Although the data show considerable variability (particularly for the more specific modes of action other than narcosis), it is still useful to compare the critical body burden for narcosis with the expected maximum body burden for LCCPs.

**Table 4.5 Summary of critical body burdens for lethality (taken from the draft Reference Technical Guidance Document being developed for REACH)**

Reference	Critical body burden for lethality by mode of action (mmol/kg wet weight)		
	Narcosis	AChE inhibitors	Respiratory inhibitors
Sijm (2004)	2	0.01	0.001
Thompson and Stewart (2003)	2–8	$1 \times 10^{-6}$ –10	$1 \times 10^{-6}$ –10
Barron <i>et al.</i> (2002)	0.03–450	$4 \times 10^{-5}$ –29	$2 \times 10^{-5}$ –1.1 (CNS seizure agents)
McCarty and Mackay (1993)	1.7–8	0.05–27	$5 \times 10^{-5}$ –0.02 (CNS seizure agents)

Notes: AChE = acetylcholinesterase.  
CNS = central nervous system.

<sup>13</sup> Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directive 91/155/EEC, 93/105/EC and 2000/21/EC. Official Journal of the European Union, L396, 30.12.2006, pp1-849.

Assuming a water solubility of around 5 µg/l, the following body burdens can be estimated in fish exposed to a saturated solution of LCCPs:

$C_{18-20}$ liquid	BCF = 1,096 l/kg Molecular weight = ~500 g/mole Internal body burden = ~0.01 mmol/kg wet weight
$C_{>20}$ liquid	BCF = 192 l/kg Molecular weight = ~700 g/mole Internal body burden = $\sim 1 \times 10^{-3}$ mmol/kg wet weight
$C_{>20}$ solid	BCF = 1 l/kg Molecular weight = ~1,000 g/mole Internal body burden = $\sim 5 \times 10^{-6}$ mmol/kg wet weight

As can be seen from this analysis, the body burdens predicted are all below the ranges for critical body burdens for narcosis defined by Sijm (2004), Thompson and Stewart (2003), Barron *et al.* (2002) and McCarty and Mackay (1993). This indicates that none of the LCCPs would be expected to be toxic (lethal) to fish over long-term exposure to concentrations at or below the water solubility if they act by a narcotic mode of action.<sup>14</sup> It should be noted, however, that the above approach requires a reliable value for the water solubility and the BCF. The available data for LCCPs is limited, particularly for the  $C_{18-20}$  liquid chlorinated paraffins (see Section 1.4.5 and Section 3.2.9.1).

#### 4.1.5 Overall summary of standard endpoint toxicity data

There is a relatively large amount of aquatic toxicity data available for LCCPs. The substance generally shows little or no toxicity at concentrations well in excess of its water solubility in acute tests. Effects have been seen on *Daphnia* at high concentrations, but these are likely to be physical effects rather than direct toxicity of the substance itself. However, there is no fully valid algal test available for LCCPs.

In long-term tests, significant effects have only been seen in *Daphnia* reproduction studies. Here a 21-day NOEC of 29–32 µg/l was determined for a  $C_{18-20}$ , 52% wt. Cl product. This result was obtained using water-soluble fractions from a loading rate of 10 g/l and, as such, is difficult to interpret as the toxicity seen could be due to impurities or additives present in the substance tested rather than the chlorinated paraffin itself. It should be noted that this value is slightly above the expected water solubility for LCCPs of around 5 µg/l (see Section 1.4.5), but no experimental water solubility data for the  $C_{18-20}$  liquid chlorinated paraffins are available. Another 21-day *Daphnia* reproduction study using a loading rate of 100 mg/l gave an apparent NOEC/LOEC of <1.2 µg/l. A third 21-day *Daphnia* reproduction study with a  $C_{18-20}$ , 52% wt. Cl product, this time using a single concentration prepared by a column method, resulted in reduced reproduction compared with the control population at a concentration around 2 µg/l but the statistical significance of this result is debatable and the NOEC from this study can be taken as  $\geq 2$  µg/l. A 21-day *Daphnia* reproduction study is also available for a  $C_{>20}$ , 43% wt. Cl substance. This showed no effects on reproduction at concentrations up to 55 µg/l.

No effects were reported to be seen in 60-day studies with fish and mussels using both a  $C_{22-26}$ , 43% wt. Cl product and a  $C_{>20}$ , 70% wt. Cl product. This finding is in

<sup>14</sup> Given the relatively non-polar nature of LCCPs, and the lack of reactive groups present in the molecule, it would be expected that a non-specific narcotic mode of action would be most applicable.

accordance with calculations for lethality using the critical body burden concept assuming a narcotic mode of toxic action. However, the fish toxicity test is not equivalent to the fish early lifestage test that is currently recommended in the TGD to assess the long-term toxicity potential of this type of substance. In particular, the 60-day tests reported do not include any of the potentially sensitive early lifestages.

#### **4.1.6 Endocrine disruption**

No tests investigating the effects of LCCPs on the endocrine system in aquatic organisms have been located.

#### **4.1.7 Waste water treatment plant (WWTP) microorganisms**

Madeley and Birtley (1980) found that a C<sub>20-30</sub>, 42% wt. Cl caused no significant increase or decrease in bacterial activity in laboratory-scale digesters over 30 days at concentrations of the chlorinated paraffin of up to 10% by weight of dry sludge solids.

The toxicity of several C<sub>18-20</sub> chlorinated paraffins has been tested in a three-hour respiration inhibition test (unpublished study). The chlorinated paraffin was emulsified in water using 0.5 g/l nonylphenol ethoxylate surfactant and then incubated for three hours with activated sludge from a municipal sewage treatment plant. No effect on respiration was seen up to the highest concentration tested (2,000 mg/l) with a C<sub>18-20</sub>, 35% wt. Cl product or a C<sub>18-20</sub>, 44% wt. Cl product, but inhibition was seen at concentrations above 1,000 mg/l with a C<sub>18-20</sub>, 49% wt. Cl product (Hoechst AG, 1985; BUA, 1992).

The toxicity of LCCPs to anaerobic bacteria from a domestic waste water treatment plant (wwtp) has been studied using the ETAD fermentation tube method (Hoechst AG, 1976 and 1977). The full details of the test are not available and so it is not possible to fully validate the results. The reported results are shown in Table 4.6.

Howard *et al.* (1975) report the results of tests carried out by Hildebrecht (1972) on the toxicity of two LCCPs to sewage microorganisms. The two chlorinated paraffins tested were a C<sub>>20</sub>, 40–42% wt. Cl product and a C<sub>>20</sub>, 70% wt. Cl product. The experiments were carried out using bottles containing potassium acid phthalate (reported to be readily biodegradable), bionutrients and bacterial seed (sewage). The effect of various concentrations (1, 10, 50, 100 and 200 mg/l) of the chlorinated paraffins on the residual dissolved oxygen level in the bottles was determined after five days of incubation. In the controls (containing no chlorinated paraffin), the residual dissolved oxygen concentration at the end of the test was 4.6 mg/l. The residual dissolved oxygen concentration in the chlorinated paraffin treatments were all less than 1 mg/l, indicating that the substance had no effect on the degrading bacteria. Few other details of this test are available. The overall 5-day NOECs for both chlorinated paraffins from this test can be tentatively set as >200 mg/l.

**Table 4.6 Summary of toxicity data for microorganisms**

Substance	Comments	Result	Reference
C <sub>18-20</sub> , 35% wt. Cl	Activated Sludge Respiration Inhibition Test (equivalent to OECD 209)	3 hour NOEC >2,000 mg/l	Hoechst AG, 1985
	Anaerobic bacteria from a domestic wwtp – ETAD Fermentation Tube Method	24 hour harmful threshold = 1,250 mg/l	Hoechst AG, 1976
C <sub>20-30</sub> , 42% wt. Cl	Anaerobic bacteria in laboratory-scale digester	30 day NOEC >10% by weight of dry sludge solids	Madeley and Birtley, 1980
C <sub>18-20</sub> , 44% wt. Cl	Activated Sludge Respiration Inhibition Test (equivalent to OECD 209)	3 hour NOEC >2,000 mg/l	Hoechst AG, 1985
	Anaerobic bacteria from a domestic wwtp – ETAD Fermentation Tube Method	24 hour harmful threshold = 600 mg/l	Hoechst AG, 1976
C <sub>18-20</sub> , 49% wt. Cl	Activated Sludge Respiration Inhibition Test (equivalent to OECD 209)	3 hour EC <sub>0</sub> = 1000 mg/l	Hoechst AG, 1985
	Anaerobic bacteria from a domestic wwtp – ETAD Fermentation Tube Method	24 hour harmful threshold = 1,250 mg/l	Hoechst AG, 1976
C <sub>18-20</sub> , 52% wt. Cl	Anaerobic bacteria from a domestic wwtp – ETAD Fermentation Tube Method	24 hour harmful threshold = 1,250 mg/l	Hoechst AG, 1977

#### 4.1.8 Toxicity to sediment organisms

No data are available on the toxicity of LCCPs to sediment organisms.

#### 4.1.9 Derivation of PNEC for the aquatic compartment

##### 4.1.9.1 PNEC for surface water

In long-term tests, significant effects have only been seen in *Daphnia* reproduction studies. Here a 21-day NOEC of 29–32 µg/l was determined for a C<sub>18-20</sub>, 52% wt. Cl product. This result was obtained using water-soluble fractions from a loading rate of 10 g/l and, as such, is difficult to interpret because the observed toxicity could be due to impurities or additives present in the substance tested rather than the chlorinated paraffin itself. In addition, the high loading rate used in this test could affect the composition of the substance(s) present in the solutions tested such that they may not



have been entirely representative of the commercial substance. The proportion of more soluble (e.g. shorter-chain length) components present in solution may have been enhanced compared to the composition of the commercial product).

It should be noted that this NOEC value is slightly above the expected water solubility for LCCPs of around 5 µg/l (see Section 1.4.5), but no experimental water solubility data for the C<sub>18-20</sub> liquid chlorinated paraffins are available. Another 21-day *Daphnia* reproduction study using a loading rate of 100 mg/l gave an apparent NOEC/LOEC of <1.2 µg/l. Despite the shortcomings associated with the WAF technique in this case, of these two studies the value obtained from the 10 g/l loading is considered to be more reliable for use in the risk assessment because:

- i. The concentration in the water-soluble fraction for the 10 g/l loading was measured at the start of the test and was shown to contain at least a chlorinated compound (as determined by AOX measurement). The level of AOX in the water-soluble fraction from the 100 mg/l loading was below the limit of detection and so this solution is much less well categorised for chlorinated substances.
- ii. It was shown that the AOX concentration for the 10 g/l loading was maintained within 80 per cent of the starting concentration over the 2–3 day renewal period used in the test.
- iii. The statistical methodology used to obtain the NOEC/LOEC of <1.2 µg/l was probably similar to that used in the 10 g/l loading in the original paper and is therefore questionable. The NOEC of 29–32 µg/l has been obtained using several reliable statistical techniques.

A third 21-day *Daphnia* reproduction study with a C<sub>18-20</sub>, 52% wt. Cl product, this time using a single concentration prepared by a column method, resulted in reduced reproduction compared with the control population at a concentration around 2 µg/l but the statistical significance of this result is debatable. Unfortunately, as only one concentration was tested, no dose-response was generated in this study. Overall the value of 2 µg/l from this study will be taken as a NOEC or a value close to the NOEC. It should be noted that, as this was the highest concentration tested, it is possible that the true NOEC for this substance could be higher than 2 µg/l.

A C<sub>18-27</sub>, 60% wt. Cl product was also found to caused effects on *Daphnia* in a 21-day study, but these are most likely to be due to physical effects as a result of the high concentrations tested.

A further 21-day *Daphnia* reproduction study is available for a C<sub>>20</sub>, 43% wt. Cl substance. Overall, this test gave a NOEC for reproduction of 55 µg/l but the interpretation of this result is complicated; it is likely that some of the concentrations used were above the water solubility of the test substance.

No effects were reported to be seen in 60-day studies with fish and mussels using both a C<sub>22-26</sub>, 43% wt. Cl product and a C<sub>>20</sub>, 70% wt. Cl product. However, the fish toxicity test is not equivalent to the fish early lifestage test that is currently recommended in the TGD to assess the long-term toxicity potential of this type of substance. In particular, the 60-day tests reported do not include any of the potentially sensitive early lifestages.

Based on the available data, there are considerable uncertainties over the toxicity of LCCPs to aquatic organisms. The pattern of toxicity appears to be similar to that observed for medium-chain chlorinated paraffins, where again effects were seen

mainly in *Daphnia*. The database for LCCPs is smaller, however, and the available long-term *Daphnia* results appear to be conflicting.

As a preliminary approach, it is suggested that the 21-day *Daphnia* NOEC should be taken as 29 µg/l for the C<sub>18-20</sub>, chlorinated paraffin. This is the result from the study using a water-soluble fraction derived from a 10 g/l loading, where the actual exposure concentration in terms of AOX (i.e. chlorine-containing substances) was best determined. This value may represent the more reliable value from the available studies using water-soluble fractions. The shortcomings of this study have been discussed previously, and although the value is in excess of the water solubility values used in the assessment<sup>15</sup>, a clear dose-response was evident in this study, and the statistical significance of the effects seen was clearly established.

There are two NOEC values for C<sub>18-20</sub> chlorinated paraffins below this value. One was a NOEC of <1.2 µg/l from a water-soluble fraction using a 100 mg/l loading, but there are uncertainties over the actual exposure concentrations and the statistical method used to analyse the data in this particular study. The second is a NOEC of ≥2 µg/l obtained in a study using a single concentration prepared using a column method.

Since there are no reliable long-term NOECs for alga, and the available long-term fish test does not include exposure to potentially sensitive early lifestages, an assessment factor of 100 would normally be applied to the *Daphnia* NOEC when deriving a PNEC using the TGD methodology. However, in this case it can be argued that a lower assessment factor should be applied to the data, as *Daphnia* appear to be the most sensitive species for chlorinated paraffins as a whole.

Table 4.7 outlines the available data for short-, medium and long-chain chlorinated paraffins. A PNEC of 0.5 µg/l and a PNEC of 1 µg/l have been derived for short-chain chlorinated paraffins (ECB, 2000) and medium-chain chlorinated paraffins (ECB, 2005a), respectively. These have been derived from more complete and reliable datasets using an assessment factor of 10 in both cases. When the underlying data behind these PNECs are considered it can be seen that *Daphnia* appears to be the most sensitive species for chlorinated paraffins as a whole, and that the toxicity to *Daphnia* decreases with increasing carbon chain length. This provides some justification for deriving the PNEC for the C<sub>18-20</sub> liquid chlorinated paraffins using an assessment factor of 10 on the *Daphnia* NOEC of 29 µg/l. This gives a PNEC for the C<sub>18-20</sub> liquid chlorinated paraffins of 2.9 µg/l, and, as can be seen from Table 4.7, this value appears to be consistent with the trend in PNEC seen for short- and medium-chain chlorinated paraffins.

The PNEC of 2.9 µg/l could also be taken to apply to the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins. However, in the case of the C<sub>>20</sub> liquid chlorinated paraffin, the available *Daphnia* data indicate that toxicity does not occur until concentrations well in excess of the water solubility are used and so the effects seen in the *Daphnia* tests with this substance may be due to physical effects rather than direct toxicity. Thus, a PNEC of 2.9 µg/l may be overprotective for this type of chlorinated paraffin. No *Daphnia* data are available for the C<sub>>20</sub> solid chlorinated paraffin. Therefore it is not possible to derive reliable PNECs from the available data.

An approach that could be used for the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins is to calculate a tentative screening PNEC based on the NOEC of 55 µg/l from the recent study with a C<sub>>20</sub> 43% wt. Cl substance, recognising that this NOEC value is likely to be in excess of the water solubility of the substance tested. Applying an assessment factor

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<sup>15</sup> The actual water solubility of the substance tested is not known.

of 10 to this value (using similar arguments as above i.e. that *Daphnia* are likely to be the most sensitive species overall for chlorinated paraffins) would give a PNEC of around 5.5 µg/l. This screening PNEC is then reasonably consistent with those derived for other chlorinated paraffins (see Table 4.7) and is also consistent with the fact that toxic effects are considered unlikely from the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins at concentrations up to their water solubility (around 5 µg/l).

These values will be used here in a provisional assessment of these substances to determine if more reliable toxicity data for the substances themselves are required. This approach should be conservative and protective for these C<sub>>20</sub> substances because they are expected, based on QSAR estimates, to be less accumulative, and hence have a lower potential to cause long-term effects, than the shorter-chain length chlorinated paraffins.

**Table 4.7 Comparison of long-term NOEC data for chlorinated paraffins**

Endpoint	Chlorinated paraffin type				
	Short-chain	Medium-chain	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
21-day <i>Daphnia</i> reproduction study	NOEC = 5 µg/l	NOEC = 10 µg/l	NOEC = 29 µg/l	NOEC = 55 µg/l (or ≥1.6 µg/l)	
32-day early lifestage study with <i>Cyprinodon variegatus</i>	280 µg/l				
60-day study with <i>Oncorhynchus mykiss</i>	LC <sub>50</sub> 340 µg/l	no effects at solubility		no effects at solubility	no effects at solubility
20-day embryo-larval study with <i>Oryzias latipes</i>	NOEC = 9.6–62 µg/l (four substances tested)	no effects at solubility (two substances tested)			
Algal NOEC	12 µg/l	no effects at solubility			
Assessment factor used to derive PNEC	10	10	10	10	
PNEC	0.5 µg/l	1 µg/l	2.9 µg/l	5.5 µg/l	5.5 µg/l (taken to be the same as for C <sub>&gt;20</sub> liquid products)

To summarise, the PNECs that will be used for the initial assessment of the aquatic compartment are:

C <sub>18-20</sub> liquid	PNEC <sub>water</sub> = 2.9 µg/l
C <sub>&gt;20</sub> liquid	PNEC <sub>water(screening)</sub> = 5.5 µg/l
C <sub>&gt;20</sub> solid	PNEC <sub>water(screening)</sub> = 5.5 µg/l

An alternative approach that could be used for the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins would be to derive no PNEC at all for such substances and carry out a qualitative assessment for surface water. However, although a qualitative assessment for surface water would be possible, it would not necessarily be possible to extend this to other relevant compartments (for example sediment and soil). Therefore, on balance, although it is accepted that there are uncertainties associated with the PNEC<sub>water(screening)</sub> values for the C<sub>>20</sub> liquid and C<sub>>20</sub> solid products, it is useful to consider these in the risk characterisation as they allow the PECs calculated for surface water (and sediment and soil) to be put into context. Although such values cannot be used to determine whether a risk actually exists, they are useful in

determining where no risk is likely to occur and for identifying where further work might be needed to determine better the PNEC for these substances. These issues are considered further in the risk characterisation.

#### 4.1.9.2 PNEC for sediment

There are no toxicity data available for LCCPs on sediment-dwelling organisms. In the absence of any ecotoxicological data, the PNEC can provisionally be calculated using the equilibrium partitioning method as follows.

$$PNEC_{sed} = \frac{K_{susp-water} \times PNEC_{water} \times 1000}{RHO_{susp}}$$

where  $K_{susp-water}$  = suspended matter-water partition coefficient  
 =  $2.27 \times 10^6 \text{ m}^3/\text{m}^3$  for  $C_{18-20}$  liquid chlorinated paraffin  
 =  $6.93 \times 10^6 \text{ m}^3/\text{m}^3$  for  $C_{>20}$  liquid chlorinated paraffin  
 =  $>2.5 \times 10^8 \text{ m}^3/\text{m}^3$  for  $C_{>20}$  solid chlorinated paraffin  
 $RHO_{susp}$  = bulk density of suspended matter =  $1,150 \text{ kg}/\text{m}^3$

Using this equation, the following  $PNEC_{sed}$  can be derived:

$C_{18-20}$ liquid chlorinated paraffin	$PNEC_{sed} = 5,710 \text{ mg}/\text{kg wet wt.}$
$C_{>20}$ liquid chlorinated paraffin	$PNEC_{sed(screening)} = 33,100 \text{ mg}/\text{kg wet wt.}$
$C_{>20}$ solid chlorinated paraffin	$PNEC_{sed(screening)} = >1,200,000 \text{ mg}/\text{kg wet wt.}$

These PNECs assume that the exposure, and hence effects of the substance, occurs mainly via sediment pore water. The ingestion of sediment-bound substance by the exposed organisms may not be sufficiently explained by this relationship for substances with a log Kow >5. The TGD suggests that in such cases, the PEC/PNEC ratio should be increased by a factor of 10.

Toxicity tests using medium-chain chlorinated paraffins with sediment organisms (*Chironomus riparius*, *Hyalella azteca* and *Lumbriculus variegatus*) have been carried out (Thompson *et al.*, 2001a, 2001b and 2002). The lowest NOEC for these species was 50 mg/kg wet wt. obtained for both *Lumbriculus variegatus* and *Hyalella azteca* in a sediment with a 4.9–5 per cent organic carbon content. A  $PNEC_{sed}$  of 5 mg/kg wet wt. was derived from these data using an assessment factor of 5 (ECB, 2005a). This was very similar to the  $PNEC_{sed}$  of 12.6 mg/kg derived for medium-chain chlorinated paraffins using the equilibrium partitioning method (the value is different by a factor of 2.6). At least some of the difference between the two values could be explained by the fact that the NOECs underlying both PNEC determinations depend to some extent on the actual concentrations and concentration intervals used in the various tests. Similar agreement is also evident in a comparative study of the toxicity of different medium-chain chlorinated paraffins to soil organisms (see Section 4.2). Taking these results into account, the equilibrium partitioning method appears to be appropriate for medium-chain chlorinated paraffins and direct ingestion of sediment-bound substance is only a minor contributor to the toxicity seen for this class of substance.

However, LCCPs are predicted to adsorb onto sediment to a greater extent than medium-chain chlorinated paraffins and so it is possible that direct ingestion of sediment-bound substance could become a more important route of exposure for these substances than was seen in the experiments with medium-chain chlorinated paraffins.

Therefore, the PEC/PNEC ratios based on the equilibrium partitioning method will be increased by a factor of 10 to take this possibility into account in this assessment.

#### 4.1.9.3 PNEC for WWTP

There are toxicity data available for the effects of various LCCPs on bacteria. In these experiments, the lowest threshold concentration reported to cause effects (approximates to a NOEC/LOEC) was 600 mg/l for a C<sub>18-20</sub> liquid chlorinated paraffin on anaerobic bacteria. The NOECs for C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins are >200 mg/l (no effects seen). The TGD suggests that an assessment factor of 10 can be applied to the NOEC or EC<sub>10</sub> from a test using mixed bacterial populations. Therefore, the PNEC for waste water treatment plants can be estimated at 60 mg/l. This PNEC is protective for all types of LCCPs.

#### **Considerations for the marine environment**

The available dataset contains several results with marine and brackish water species. These data generally show a similar pattern of toxicity as with freshwater species. The most sensitive freshwater species to LCCPs appears to be *Daphnia magna*, where effects were seen in 21-day tests with a C<sub>18-20</sub> liquid chlorinated paraffin. There are acute toxicity data available for marine crustaceans (the brackish water harpacticoid *Nitocra spinipes*). There are few details available for this test, but no effects were seen with either a C<sub>22-26</sub>, 42% wt. Cl compound or a C<sub>18-26</sub>, 49% wt. Cl compound at concentrations in excess of the substances' solubility.

In addition, a 60-day study is available with mussels for a C<sub>22-26</sub>, 43% wt. Cl substance and a C<sub>>20</sub>, 70% wt. Cl substance, both showing no effects at water solubility. As the related C<sub>14-17</sub> chlorinated paraffins also showed effectively little or no effects at water solubility with mussels (ECB, 2005a) it can be concluded that the C<sub>18-20</sub>, liquid chlorinated paraffins are also unlikely to be toxic to mussels at concentrations below their water solubility limit.

According to the TGD, an assessment factor of 1,000, 500, 100 or 50 could be considered for this dataset, depending on the confidence to which the most sensitive species has been tested. An assessment factor of 50<sup>16</sup> will be used on the NOEC of 29 µg/l from the 21-day *Daphnia* study with the C<sub>18-20</sub>, 52% wt. Cl substance. Thus the PNEC<sub>marine water</sub> will be taken to be 0.58 µg/l for the C<sub>18-20</sub> liquid chlorinated paraffins. Similarly, for the C<sub>>20</sub> liquid and C<sub>>20</sub> solid products, a PNEC<sub>marine water(screening)</sub> of 1.1 µg/l will be used (based on an assessment factor of 50 applied to the *Daphnia* NOEC of 55 µg/l for a C<sub>>20</sub> 43% wt. Cl product).<sup>17</sup>

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<sup>16</sup> An assessment factor of 50 is used as there is a long-term NOEC for a freshwater species (*Daphnia*), the read-across from short- and medium-chain chlorinated paraffins suggests that *Daphnia* are likely to be the most sensitive freshwater species (see Section 4.1.9.1). There is also data to indicate that an additional marine taxonomic group (molluscs) is unlikely to be more sensitive than *Daphnia*.

<sup>17</sup> This is consistent with the approach taken to derive the freshwater PNEC for these substances (see Section 4.1.9.1).

No data are available on the toxicity to marine sediment organisms. According to the TGD, the PNEC for marine sediment can be estimated using the equilibrium partitioning approach. The following values for the  $PNEC_{\text{marine sediment}}$  are therefore obtained:

$C_{18-20}$ liquid	$PNEC_{\text{marine sediment}} = 1,140 \text{ mg/kg wet wt.}$
$C_{>20}$ liquid	$PNEC_{\text{marine sediment}} = 6,620 \text{ mg/kg wet wt.}$
$C_{>20}$ solid	$PNEC_{\text{marine sediment}} >239,000 \text{ mg/kg wet wt.}$

For substances with  $\log Kow >5$ , the TGD indicates that the PEC/PNEC ratios should be increased by a factor of 10 to take into account the possible direct ingestion of sediment-bound substance. This factor will be taken into account in the risk characterisation.

## 4.2 Terrestrial compartment

### 4.2.1 Terrestrial toxicity data

There are no studies available on the toxicity of LCCPs to plants, earthworms or other soil-dwelling organisms.

### 4.2.2 PNEC for the soil compartment

In the absence of any ecotoxicity data, the PNEC may be calculated provisionally using the equilibrium partitioning method as follows.

$$PNEC_{\text{soil}} = \frac{K_{\text{soil-water}} \times PNEC_{\text{water}} \times 1000}{RHO_{\text{soil}}}$$

Where $K_{\text{soil-water}}$	= soil-water partition coefficient
	= $2.72 \times 10^6 \text{ m}^3/\text{m}^3$ for $C_{18-20}$ liquid chlorinated paraffins
	= $8.31 \times 10^6 \text{ m}^3/\text{m}^3$ for $C_{>20}$ liquid chlorinated paraffins
	$>3.0 \times 10^8 \text{ m}^3/\text{m}^3$ for $C_{>20}$ solid chlorinated paraffins
$RHO_{\text{soil}}$	= bulk density of soil = $1,700 \text{ kg/m}^3$

The following  $PNEC_{\text{soil}}$  can be estimated:

$C_{18-20}$ liquid	$PNEC_{\text{soil}} = 4,640 \text{ mg/kg wet wt.}$
$C_{>20}$ liquid	$PNEC_{\text{soil}(\text{screening})} = 26,900 \text{ mg/kg wet wt.}$
$C_{>20}$ solid	$PNEC_{\text{soil}(\text{screening})} >971,000 \text{ mg/kg wet wt.}$

Similar to the case with sediment, these PNECs assume that the exposure, and hence effects, is mainly through the soil pore water. The ingestion of soil-bound substance by soil dwelling organisms may not be sufficiently explained by this relationship for substances with  $\log Kow >5$ . The TGD suggests that the PEC/PNEC ratio should be increased by a factor of 10 to take into account this route of exposure.

Toxicity tests using medium-chain chlorinated paraffins with soil organisms (plants *Triticum aestivum*, *Brassica napus* and *Phaseolus aureus*, earthworms *Eisenia fetida*, and soil nitrification processes) have recently been carried out (Thompson *et al.*, 2001c and 2001d; Thompson, 2002). The lowest NOEC from these tests was 248 mg/kg wet wt. for *Eisenia fetida* in a soil with a 4.7 per cent organic carbon content. When this value is normalised to the organic carbon content of 2 per cent used in the TGD, the

NOEC becomes 106 mg/kg wet wt. A PNEC<sub>soil</sub> of 10.6 mg/kg wet wt. was derived from these data using an assessment factor of 10 (ECB, 2005a). This value was almost identical to the PNEC<sub>soil</sub> of 10.4 mg/kg derived for medium-chain chlorinated paraffins using the equilibrium partitioning method. This agreement suggests that the equilibrium partitioning method is appropriate for medium-chain chlorinated paraffins and that direct ingestion of soil-bound substance is only a minor contributor to the toxicity seen.

LCCPs are, however, predicted to adsorb onto soil to a larger extent than medium-chain chlorinated paraffins and so it is possible that direct ingestion of soil-bound substance could become a more important route of exposure for these substances than was seen in the experiments with medium-chain chlorinated paraffins. Therefore, the PEC/PNEC ratios based on the equilibrium partitioning method will be increased by a factor of 10 to take this possibility into account.

## 4.3 Atmosphere

### 4.3.1 Toxicity data relevant to the atmospheric compartment

No data are available on possible effects of the substance on the atmosphere.

### 4.3.2 PNEC for the atmospheric compartment

It is not currently possible to derive a PNEC for the atmospheric compartment for LCCPs. However, given the low predicted environmental concentrations, neither biotic nor abiotic effects are likely.

Concern has been raised that chlorinated paraffins, particularly the short-chain ones, may be subject to long-range atmospheric transport and subsequent bioaccumulation in remote regions. This issue is currently being discussed within the appropriate international fora, but no agreement has yet been reached. The potential for long-range transport (and subsequent accumulation) of the long-chain substances appears to be less than that for short-chain products because the LCCPs generally have lower vapour pressures and are likely to adsorb more strongly to soil and sediment. However, LCCP substances contain many components and the components exhibit a range of physico-chemical properties. Some components of commercial products may have properties that make long-range transport via the atmosphere a possibility. This issue should be considered further in the appropriate international fora.

## 4.4 Non-compartment-specific effects relevant for the food chain (secondary poisoning)

### 4.4.1 Avian toxicity

The toxicity of a C<sub>22-26</sub>, 42% wt. Cl chlorinated paraffin to chicken embryos has been studied. In the study, the chlorinated paraffin was injected into fertilized hens' eggs after four days of incubation in an emulsion of peanut oil, lecithin and water at a dose of 100 or 200 mg/kg egg. No effects were seen on the incubation time, hatching rate, hatching weight, weight gain after hatch (the observations were made up to day 39 after the start of incubation) or liver weights of the chicks when compared with the control group (Brunström, 1993).



In a further injection study, Brunström (1995) investigated the effects of a C<sub>22-26</sub>, 42% wt. Cl substance on liver weight, microsomal enzyme activities and cytochrome P-450 concentration in chick embryos after 20 days of incubation. In this experiment the chlorinated paraffin concentration used was 300 mg/kg egg. No effects were seen on the viability of the chick embryos, liver weights or AHH (aryl hydrocarbon (benzo[a]pyrene) hydroxylase) activity due to the treatment. A statistically significant (p<0.01) increase in cytochrome P-450 concentration and decrease in APND (aminopyrine N-demethylase) and ECOD (7-ethoxycoumarin O-deethylase) activity was observed in the treated population when compared to the control population.

#### 4.4.2 Mammalian toxicity

There are mammalian toxicity data for representative LCCP products with carbon chain-lengths C<sub>20-30</sub> for:

- acute toxicity;
- skin and eye irritation;
- skin sensitisation;
- repeated dose toxicity;
- mutagenicity (limited to bacterial gene mutation and *in vivo* cytogenetics testing);
- carcinogenicity;
- developmental toxicity.

However, toxicokinetic information for the C<sub>20-30</sub> LCCPs is limited and there are no data on:

- repeated skin exposure (a hazardous property identified for medium-chain length chlorinated paraffins);
- the potential to induce gene mutations in mammalian cells;
- fertility;
- parturition;
- lactation.

The hazardous properties of the C<sub>20-30</sub> LCCPs in these data-gap areas will be predicted based on what is known about the toxicity of the medium-chain chlorinated paraffins (MCCPs, CAS no. 85535-85-9) (ECB, 2007b). The justification for this read-across is that the C<sub>20-30</sub> LCCPs have a similar chemical structure to the MCCPs and certain physico-chemical properties are similar (log Kow, water solubility). Further, the profiles of both groups of chlorinated paraffins are broadly similar where studies have been conducted on their adverse health effects. Therefore, the toxicity of LCCPs in other areas is likely to be similar to MCCPs. There are also data gaps for the MCCPs, so the European risk assessment for the MCCPs involves a read-across from the short-chain chlorinated paraffins (SCCPs, CAS no. 85535-84-8) (ECB, 2000). A summarised comparison of the physico-chemical and toxicological properties of these three categories of chlorinated paraffins is provided in Appendix I.

With the exception of a skin irritation study, no mammalian toxicity data are available for the LCCPs with carbon chain lengths C<sub>18-20</sub>. Additionally, information on the physico-chemical properties, in particular water solubility and log K<sub>ow</sub>, are limited.

The hazardous properties of the C<sub>18-20</sub> LCCPs have been predicted on the basis of what is known about the toxicity of the MCCPs and the LCCPs that have carbon chain lengths C<sub>20-30</sub>. The justification for this read-across is that the C<sub>18-20</sub> LCCPs have a similar chemical structure to the MCCPs and C<sub>20-30</sub> LCCPs and therefore their toxic properties are likely to be similar. There are uncertainties in this read-across, so the most conservative toxicology positions possible will be taken as the prediction for the C<sub>18-20</sub> LCCPs (based on data for the MCCPs and C<sub>20-30</sub> LCCPs). Furthermore, an additional assessment factor will be used in the risk assessment for C<sub>18-20</sub> LCCPs to account for uncertainty in these predictions.

#### 4.4.2.1 Toxicokinetics

##### **Studies in animals**

Limited toxicokinetic information is available for a C<sub>22-26</sub>, 43% chlorination product and a C<sub>22-26</sub>, 70% chlorination product.

In conjunction with a standard 13-week repeated dose toxicity study, 18 rats of each gender received a single dose of a radiolabelled C<sub>22-26</sub>, 43% chlorinated LCCP by the oral (gavage) route at 100 or 3,750 mg/kg (IRDC, 1981). The animals were dosed either after having received the respective dose level of unlabelled LCCP daily for 13 weeks or having previously not been exposed to LCCP. Radioactivity in faeces and urine was monitored during the first seven days after radiolabelled LCCP dosing. Three animals per gender per group were killed at 0.5, 1, 2, 7, 28 and 90 days for collection of tissue and/or blood samples for radioactivity measurement.

It was found that between 82 and 95 per cent of the administered radioactivity was recovered in the faeces during the seven-day collection period, most of which was recovered during the first two days. Between 0.1 and 0.8 per cent of the radiolabel was excreted in the urine. Blood concentrations of radioactivity in animals from the two-dose groups were very similar. Also, the inter-group differences in the concentration of radioactivity for any given tissue were much less than the differences between the administered dose. Tissue radioactivity levels were initially greatest in the liver but by 90 days a redistribution to adipose tissue had occurred. This study suggests that absorption of the LCCP product may be saturable, but the extent of systemic absorption and systemic elimination of LCCP could not be determined from this study.

Toxicokinetics of the C<sub>22-26</sub>, 70% chlorination product were investigated in a study of identical design (IUCLID, 2008). It was found that between 61 per cent and 88 per cent of the administered radioactivity was recovered in the faeces during the seven-day collection period. Only a very small proportion of the radioactivity (<0.1–1 per cent) was excrete in the urine. The highest levels of radioactivity were found in the liver, gonads and adipose tissue seven days after dosing, with lower levels being found in the brain, kidney, blood and heart. As was the case with the C<sub>22-26</sub>, 43% chlorination LCCP study, the extent of systemic absorption and systemic elimination could not be determined.

##### **Studies in humans**

No data are available.

### **Summary of toxicokinetics**

Limited toxicokinetic information is available for the LCCP products. Based on this information and that available for MCCPs, it is predicted that absorption via the oral and inhalation routes will be significant (about 50 per cent of the administered dose). Absorption via the dermal route is predicted to be lower (about 1 per cent of administered dose). It can be predicted that LCCPs could be preferentially distributed to fatty tissues in the body, and that excretion via breast milk could occur. It is possible that there will be some metabolism of LCCPs to CO<sub>2</sub>.

#### **4.4.2.2 Acute toxicity**

##### **Studies in animals**

###### Inhalation

No data are available.

###### Oral

Valid acute toxicity investigations by the oral route (gavage) have been conducted on five LCCP products: C<sub>20-30</sub> 41–50% chlorination, C<sub>22-26</sub> 42% chlorination, C<sub>23</sub> 43% chlorination, C<sub>20-30</sub> 61–70% chlorination, C<sub>24</sub> 70% chlorination (IUCLID, 2003). Most of the studies were conducted in rats, but the dog and mouse have also been used as test species. The maximum dose levels used in these studies ranged from 4,000 to 50,000 mg/kg.

The LCCP products were all found to have very low acute toxicity. No deaths were reported in any of the studies. Furthermore, non-lethal toxicity was reported in only one of the studies; in the exception, incontinence was observed during the two days following dosing.

###### Dermal

No data are available.

##### **Studies in humans**

No data are available.

##### **Summary of acute toxicity**

Acute oral toxicity data in animals are available for a number of LCCP products with carbon chain lengths ranging from C<sub>20</sub> to C<sub>30</sub>. These data show that the LCCP products are of low acute toxicity. Based on the low oral toxicity and absence of any significant irritant hazard (see Section 4.4.2.3), it can be predicted that the LCCP products will also be of low acute toxicity by the inhalation and dermal routes. As both MCCPs and C<sub>20-30</sub> LCCPs are known to be of low acute toxicity, it is assumed that the C<sub>18-20</sub> LCCPs will also be of low acute toxicity.

#### **4.4.2.3 Irritation**

##### **Studies in animals**

###### Skin

Valid skin irritation testing has been conducted on four LCCP products: C<sub>19</sub> 44% chlorination, C<sub>20-30</sub> 70% chlorination, C<sub>22-26</sub> 42% chlorination and C<sub>20-30</sub> 41–50% chlorination products (IUCLID, 2003). No evidence of irritation was seen in the testing

of three products. However, for the C<sub>22-26</sub> 42% chlorination product tested, erythema was observed in two out of six animals, indicating a potential to cause slight irritation, albeit below the severity threshold for classification according to the EU system.

No information is available on the effects on the skin of repeated application of LCCPs so information from MCCPs is taken into account in the summary.

#### Eye

Valid eye irritation testing has been conducted on two LCCP products (IUCLID, 2003). A C<sub>20-30</sub> 61–70% chlorination product caused no eye irritation. Evidence of slight irritation was seen in a test of a C<sub>22-26</sub> 42% chlorination product, but the criteria for classification as an eye irritant were not met.

#### Respiratory Tract

No data are available.

#### **Studies in humans**

No data are available.

#### **Summary of irritation**

Skin and eye irritation have been investigated in animal studies for a number of LCCP products with carbon chain lengths ranging from C<sub>19</sub> to C<sub>30</sub>. These studies suggest that the LCCPs have the potential to cause slight irritation, albeit below the severity threshold for classification according to the EU system. Single exposure to MCCPs also caused slight irritation in standard tests, but somewhat more pronounced irritation has been reported following repeated exposure, presumably due to defatting properties. In the absence of studies on repeated application of LCCPs to skin, a conservative assumption is made that LCCPs will have a similar effect as MCCPs.

There are no specific data on respiratory tract irritation, but on the basis of the low skin and eye irritation potential, it is anticipated that the LCCP products are unlikely to cause such an effect.

#### **4.4.2.4 Corrosivity**

The skin and eye irritation studies summarised above in Section 4.4.2.3 demonstrate that LCCPs are not corrosive.

#### **4.4.2.5 Sensitisation**

##### **Studies in animals**

Guinea pig maximisation tests have been conducted on two LCCP products (IUCLID, 2003; IUCLID, 2000a). A C<sub>22-26</sub> 42% chlorination product tested negative in a test considered to be valid. A C<sub>18-27</sub> 40% chlorination product elicited a positive response; no information is available on the quality of this study.

A Buehler guinea pig test has been conducted on a C<sub>22-26</sub> product (chlorination level not stated) (Bailey and Sheldon, 1998). Negative results were reported for the LCCP product in mineral oil. This study was reported as a brief abstract, so it is not possible to assess the quality of the study.

## **Studies in humans**

### Skin

No data are available.

### Respiratory Tract

No data are available.

## **Summary of sensitisation**

Both positive and negative results have been obtained in standard guinea pig skin sensitisation tests. Although firm conclusions cannot be drawn from the available data, it is possible that the LCCPs may have the potential to cause skin sensitisation reactions.

### **4.4.2.6 Repeated dose toxicity**

## **Studies in animals**

### Inhalation

No data are available.

### Oral

Standard repeated dose toxicity studies in rats are available for two similar LCCP products with 43% chlorination, one with a carbon chain length  $C_{22-26}$ , and one with  $C_{23av}$ , and a 70% chlorination LCCP product with a carbon chain length  $C_{20-26}$ . The studies were conducted in compliance with GLP.

#### *$C_{22-26}$ , 43% chlorination product*

In a preliminary 14-day study, the LCCP product was administered by gavage to groups of five Fischer rats of each gender at dose levels of 0 (corn oil vehicle control), 30, 100, 300, 1,000 or 3,000 mg/kg/day (IRDC, 1981a). Bodyweights, food and water consumption and the presence of clinical signs of toxicity were monitored throughout the study. At termination, a necropsy was conducted in which macroscopic abnormalities and selected organ weights were recorded. Liver microsomal Lowry protein and cytochrome P-450 levels and aminopyridine demethylase activity were determined. Liver and kidneys were subject to microscopic examination. There were no intergroup differences that were considered to be treatment-related and therefore a NOAEL of 3,000 mg/kg/day for a 14-day exposure period was identified.

In a standard 13-week repeated dose toxicity study the LCCP product was administered by gavage to groups of fifteen Fischer rats of each gender at dose levels of 0 (corn oil vehicle control), 100, 900 or 3,750 mg/kg/day (IRDC, 1984). Bodyweights, food consumption and the presence of clinical signs of toxicity were monitored throughout the study. Water consumption was measured during the first three weeks of the study. Standard haematology and clinical chemistry investigations were conducted on blood samples taken at weeks 4/5, 8 and 13. Ophthalmoscopy examinations were conducted at the start and end of the study and urinalysis was conducted during week 5. At termination, a necropsy was conducted in which macroscopic abnormalities and selected organ weights were recorded. A standard range of tissues, including reproductive organs, were examined microscopically.

There were no treatment-related deaths, clinical signs of toxicity or effects on bodyweight or water consumption. Food consumption was slightly increased in both

males and females receiving 3,500 mg/kg/day. Haematological, clinical chemistry, urinalysis and ophthalmoscopy findings were similar for all groups.

At necropsy, the only changes considered to be treatment-related were on liver weight, among females only. Absolute liver weight was significantly increased at all treatment levels. Bodyweight-related liver weight was also increased at all treatment levels, although the differences were statistically significant only at 900 and 3,750 mg/kg/day. The increases were of similar magnitude (~15 per cent greater than controls) at all treatment levels. Microscopic examination revealed treatment related inflammatory changes in the liver of a number of females in all LCCP-exposed groups. The microscopic changes were granulomatous inflammation and/or necrosis and increased intensity of Oil Red O staining (an indicator of intracellular lipid accumulation). The incidence and severity of the liver lesions did not follow an obvious dose-dependant pattern. The microscopic examination also revealed the presence of nephrosis (graded as either trace or mild) in four males at 3,750 mg/kg/day; nephrosis was not seen in the controls or other LCCP treated groups.

A NOAEL could not be identified in this study. A LOAEL of 100 mg/kg/day is established based on the presence of liver changes in females at all treatment levels.

#### *C<sub>23av</sub>, 43% chlorination*

A series of rat studies commenced with a 16-day preliminary study. The LCCP product was administered by gavage to groups of five Fischer rats of each gender at dose levels of 0 (corn oil vehicle control), 235, 469, 938, 1,875 or 3,750 mg/kg/day for five days/week (NTP, 1986). Bodyweights and the presence of clinical signs of toxicity were monitored throughout the study. At termination, a necropsy was conducted in which any macroscopic abnormalities were recorded. No treatment related effects were observed in this study.

In a 13-week study designed as a rangefinder for a carcinogenicity study, the LCCP product was administered by gavage to groups of 10 Fischer rats of each gender at dose levels of 0 (corn oil vehicle control) 235, 469, 938, 1,875 or 3,750 mg/kg/day for five days per week (NTP, 1986). Bodyweights and the presence of clinical signs of toxicity were monitored throughout the study. At termination, a necropsy was conducted in which any macroscopic abnormalities were recorded. A standard range of tissues, including reproductive organs, were examined microscopically.

There were no treatment-related deaths, clinical signs of toxicity, effects on bodyweight or macroscopic abnormalities observed at necropsy. Microscopic abnormalities were reported in the liver in females in all LCCP exposed groups. There was a dose related increase in the incidence of granulomatous inflammation in the liver; the incidence ranged from 1/10 at 235 mg/kg/day to 9/10 at 3,750 mg/kg/day, compared with 0/10 in the control group. A LOAEL of 235 mg/kg/day is established for a 13-week exposure period, based on the presence of liver changes at all treatment levels.

In a carcinogenicity study (cancer findings are presented in Section 4.4.2.8), the LCCP product was administered by gavage to Fischer rats, for five days each week, for up to either six months, 12 months or two years (NTP, 1986). The dose levels were 0 (corn oil vehicle control), 1,875 or 3,750 mg/kg/day for males and 0, 100, 300 or 900 mg/kg/day for females. The group sizes were 20 rats for each gender for the six and 12 month exposure periods and 50 of each gender for the two year exposure period. Bodyweights and the presence of clinical signs of toxicity were monitored throughout the study. At termination, a necropsy was conducted in which any macroscopic abnormalities were recorded. A standard range of tissues, including

reproductive organs, were examined microscopically. For the six and 12 month exposure groups, blood was collected just prior to necropsy for standard haematological and clinical chemistry investigations; additionally the weights of major organs were measured.

In the groups exposed for six or 12 months there were no treatment-related deaths or effects on bodyweight. The activities of several serum enzymes that serve as markers for liver injury were significantly increased in males (at 1,875 and 3,750 mg/kg/day) and females (at 300 and 900 mg/kg/day) at both time intervals. Bodyweight-related liver weights were increased in males at 3,750 mg/kg/day at 12 months and in females at 300 mg/kg/day at 12 months and at 900 mg/kg/day at six and 12 months. Microscopically, there was a dose- and time-related increase in the incidence and severity of granulomatous and lymphohistiocytic hepatitis throughout all the LCCP exposed groups.

In the two year study survival was not affected by LCCP treatment. In males there were no effects on bodyweights, but for females at 300 and 900 mg/kg/day bodyweights were about five per cent lower than controls from week 70. The only clinical signs that could be related to treatment were brown staining around the mouth of some males from week 44 and a high incidence of distended abdomen for females towards the end of the study. Microscopically, treatment-related non-neoplastic lesions were reported in all LCCP treated groups in the liver (granulomatous focal inflammation, hyperplasia, pigmentation), pancreatic lymph node (granulomatous inflammation, lymphoid hyperplasia) for both males and females, and in the eye (retinopathy, cataracts) among males. Generally, the incidence of microscopic lesions was similar in all LCCP groups. A LOAEL of 100 mg/kg/day is established for non-neoplastic changes, based on the presence of microscopic changes in the liver and lymph nodes at the lowest dose level.

The series of mouse studies commenced with a 16-day preliminary study. The LCCP product was administered by gavage to groups of five B6C3F<sub>1</sub> mice of each gender at dose levels of 0 (corn oil vehicle control), 469, 938, 1,875, 3,750 or 7,500 mg/kg/day for five days per week (NTP, 1986). Bodyweights and the presence of clinical signs of toxicity were monitored throughout the study. At termination, a necropsy was conducted in which macroscopic abnormalities were recorded. No treatment-related effects were observed in this study.

In a 13-week study designed as a rangefinder for a carcinogenicity study, the LCCP product was administered by gavage to groups of 10 B6C3F<sub>1</sub> mice of each gender at dose levels of 0 (corn oil vehicle control) 469, 938, 1,875, 3,750 or 7,500 mg/kg/day for five days per week (NTP, 1986). Bodyweights and the presence of clinical signs of toxicity were monitored throughout the study. At termination, a necropsy was conducted in which any macroscopic abnormalities were recorded. A range of tissues were examined microscopically. No treatment related effects were observed in this study.

In a carcinogenicity study (cancer findings are presented in Section 4.4.2.8) the LCCP product was administered by gavage to groups of 50 B6C3F<sub>1</sub> mice of each gender at dose levels of 0 (corn oil vehicle control) 2,500 or 5,000 mg/kg/day, five days per week, for two years (NTP, 1986). Bodyweights and the presence of clinical signs of toxicity were monitored throughout the study. At termination, a necropsy was conducted in which macroscopic abnormalities were recorded. A standard range of tissues, including reproductive organs, were examined microscopically.

Survival and bodyweights were not affected by LCCP treatment. There were no treatment-related clinical signs. There were no non-neoplastic microscopic findings that

could be clearly attributed to LCCP treatment. Thus, a NOAEL of 5,000 mg/kg/day is established in the mouse for a two-year exposure period.

#### *C<sub>20-26</sub>, 70% chlorination*

In a five-day study designed as a rangefinder for a cytogenetics study, the LCCP product was administered by gavage to groups of eight Fischer 344 rats of each gender at dose levels of 0 (1% carboxymethylcellulose vehicle control), 1,000, 2,500 or 5,000 g/kg/day (IRDC, 1982). Bodyweights and food consumption were measured and clinical signs of toxicity were monitored. At termination a necropsy was conducted in which macroscopic abnormalities were recorded. There were no treatment-related effects and therefore a NOAEL of 5,000 mg/kg/day for a five-day exposure period was identified.

In a preliminary 14-day study, the LCCP product was administered via the diet to groups of five Fischer rats of each gender at concentrations resulting in dose levels of about 0, 17, 55, 179, 565 and 1,715 mg/kg/day (IRDC, 1981b). Bodyweights, food consumption and the presence of clinical signs of toxicity were monitored throughout the study. At termination a necropsy was conducted in which macroscopic abnormalities and selected organ weights were recorded. Liver microsomal Lowry protein and cytochrome P-450 levels and aminopyridine demethylase activity were determined. Liver, kidneys and spleen were subject to microscopic examination. There were no intergroup differences that were considered to be treatment-related and therefore a NOAEL of 1,715 mg/kg/day for a 14-day exposure period was identified.

In a standard 13-week repeated exposure toxicity study the LCCP product was administered via the diet to groups of 15 Fischer rats of each gender at concentrations resulting in dose levels of 0, 100, 900 or 3,750 mg/kg/day (IUCLID, 2003). Bodyweights, food consumption and the presence of clinical signs of toxicity were monitored throughout the study. Water consumption was measured during the first three weeks of the study. Standard haematology and clinical chemistry investigations were conducted on blood samples taken at weeks 4/5, 8 and 13. Ophthalmoscopy examinations were conducted at the start and end of the study and urinalysis was conducted during week 5. At termination, a necropsy was conducted in which macroscopic abnormalities and selected organ weights were recorded. A standard range of tissues, including reproductive organs, from the control and the 3,750 mg/kg/day group were examined microscopically.

There were no treatment-related deaths, clinical signs of toxicity or effects on water consumption. Bodyweight gain was significantly reduced at 3,750 mg/kg/day, with weights at 13 weeks being seven per cent or three per cent less than controls for males and females, respectively. Food consumption was significantly increased in both males (by ~11 per cent) and females (by ~7 per cent) at 3,750 mg/kg/day. There was a significant reduction in urine volume, with an associated increase in urine specific gravity, in males at 3,750 mg/kg/day. Haematological, clinical chemistry (except for aspartate (AST) and alanine (ALT) aminotransferase, see below) and ophthalmoscopy findings were similar for all groups.

Effects on the liver were reported at 3,750 mg/kg/day. There was a statistically significant increase in bodyweight-related liver weight in males and females; absolute liver weight was also increased in females at this dose level. Microscopic findings in the liver of rats from the 3,750 mg/kg/day were increased cytoplasmic vacuolation, hepatocellular hypertrophy and positive Oil Red O staining. The microscopic changes were more prominent among females. Additionally, AST (females) and ALT (males and



females) were slightly, though statistically significant, increased at this dose level, confirming an effect on the liver.

Overall, a NOAEL of 900 mg/kg/day was identified, based on the observation of effects on bodyweight gain, food consumption and the liver at the higher dose level of 3,750 mg/kg/day.

#### Dermal

No data are available.

#### **Studies in humans**

No data are available.

#### **Summary of repeated dose toxicity**

No information is available on the effects of repeated exposure in humans. In animals there are no data relating to the inhalation or dermal routes. Repeated dose toxicity data in animals for the oral route are available for two LCCP products with 43% chlorination (by gavage administration), one with carbon chain length  $C_{22-26}$  and one with  $C_{23av}$ , and for a 70% chlorinated LCCP product (by dietary administration) with carbon chain length  $C_{20-26}$ . A specific comparison of the toxicities of the low and high chlorination states is not possible because of differences in methods of administration.

The liver was identified as the main target organ in the rat for both the 43% and 70% chlorination products. For the 43% chlorination products, inflammatory and necrotic histopathological changes, intracellular lipid accumulation and hyperplasia were seen in rats at dose levels of 100 mg/kg/day and above. As 100 mg/kg/day was the lowest dose level investigated, this is identified as a LOAEL for liver toxicity for 43% chlorination LCCP products. For the 70% chlorination product, effects in the liver (i.e. hyperplasia, intracellular lipid accumulation and increased cytoplasmic vacuolation) occurred only at a very high exposure level of 3,750 mg/kg/day; the NOAEL for liver toxicity was 900 mg/kg/day.

Other target organs for the 43% chlorinated LCCP products were also identified in the rat. Kidney toxicity, manifested as histopathological-detected mild nephrosis was seen in several male rats only dosed with the 43% chlorination product at 3,750 mg/kg/day for 13 weeks. Additionally, changes were observed in the pancreatic lymph node (i.e. granulomatous inflammation, lymphoid hyperplasia) at 100 mg/kg/day and above, and in the eye (retinopathy, cataracts) at 1,875 mg/kg/day and above.

Overall, a repeated dose toxicity LOAEL of 100 mg/kg/day for 43% chlorinated LCCPs and a NOAEL 900 mg/kg/day for 70% chlorinated LCCPs were identified. The uncertainties regarding the influence of the chlorination state on the toxicity of the LCCPs means that the more conservative LOAEL of 100 mg/kg/day is taken forward to the risk assessment for all  $C_{20-30}$  LCCPs, irrespective of their chlorination state. For the  $C_{18-20}$  LCCPs a NOAEL of 23 mg/kg/day (300 mg/kg food) for repeated dose toxicity will be assigned, based on the data for MCCPs.

#### **4.4.2.7 Mutagenicity**

Because testing of the LCCPs is limited, data for SCCPs and MCCPs are also covered in the summary of this section.

## ***In vitro studies***

### **Bacterial studies**

Ames testing, using valid methods, has been conducted on two LCCP products: C<sub>22-26</sub>, 43% chlorination and C<sub>23av</sub>, 43% chlorination (IUCLID, 2003).

The C<sub>22-26</sub>, 43% chlorination product was tested using *Salmonella* strains TA98, TA100, TA1535, TA1537. The C<sub>23av</sub>, 43% chlorination product test was conducted in compliance with GLP, using *Salmonella* strains TA98, TA100, TA1535, TA1538. The test result for both products was negative.

Several other bacterial tests are reported in the IUCLID (2003), but these did not use standard methodology and are therefore considered invalid.

### **Mammalian cell studies**

A C<sub>23</sub>, 43% chlorination product has been investigated in a chromosome aberration and sister chromatid exchange test conducted in Chinese hamster ovary cells (Anderson *et al.*, 1990). The design of the studies was comparable to the OECD test guidelines 473 and 479. A positive result was obtained in the absence of S9 in the chromosome aberration test. Positive results were reported both in the presence and absence of S9 in the sister chromatid exchange test.

## ***In vivo studies***

*In vivo* chromosome aberration tests have been conducted on two LCCP products: C<sub>22-26</sub>, 43% chlorination and C<sub>20-26</sub>, 70% chlorination (IUCLID, 2003). Both tests were conducted in compliance with GLP and were considered to be valid.

The test result for both products was negative.

## ***Studies in humans***

No data are available.

## ***Summary of mutagenicity***

Limited data are available on the mutagenicity of the LCCPs. C<sub>23av</sub>, 43% chlorinated and C<sub>22-26</sub>, 42% chlorinated LCCP products are not mutagenic in bacteria, but an LCCP product with a higher chlorination state has not been tested in bacteria. No *in vitro* or *in vivo* mammalian cell gene mutation tests are available for the LCCPs. A C<sub>23</sub>, 43% chlorination product tested positive in an *in vitro* chromosome aberration and sister chromatid exchange test. However, negative results were obtained in *in vivo* chromosome aberration tests on a C<sub>22-26</sub>, 43% chlorination and a C<sub>20-26</sub>, 70% chlorination LCCP product, suggesting that genotoxic activity would not be expressed *in vivo*.

The mutagenicity data available for the other chlorinated paraffin categories are also limited. Several short-chain chlorinated paraffins (SCCPs) have tested negative in bacterial tests and one SCCP has been tested in an *in vitro* mammalian gene cell mutation test which was negative. *In vivo*, an SCCP product tested negative in a chromosome aberration test and in a dominant lethal test. The MCCPs that have been tested in bacteria are also not mutagenic, but no members of this category have been tested in *in vitro* or *in vivo* mammalian cell gene mutation tests, as is the case for the LCCPs. Two similar MCCP products have tested negative in *in vivo* micronucleus tests and another MCCP product was negative in an *in vivo* chromosome aberration test.

Overall, the chlorinated paraffins have not been comprehensively tested for mutagenicity. However, given the lack of evidence of mutagenicity for the chlorinated paraffins generally, it can be predicted that the LCCPs will not be mutagenic.

#### 4.4.2.8 Carcinogenicity

##### **Studies in animals**

The carcinogenicity of a C<sub>23av</sub>, 43% chlorination LCCP product has been investigated in rats and mice in standard studies (NTP, 1986). Non-neoplastic findings reported in these studies are presented in Section 4.4.2.6.

In the rat study, groups of 50 Fischer rats of each gender were administered the LCCP product by gavage, five days per week, for up to two years. The dose levels were 0 (corn oil vehicle control), 1,875 or 3,750 mg/kg/day for males and 0, 100, 300 or 900 mg/kg/day for females. The incidence of tumours in males was not affected by LCCP treatment. However, a dose-related increased incidence in adrenal gland medullary pheochromocytoma was seen in females in all the LCCP treated groups (1/50, 4/50, 6/50 and 7/50 in the control, 100, 300 or 900 mg/kg/day, respectively). All the tumours, except for one at 100 mg/kg/day, were benign. The historical incidence of this type of tumour in corn-oil vehicle control female Fischer rats is 5–6 per cent. The NTP report concludes that there was no evidence of carcinogenicity in male rats and equivocal evidence of carcinogenicity in female rats.

In the mouse study, groups of 50 B6C3F<sub>1</sub> mice of each gender were administered the LCCP product by gavage at dose levels of 0 (corn oil vehicle), 2,500 or 5,000 mg/kg/day, five days/week, for two years. The number of female deaths after week 65 was unusually high, probably the result of a *Klebsiella oxytoca* infection. This may have reduced the power of the study to detect a carcinogenic effect. In males there was a dose-related increased incidence of malignant lymphomas (6/50 (12 per cent), 12/50 (24 per cent) and 16/50 (32 per cent) in the control, 2,500 and 5,000 mg/kg/day groups, respectively). The historical incidence of this type of tumour in corn-oil vehicle control male B6C3F<sub>1</sub> mice is 22 per cent, similar to that observed at the lower dose level of 2,500 mg/kg/day, so only the increased incidence at 5,000 mg/kg/day can be considered to be treatment-related.

In females there was a marginal increase in the incidence of hepatocellular carcinomas (1/50, 1/49 and 6/50 in the control, 2,500 and 5,000 mg/kg/day groups, respectively) and of adenomas and carcinomas combined (4/50, 3/49 and 10/50). The historical incidence of hepatocellular carcinomas in corn-oil vehicle control females was about half that observed in the high dose group. The NTP report concludes that there was clear evidence of carcinogenicity in male mice and equivocal evidence of carcinogenicity in female mice.

##### **Studies in humans**

No data are available.

##### **Summary of carcinogenicity**

The carcinogenicity of a C<sub>23av</sub>, 43% chlorination LCCP product has been investigated in rats and mice in standard studies. An increased incidence of malignant lymphoma in male mice was reported at the highest dose tested, 5,000 mg/kg/day, providing evidence that LCCPs are carcinogenic. Marginal increases in the incidence of adrenal medullary pheochromocytomas observed in female rats from 100 mg/kg/day and in

hepatocellular carcinomas in female mice at 5,000 mg/kg/day were not considered to represent convincing evidence of carcinogenicity.

Overall, there is evidence that LCCPs are carcinogenic, but only at very high exposure levels. Because the chlorinated paraffins do not appear to have mutagenic potential it is likely that this carcinogenic activity is the result of a non-genotoxic mode of action and it can therefore be assumed that the carcinogenicity will have a threshold exposure level. Accordingly, a NOAEL of 2,500 mg/kg/day, at which the incidence of malignant lymphomas was similar to historical controls, can be identified.

#### 4.4.2.9 Toxicity for reproduction

##### **Effects on fertility**

###### Studies in animals

There are no studies in which effects on fertility and reproductive performance have been specifically investigated. No changes in the weight or macroscopic and microscopic appearance of the reproductive organs were reported in the repeated dose toxicity studies, available for C<sub>22-26</sub>, 43% chlorination, C<sub>23av</sub>, 43% chlorination and C<sub>20-26</sub>, 70% chlorination LCCP products (see Section 4.4.2.6).

Limited testing that has been conducted into the effects of LCCPS on fertility and reproductive performance, therefore data for MCCPs is taken into account in the summary of this section.

###### Studies in humans

No data are available.

##### **Developmental toxicity**

###### Studies in animals

Valid studies are available in rat and rabbits for a C<sub>22-26</sub>, 43% chlorination and a C<sub>22-26</sub>, 70% chlorination LCCP product. The studies were conducted in compliance with GLP.

###### *C<sub>22-26</sub>, 43% chlorination*

In a standard developmental toxicity study, the LCCP product was administered to groups of 25 timed mated female Sprague-Dawley rats at dose levels of 0 (corn oil vehicle control), 500, 2,000 or 5,000 mg/kg/day, from days 6 to 19 of gestation (IRDC 1983a). Clinical signs and maternal bodyweights were monitored throughout the study. The mothers were killed on day 20 of gestation and a necropsy was performed. Maternal organs were examined for gross abnormalities. Numbers of corpora lutea and implantation sites were counted and foetal weights were recorded. All foetuses were examined externally. Approximately half of the foetuses from each litter were processed for skeletal examination and the remainder were processed for soft tissue examination.

In the mothers there were no treatment-related clinical signs, effects on bodyweight gain or maternal necropsy findings. There was one premature maternal death, at 5,000 mg/kg/day on day 18 of gestation, but a relationship with treatment could not be established. Pre- and post-implantation loss was not affected by treatment. Foetal weights and the incidence of external, visceral and skeletal variations and abnormalities in the foetuses were similar to the controls for all LCCP treated groups. A NOAEL of 5,000 mg/kg/day was identified for maternal and developmental toxicity.

In a standard developmental toxicity study, the LCCP product was administered to groups of 16 timed mated female Dutch belted rabbits at dose levels of 0 (corn oil vehicle control), 500, 2,000 or 5,000 mg/kg/day, from days 6 to 27 of gestation (IUCLID, 2003). Clinical signs and maternal bodyweights were monitored throughout the study. The mothers were killed on day 28 of gestation and a necropsy was performed. Maternal organs were examined for gross abnormalities. Numbers of corpora lutea and implantation sites were counted and foetal weights were recorded. All foetuses were examined for external, visceral and skeletal variations and abnormalities.

Among mothers from all LCCP-treated groups there was an increased incidence of soft faeces and matted hair in the anogenital region. There were no treatment-related effects on maternal bodyweight gain or necropsy findings. There was one premature maternal death, at 5,000 mg/kg/day, due to a dosing error. Three mothers aborted during the study, one at 2,000 mg/kg/day group and two at 5,000 mg/kg/day. However, abortions are relatively common in rabbit developmental toxicity studies, so these abortions could not be attributed to LCCP treatment. Post-implantation loss was slightly increased at 5,000 mg/kg/day, with a consequent slight reduction in the numbers of viable foetuses. Foetal weights and the incidence of foetal external, visceral and skeletal variations and abnormalities were similar to the controls for all the LCCP treated groups. The comparison of the incidence of variations and abnormalities with controls was of limited value owing to the reduced numbers of live foetuses at 5,000 mg/kg/day. As there were clinical signs that were possibly related to treatment in all LCCP-treated groups, a NOAEL for maternal toxicity could not be identified and therefore a LOAEL of 500 mg/kg/day is declared. The NOAEL for developmental toxicity is 2,000 mg/kg/day, based on the observation of increased post-implantation loss at 5,000 mg/kg/day. It is considered likely that this post-implantation loss was a secondary non-specific consequence of maternal toxicity.

#### *C<sub>22-26</sub>, 70% chlorination*

In a standard developmental toxicity study, the LCCP product was administered to groups of 25 timed mated female Sprague-Dawley rats at dose levels of 0 (aqueous carboxymethyl cellulose vehicle control), 500, 2,000 or 5,000 mg/kg/day, from days 6 to 19 of gestation (IRDC 1984b). The design of the study was identical to the rat developmental toxicity study for the C<sub>22-26</sub>, 43% chlorination LCCP product, described above (IRDC 1983a). There were no treatment-related effects in either the mothers or offspring, and therefore a NOAEL of 5,000 mg/kg/day was identified for maternal and developmental toxicity.

In a standard developmental toxicity study, the LCCP product was administered to groups of 16 timed mated female Dutch belted rabbits at dose levels of 0 (aqueous carboxymethyl cellulose vehicle control), 500, 2,000 or 5,000 mg/kg/day, from days 6 to 27 of gestation (IRDC 1983b). The dose levels were chosen on the basis of range finding studies in which evidence of maternal toxicity and a high incidence of abortions were reported at dose levels of 2,000 and 5,000 mg/kg/day. The design of the study was identical to the rabbit developmental toxicity study for the C<sub>22-26</sub>, 43% chlorination LCCP product, described above (IUCLID, 2003).

There were no treatment-related maternal clinical signs of effects on bodyweight gain. Two mothers at 1,000 mg/kg/day died due to dosing errors and one mother at 500 mg/kg/day died of an undetermined cause. At the maternal necropsy a slight increase in the incidence of congested lungs was reported in the LCCP-treated groups, but there was no dose-response relationship so this was considered likely to be a chance finding. Pre- and post-implantation loss, foetal weights and the incidence of

foetal variations and abnormalities were not affected by treatment. Overall, a NOAEL of 1,000 mg/kg/day for maternal and developmental toxicity was identified.

### ***Studies in humans***

No data are available.

### ***Summary of toxicity for reproduction***

There are no studies in which effects on fertility and reproductive performance have been specifically investigated. No changes in the weight or macroscopic and microscopic appearance of the reproductive organs were reported in the repeated dose toxicity studies, available for C<sub>22-26</sub>, 43% chlorination, C<sub>23av</sub>, 43% chlorination and C<sub>20-26</sub>, 70% chlorination LCCP products. Taking account of this information from the repeated dose toxicity studies and the fact that no effects on fertility were observed in two MCCP reproductive toxicity studies, it is predicted that the LCCPs do not have the capacity to affect fertility. In one MCCP study using dietary administration, maternal deaths during parturition were reported at 538 mg/kg/day as a consequence of haemorrhaging due to low vitamin K levels. A NOAEL of 100 mg/kg/day was identified for this effect. In the absence of studies on the effects of LCCPs during the time of parturition and on vitamin K levels, a conservative assumption is made that LCCPs will have a similar effect.

In relation to developmental effects, no evidence of a specific effect on development was observed in standard rat and rabbit studies on a C<sub>22-26</sub>, 43% chlorination and a C<sub>22-26</sub>, 70% chlorination LCCP product. However, maternal dietary exposure to MCCPs has been shown to cause haemorrhaging and death in neonates, thought to be mainly due to reduced vitamin K levels in the milk. A NOAEL of 47 mg/kg/day as a maternal dose was identified for this effect. In the absence of studies on the effects of LCCPs on neonates and on vitamin K levels, a conservative assumption is made that LCCPs will have a similar effect.

#### ***4.4.2.10 Summary of mammalian toxicity***

No human data are available for the LCCPs.

No toxicokinetic data are available for the LCCP products. Based on information available for MCCPs, it is predicted that absorption via the oral and inhalation routes will be significant (about 50 per cent of the administered dose). Absorption via the dermal route is predicted to be lower (about one per cent of administered dose). It can be predicted that LCCPs could be preferentially distributed to fatty tissues in the body, and that excretion via breast milk could occur.

Acute oral toxicity data in animals are available for a number of LCCP products with carbon chain lengths ranging from C<sub>20</sub> to C<sub>30</sub>. These data show that the LCCP products are of low acute toxicity. Based on the low oral toxicity and absence of significant irritant hazard (see Section 4.4.2.3) it can be predicted that the LCCP products will also be of low acute toxicity by the inhalation and dermal routes.

Skin and eye irritation has been investigated in animal studies for a number of LCCP products with carbon chain lengths ranging from C<sub>20</sub> to C<sub>30</sub>. These studies show that LCCPs have the potential to cause slight irritation, albeit below the severity threshold for classification according to the EU system. Single exposure to MCCPs also causes slight irritation in standard tests, but somewhat more pronounced irritation has been reported following repeated exposure, presumably due to defatting properties. In the

absence of studies on repeated application of LCCPs to skin, a conservative assumption is made that LCCPs will have a similar effect. There are no specific data on respiratory tract irritation, but on the basis of the low skin and eye irritation potential it is anticipated that LCCP products are unlikely to cause such an effect.

Both positive and negative results have been obtained in standard guinea pig skin sensitisation tests. It is possible that the LCCPs may have the potential to cause skin sensitisation reactions, although firm conclusions cannot be drawn from the available data.

On the basis of a positive result in a standard guinea pig maximisation test using an LCCP C<sub>18-27</sub> 40% chlorination product, it is assumed that LCCPs have the potential to cause skin sensitisation reactions.

No information is available on the effects of repeated exposure in humans. In animals there are no data relating to the inhalation or dermal routes. Repeated dose toxicity data in animals for the oral route are available for two LCCP products with 43% chlorination (by gavage administration), one with carbon chain length C<sub>22-26</sub> and one with C<sub>23av</sub>, and for a 70% chlorinated LCCP product (by dietary administration) with carbon chain length C<sub>20-26</sub>. A specific comparison of the toxicities of the low and high chlorination states is not possible because of differences in the methods of administration and the absence of investigation into the influence of chlorination on the toxicokinetic profile.

The liver was identified as the main target organ in the rat for both the 43% and 70% chlorination products. For the 43% chlorination products, inflammatory and necrotic histopathological changes, intracellular lipid accumulation and hyperplasia were seen in rats at dose levels of 100 mg/kg/day and above. As 100 mg/kg/day was the lowest dose level investigated, this is identified as a LOAEL for liver toxicity for 43% chlorination LCCP products. For the 70% chlorination product, effects in the liver (hyperplasia, intracellular lipid accumulation and increased cytoplasmic vacuolation) occurred only at a very high exposure level of 3,750 mg/kg/day; the NOAEL for liver toxicity was 900 mg/kg/day.

Other target organs for the 43% chlorinated LCCP products were also identified in the rat. Kidney toxicity, manifested as histopathological detected mild nephrosis was seen in several male rats only dosed with the 43% chlorination product at 3,750 mg/kg/day for 13 weeks. Additionally, changes were observed in the pancreatic lymph node (granulomatous inflammation, lymphoid hyperplasia) at 100 mg/kg/day and above, and in the eye (retinopathy, cataracts) at 1,875 mg/kg/day and above.

Overall, a repeated dose toxicity LOAEL of 100 mg/kg/day for 43% chlorinated LCCPs and a NOAEL 900 mg/kg/day for 70% chlorinated LCCPs were identified. It is recommended that the more conservative LOAEL of 100 mg/kg/day is taken forward to the risk assessment for the C<sub>20-30</sub> LCCPs, regardless of the chlorination state, owing to the uncertainties regarding the influence of the chlorination state on the toxicity of LCCPs. For the C<sub>18-20</sub> LCCPs a NOAEL of 23 mg/kg/day (equivalent to 300 mg/kg food) for repeat dose toxicity is assigned, based on the data for MCCPs.

Limited data are available on the mutagenicity of the LCCPs. A C<sub>23av</sub>, 43% chlorinated and a C<sub>22-26</sub>, 42% chlorinated LCCP product were not mutagenic in bacteria, but an LCCP product with a higher chlorination state has not been tested in bacteria. No *in vitro* or *in vivo* mammalian cell gene mutation tests are available for the LCCPs. A C<sub>23</sub>, 43% chlorination product tested positive in an *in vitro* chromosome aberration and sister chromatid exchange test. However, negative results were obtained in *in vivo*

chromosome aberration tests on a C<sub>22-26</sub>, 43% chlorination and a C<sub>22-26</sub>, 70% chlorination LCCP product, suggesting that genotoxic activity would not be expressed *in vivo*. The mutagenicity data available for other categories of chlorinated paraffins are also limited. Several SCCPs have tested negative in bacterial tests and one SCCP has been tested in an *in vitro* mammalian gene cell mutation test which was negative. *In vivo*, an SCCP product tested negative in a chromosome aberration test and in a dominant lethal test. The MCCPs that have been tested in bacteria are also not mutagenic, but no members of this category of chlorinated paraffin have been tested in *in vitro* or *in vivo* mammalian cell gene mutation tests, as is the case for the LCCPs. Two similar MCCP products have tested negative in *in vivo* micronucleus tests and another MCCP product was negative in an *in vivo* chromosome aberration test. Overall, the chlorinated paraffins have not been comprehensively tested for mutagenicity. However, given the lack of evidence of mutagenicity for the chlorinated paraffins generally, it can be predicted that the LCCPs will not be mutagenic.

The carcinogenicity of a C<sub>23av</sub>, 43% chlorination LCCP product has been investigated in rats and mice in standard studies. An increased incidence of malignant lymphoma in male mice reported at the highest dose tested (5,000 mg/kg/day) provides evidence that LCCPs are carcinogenic. Marginal increases in the incidence of adrenal medullary pheochromocytomas observed in female rats from 100 mg/kg/day and in hepatocellular carcinomas in female mice at 5,000 mg/kg/day were not considered to be convincing evidence of carcinogenicity. Overall, there is evidence that LCCPs are carcinogenic, but only at very high exposure levels. The chlorinated paraffins do not appear to have mutagenic potential, so it is likely that this carcinogenic activity is the result of a non-genotoxic mode of action. It can therefore be assumed that the carcinogenicity will have a threshold exposure level. Accordingly, a NOAEL of 2,500 mg/kg/day, at which the incidence of malignant lymphomas was similar to historical controls, can be identified. It is assumed that this NOAEL is applicable to all LCCPs.

There are no studies in which effects on fertility and reproductive performance have been specifically investigated. No changes in the weight or macroscopic and microscopic appearance of the reproductive organs were reported in the repeated dose toxicity studies, available for C<sub>22-26</sub>, 43% chlorination, C<sub>23av</sub>, 43% chlorination and C<sub>20-26</sub>, 70% chlorination LCCP products. Taking account of this information from the repeated dose toxicity studies and the fact that no effects on fertility were observed in two MCCP reproductive toxicity studies, it is predicted that the LCCPs do not have the capacity to affect fertility. In one MCCP study using dietary administration, maternal deaths during parturition were reported at 538 mg/kg/day as a consequence of haemorrhaging due to low vitamin K levels. A NOAEL of 100 mg/kg/day was identified for this effect. In the absence of studies on the effects of LCCPs during the time of parturition and on vitamin K levels, a conservative assumption is made that LCCPs will have a similar effect.

In relation to developmental effects, no evidence of a specific effect on development was observed in standard rat and rabbit studies on a C<sub>22-26</sub>, 43% chlorination and a C<sub>22-26</sub>, 70% chlorination LCCP product. However, maternal dietary exposure to MCCPs has been shown to cause haemorrhaging and death in neonates, thought to be mainly due to reduced vitamin K levels in the milk. A NOAEL of 47 mg/kg/day as a maternal dose was identified for this effect. In the absence of studies of the effects of LCCPs on neonates and on vitamin K levels, a conservative assumption is made that all the LCCPs will have a similar effect.



### 4.4.3 PNEC for secondary poisoning

Avian toxicity data are available for LCCPs. However, the mode of administration (direct injection into eggs) means that these data cannot be used to estimate a PNEC.

There is a large database of repeated dose mammalian studies available for both a  $C_{>20}$ , 43% wt. Cl product and a  $C_{>20}$ , 70% wt. Cl product that is suitable for derivation of a PNEC. There appear to be few mammalian toxicity data available for  $C_{18-20}$  liquid products. The available data are summarised in the preceding sections.

The conclusion from this analysis is that a LOAEL of 100 mg/kg/day for  $C_{20-30}$  LCCPs and a NOAEL of 23 mg/kg/day (equivalent to 300 mg/kg food) for  $C_{18-20}$  LCCPs (based on read-across from MCCPs) should be used for the assessment of secondary poisoning, based on the most sensitive LOAEL or NOAELs identified for repeated dose effects (liver or kidney toxicity, respectively).

For the secondary poisoning assessment it is suggested that the LOAEL of 100 mg/kg/day for  $C_{20-30}$  LCCPs is divided by three to provide an estimate of the NOAEL (i.e. assumed NOAEL = 33.3 mg/kg/day).

Using the conversion factors given in the TGD, a dose of 33.3 mg/kg bw/day is equivalent to a dietary exposure of 667 mg/kg food. A tentative  $PNEC_{oral}$  of 22.2 mg/kg food can be estimated using an assessment factor of 30 (chronic toxicity data are available). This  $PNEC_{oral}$  is considered in the assessment for both the  $C_{>20}$  liquid and  $C_{>20}$  solid products.

It is not possible to derive a PNEC for the  $C_{18-20}$  liquid chlorinated paraffins. As a pragmatic approach, a conservative  $PNEC_{oral(screening)}$  of 5 mg/kg food will be used. This value is based on the  $PNEC_{oral}$  that has been derived for MCCPs<sup>18</sup> but includes a further assessment factor of two to account for uncertainty resulting from the limited availability of toxicity data for the  $C_{18-20}$  liquid chlorinated paraffins. This approach assumes that the  $C_{18-20}$  liquid chlorinated paraffins have a similar toxicity profile to the medium-chain ( $C_{14-17}$ ) chlorinated paraffins ( $C_{17}$  and, to a lesser extent,  $C_{16}$  chlorinated paraffins are present at quite high levels in the  $C_{18-20}$  chlorinated paraffin products). It is known that the frequency and severity of toxicity of chlorinated paraffins generally decreases with increasing chain length of the chlorinated paraffin (BUA, 1992) and so this approach is probably conservative.

In summary, the following PNECs will be used in the assessment of secondary poisoning.

$C_{18-20}$ liquid chlorinated paraffin	$PNEC_{oral(screening)}$	= 5 mg/kg food
$C_{>20}$ liquid chlorinated paraffin	$PNEC_{oral}$	= 22 mg/kg food
$C_{>20}$ solid chlorinated paraffin	$PNEC_{oral}$	= 22 mg/kg food

<sup>18</sup> The  $PNEC_{oral}$  for MCCPs in the published risk assessment is currently 0.17 mg/kg (ECB, 2005a). However, since the assessment was published, further information has become available that shows that the actual NOAEL from mammalian studies for MCCPs is around 300 mg/kg food (23 mg/kg/day) for repeated dose exposure (90-day studies) and a revised  $PNEC_{oral}$  of 10 mg/kg food has been agreed using an assessment factor of 30 on these data (ECB, 2007a). The  $PNEC_{oral}$  of 10 mg/kg food is considered to be most reliable for MCCPs.

## 4.5 Classification

### 4.5.1 Current classification

LCCPs are not listed in Annex 1 of the Directive 67/548/EEC. Since there is no agreed harmonised classification, suppliers have the responsibility to self-classify.

### 4.5.2 Proposal

#### 4.5.2.1 Environment

No reliable values for an L(E)C<sub>50</sub> have been determined in acute tests with aquatic organisms. Effects have generally only been seen when the substances have been tested at concentrations well in excess of the water solubility and so may represent physical effects rather than direct toxicity of the substance itself.

The one exception to this observation may be a C<sub>18-20</sub>, 52% wt. Cl substance when tested as a water-soluble fraction with *Daphnia magna*. Here a 48h-hour EC<sub>15</sub> was determined as 0.4–0.5 mg/l. Effects were also seen at much lower concentrations with this substance in a long-term *Daphnia* reproduction study. It is not possible to determine from the study if the effects seen were due to the substance itself, to physical effects or to preferential solubility of a toxic impurity present in the test substance.

LCCP substances are not readily biodegradable, they are poorly soluble and have log Kow values  $\geq 7.5$ . There are several studies investigating the accumulation of these substances in aquatic organisms, but it is not possible to derive reliable BCF values from these experiments. Predicted BCF data indicate that some types of LCCPs may have the potential to be taken up by and accumulate in fish. Based on this information, a classification of R53 could be proposed for LCCPs.

The C<sub>18-20</sub> products are also likely to contain a significant amount of other chlorinated paraffin impurities (typically <1 per cent C<sub>16</sub> and 17 per cent C<sub>17</sub>) which are also constituents of MCCP products. The proposal for classifying the MCCPs as dangerous for the environment (N; R50/53) was agreed at the Environmental Classification and Labelling Expert Meeting in September 2004. This decision was based on the acute toxicity seen with *Daphnia magna* (48-hour EC<sub>50</sub> = 0.0059 mg/l), a high fish bioconcentration factor of 1,087 and the lack of degradation expected in standard ready biodegradation tests. This may also have some impact on the classification of the C<sub>18-20</sub> chlorinated paraffins in particular.

#### 4.5.2.2 Human health

The classification for human health has not been considered in this hazard assessment.

# 5. Risk characterisation

PECs and PNECs have been derived for three subgroups of LCCPs:

- the  $C_{18-20}$  liquid products;
- the  $C_{>20}$  liquid products;
- the  $C_{>20}$  solid products.

This approach allows differences in environmental fate, behaviour and effects between the three groups to be taken into account in the assessment. However, when it comes to risk characterisation, consideration must be given to whether a local site could be using more than one type of LCCP. PEC/PNEC ratios have been derived for each of the three subgroups, as well as for the total LCCPs that may be used at a site, to take this possibility into account.

Similarly, at a regional level, exposure to total LCCPs will occur. The approach outlined above also has the advantage of making it clearer from which type of LCCP any risk identified arises.

The one exception to this general approach to the risk characterisation is for the use of LCCPs in leather fat liquors. Here, the local PEC is calculated based on the total release from a site being either  $C_{18-20}$  liquid or  $C_{>20}$  liquid. In this instance it is unrealistic to add these two PECs (and hence obtain PEC/PNEC ratios) for a site. If both types of LCCP are used in the leather processing, then the amount of each type would be lower than assumed in the calculation (i.e. the total LCCP release would be the same, but it would be split between the two types); the total PECs and hence total PEC/PNECs would be intermediate between these two extremes.

The PNECs used in the risk characterisation for a given type of LCCP (i.e.  $C_{18-20}$  liquid,  $C_{>20}$  liquid and  $C_{>20}$  solid chlorinated paraffins) have, wherever possible, been derived from toxicity data obtained on that specific type of chlorinated paraffin. Where this was not possible, due to a lack of suitable experimental data, worst case “screening” PNECs have been derived, based on the available toxicity data for other types of chlorinated paraffins. The manner in which these screening values have been derived means that they are likely to be protective for, and will overestimate the actual risk from, the type of chlorinated paraffin under consideration. Therefore, although this approach can be used to show where the PEC/PNEC ratio is likely to be less than 1, it cannot be used reliably to indicate a risk if the PEC/PNEC ratio is greater than 1. However, this approach is useful for identifying if there is a need to generate more toxicity data for the chlorinated paraffin in question.

## 5.1 Aquatic compartment

### 5.1.1 Risk characterisation ratios for surface water

A  $PNEC_{water}$  of 2.9  $\mu\text{g/l}$  for  $C_{18-20}$  liquid chlorinated paraffin and a tentative  $PNEC_{water(screening)}$  of 5.5  $\mu\text{g/l}$  for  $C_{>20}$  liquid and  $C_{>20}$  solid chlorinated paraffins have been derived. The resulting PEC/PNEC ratios for the various scenarios considered in

this assessment are shown in Table 5.1 and are also displayed in the bar chart in Figure 5.1.

Based on this analysis, the PEC/PNEC ratios are all <1 for all scenarios considered. It can therefore be concluded that the risk to aquatic organisms from the production and use of LCCPs is low.

### **5.1.2 Risk characterisation ratios for waste water treatment plant (WWTP) micro-organisms**

A PNEC of 60 mg/l was derived for sewage treatment microorganisms. This concentration is well above those predicted to occur in waste water treatment plants and the resulting PEC/PNEC ratios are all <<1 for all scenarios considered. Therefore it can be concluded that the risk to waste water treatment plants from the production and use of LCCPs is low.

### **5.1.3 Risk characterisation ratios for sediment**

There are no toxicity studies available on sediment-dwelling organisms. A  $PNEC_{sed}$  of 5,710 mg/kg wet weight has been derived for the  $C_{18-20}$  liquid chlorinated paraffins; a  $PNEC_{sed(screening)}$  of 33,100 mg/kg wet weight and  $>1.2 \times 10^6$  mg/kg wet weight have been derived for the  $C_{>20}$  liquid and  $C_{>20}$  solid chlorinated paraffins, respectively. The resulting PEC/PNEC ratios are shown in Table 5.2 and Figure 5.2. The PEC/PNEC ratios have been increased by a factor of 10, as suggested in the TGD, in order to take into account possible exposure by direct ingestion of sediment-bound substance.

A PEC/PNEC ratio >1 is obtained for one scenario only – the intermittent release scenario<sup>19</sup> for  $C_{18-20}$  liquids used in emulsifiable metal cutting/working fluids.

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<sup>19</sup> According to an analysis by Entec (2004), intermittent disposal of such emulsified metal cutting/working fluids to drain is not necessarily prohibited under existing legislation in the UK, provided the site operator obtained relevant permission from the sewerage undertaker. However most companies are expected to separate the oil phase from the emulsified fluid prior to disposal to drain (with the oil being disposed of by processes such as incineration). In addition, Euro Chlor (2008) indicates that, as far as they are aware, there is no current use of LCCPs in emulsified fluids in the EU. Therefore this scenario is not relevant to the vast majority of sites using emulsifiable metal cutting/working fluids containing LCCPs.

**Table 5.1 Estimated PEC/PNEC ratios for surface water**

Scenario	Step	PEC/PNEC ratio			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Production	Generic	6.9×10 <sup>-4</sup>	5.8×10 <sup>-4</sup>	4.2×10 <sup>-7</sup>	1.3×10 <sup>-3</sup>
Use in PVC – plastisol coating	Compounding (O)	3.6×10 <sup>-4</sup>	b	b	3.6×10 <sup>-4</sup>
	Conversion (O)	3.6×10 <sup>-4</sup>	b	b	3.6×10 <sup>-4</sup>
	Compounding/conversion (O)	5.8×10 <sup>-4</sup>	b	b	5.8×10 <sup>-4</sup>
Use in PVC – extrusion/other	Compounding (O)	5.3×10 <sup>-4</sup>	b	b	5.3×10 <sup>-4</sup>
	Compounding (PO)	2.3×10 <sup>-3</sup>	b	b	2.3×10 <sup>-3</sup>
	Compounding (C)	3.1×10 <sup>-4</sup>	b	b	3.1×10 <sup>-4</sup>
	Conversion (O)	4.6×10 <sup>-4</sup>	b	b	4.6×10 <sup>-4</sup>
	Conversion (PO)	4.9×10 <sup>-4</sup>	b	b	4.9×10 <sup>-4</sup>
	Conversion (C)	4.3×10 <sup>-4</sup>	b	b	4.3×10 <sup>-4</sup>
	Compounding/conversion (O)	8.5×10 <sup>-4</sup>	b	b	8.5×10 <sup>-4</sup>
	Compounding/conversion (PO)	2.6×10 <sup>-3</sup>	b	b	2.6×10 <sup>-3</sup>
Use in rubber Use in sealants	Compounding/conversion	b	1.5×10 <sup>-4</sup>	2.2×10 <sup>-5</sup>	1.7×10 <sup>-4</sup>
	Formulation and use	<1	<1	b	<1
Use in paints	Formulation	<1	<1	2.5×10 <sup>-7</sup>	2.5×10 <sup>-7</sup>
	Industrial application	6.6×10 <sup>-4</sup>	1.8×10 <sup>-4</sup>	4.8×10 <sup>-6</sup>	8.4×10 <sup>-4</sup>
	Domestic application	<1	<1	<1	<1
Use in metal cutting/working fluids	Formulation	1.4×10 <sup>-4</sup>	8.8×10 <sup>-5</sup>	b	2.3×10 <sup>-4</sup>
	Use in oil-based fluids (large site – 5% LCCP content)	b	5.9×10 <sup>-4</sup>	b	5.9×10 <sup>-4</sup>
	Use in oil-based fluids (large site – 10% LCCP content)	b	1.1×10 <sup>-3</sup>	b	1.1×10 <sup>-3</sup>
	Use in oil-based fluids (small site – 5% LCCP content)	2.8×10 <sup>-3</sup>	5.5×10 <sup>-4</sup>	b	3.4×10 <sup>-3</sup>
	Use in oil-based fluids (small site – 10% LCCP content)	5.4×10 <sup>-3</sup>	1.0×10 <sup>-4</sup>	b	5.5×10 <sup>-3</sup>
	Use in emulsifiable fluids	3.6×10 <sup>-4</sup>	1.3×10 <sup>-4</sup>	b	4.9×10 <sup>-4</sup>
	Use in emulsifiable fluids – intermittent release	0.22 <sup>a</sup>	0.038 <sup>a</sup>	b	0.26 <sup>a</sup>

Table 5.1 continued overleaf

**Table 5.1 continued**

Scenario	Step	PEC/PNEC ratio			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Use in leather fat liquors	Formulation	1.0×10 <sup>-3</sup>	2.4×10 <sup>-4</sup>	b	1.2×10 <sup>-3</sup>
	Use – complete processing of raw hides	8.1×10 <sup>-3</sup>	1.5×10 <sup>-3</sup>	b	NA
Use in textile applications		0.038	b	b	0.038
<u>Regional sources</u>		1.1×10 <sup>-4</sup>	8.2×10 <sup>-5</sup>	1.5×10 <sup>-7</sup>	1.9×10 <sup>-4</sup>
		1.3×10 <sup>-4</sup>	8.7×10 <sup>-5</sup>	1.6×10 <sup>-7</sup>	2.2×10 <sup>-4</sup>

Notes: <sup>a</sup> For the intermittent scenario an assessment factor can be applied to the acute EC<sub>50</sub> to derive the PNEC. However no effects were seen in the acute tests and so it is not clear if risk actually exists from this scenario.

b = no major use of the substance in the application.

NA = not applicable – see text.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

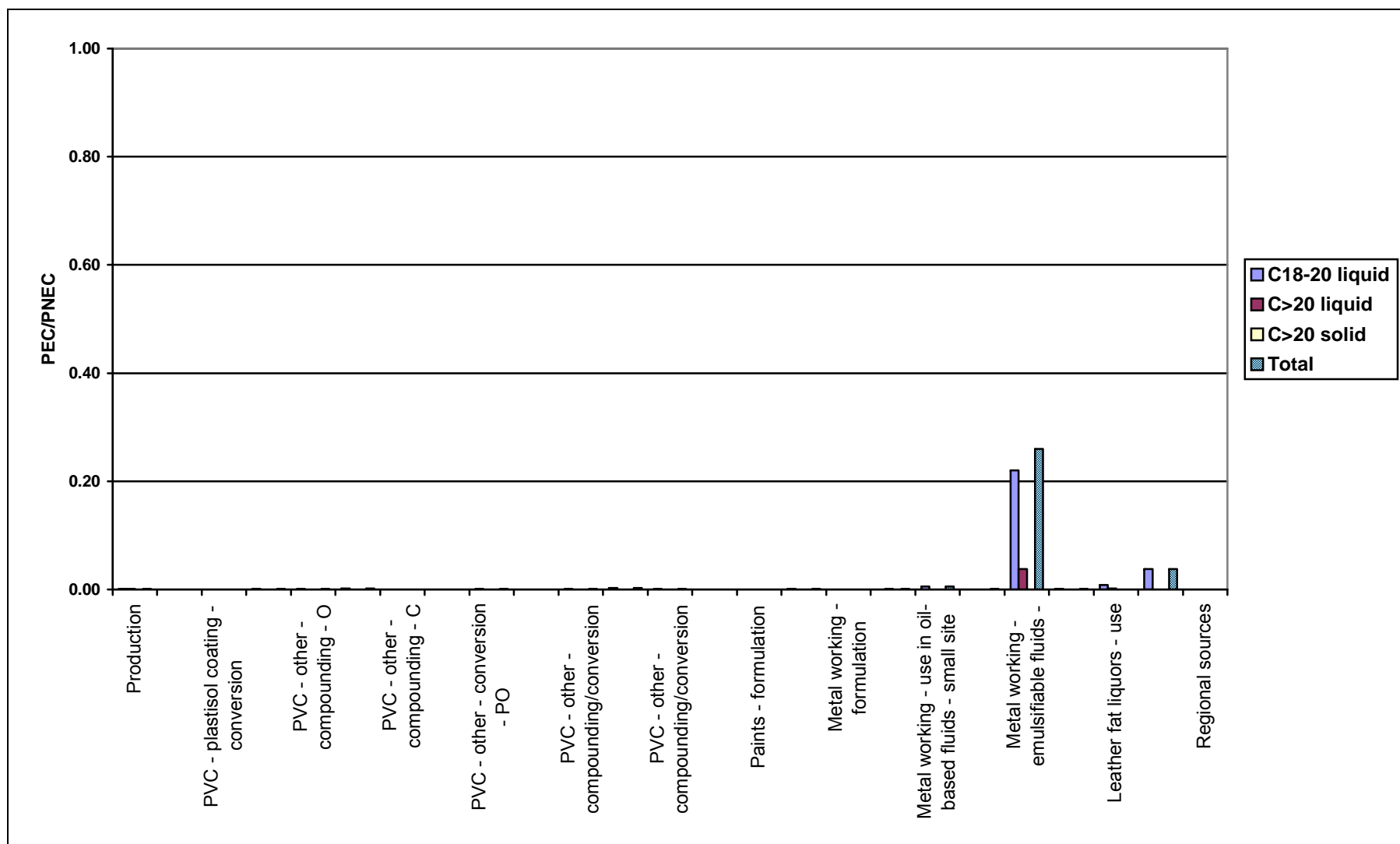


Figure 5.1 Estimated PEC/PNEC ratios for surface water

**Table 5.2 Estimated PEC/PNEC ratios for sediment**

Scenario	Step	PEC/PNEC ratio			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Production	Generic	6.9×10 <sup>-3</sup>	5.8×10 <sup>-3</sup>	<4.2×10 <sup>-6</sup>	0.013
Use in PVC – plastisol coating	Compounding (O)	3.6×10 <sup>-3</sup>	b	b	3.6×10 <sup>-3</sup>
	Conversion (O)	3.6×10 <sup>-3</sup>	b	b	3.6×10 <sup>-3</sup>
	Compounding/conversion (O)	5.8×10 <sup>-3</sup>	b	b	5.8×10 <sup>-3</sup>
Use in PVC – extrusion/other	Compounding (O)	5.3×10 <sup>-3</sup>	b	b	5.3×10 <sup>-3</sup>
	Compounding (PO)	0.023	b	b	0.023
	Compounding (C)	3.1×10 <sup>-3</sup>	b	b	3.1×10 <sup>-3</sup>
	Conversion (O)	4.6×10 <sup>-3</sup>	b	b	4.6×10 <sup>-3</sup>
	Conversion (PO)	4.9×10 <sup>-3</sup>	b	b	4.9×10 <sup>-3</sup>
	Conversion (C)	4.3×10 <sup>-3</sup>	b	b	4.3×10 <sup>-3</sup>
	Compounding/conversion (O)	8.5×10 <sup>-3</sup>	b	b	8.5×10 <sup>-3</sup>
	Compounding/conversion (PO)	0.026	b	b	0.026
	Compounding/conversion (C)	6.1×10 <sup>-3</sup>	b	b	6.1×10 <sup>-3</sup>
Use in rubber	Compounding/conversion	b	1.5×10 <sup>-3</sup>	<2.2×10 <sup>-4</sup>	1.7×10 <sup>-3</sup>
Use in sealants	Formulation and use	<1	<1	b	<1
Use in paints	Formulation	<1	<1	<2.5×10 <sup>-6</sup>	<2.5×10 <sup>-6</sup>
	Industrial application	6.6×10 <sup>-3</sup>	1.8×10 <sup>-3</sup>	<4.8×10 <sup>-5</sup>	8.4×10 <sup>-3</sup>
	Domestic application	<1	<1	<1	<1
Use in metal cutting/working fluids	Formulation	1.4×10 <sup>-3</sup>	8.8×10 <sup>-4</sup>	b	2.3×10 <sup>-3</sup>
	Use in oil-based fluids (large site – 5% LCCP content)	b	5.9×10 <sup>-3</sup>	b	5.9×10 <sup>-3</sup>
	Use in oil-based fluids (large site – 10% LCCP content)	b	0.011	b	0.011
	Use in oil-based fluids (small site – 5% LCCP content)	0.028	5.5×10 <sup>-3</sup>	b	0.034
	Use in oil-based fluids (small site – 10% LCCP content)	0.054	0.010	b	0.064
	Use in emulsifiable fluids	3.6×10 <sup>-3</sup>	1.3×10 <sup>-3</sup>	b	4.9×10 <sup>-3</sup>
	Use in emulsifiable fluids – intermittent release	2.2 <sup>a</sup> or 0.016–0.040 <sup>a</sup>	0.38 <sup>a</sup> or 3.3×10 <sup>-3</sup> –7.6×10 <sup>-3a</sup>	b	2.6 <sup>a</sup> or 0.019–0.048 <sup>a</sup>

Table 5.2 continued overleaf



**Table 5.2 continued**

Scenario	Step	PEC/PNEC ratio			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Use in leather fat liquors	Formulation	0.010	2.4×10 <sup>-3</sup>	b	0.012
	Use – complete processing of raw hides	0.081	0.015	b	NA
Use in textile applications		0.38	b	b	0.38
Regional sources		2.3×10 <sup>-3</sup> –	1.6×10 <sup>-3</sup> –	<3.0×10 <sup>-6</sup> –	3.9×10 <sup>-3</sup> –
		2.7×10 <sup>-3</sup>	1.8×10 <sup>-3</sup>	<3.1×10 <sup>-6</sup>	4.5×10 <sup>-3</sup>

Notes: <sup>a</sup> Intermittent release scenario – it is not clear how this is dealt with in the TGD for sediment (see text).

b = process makes no significant contribution to levels in sediment.

NA = not applicable.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

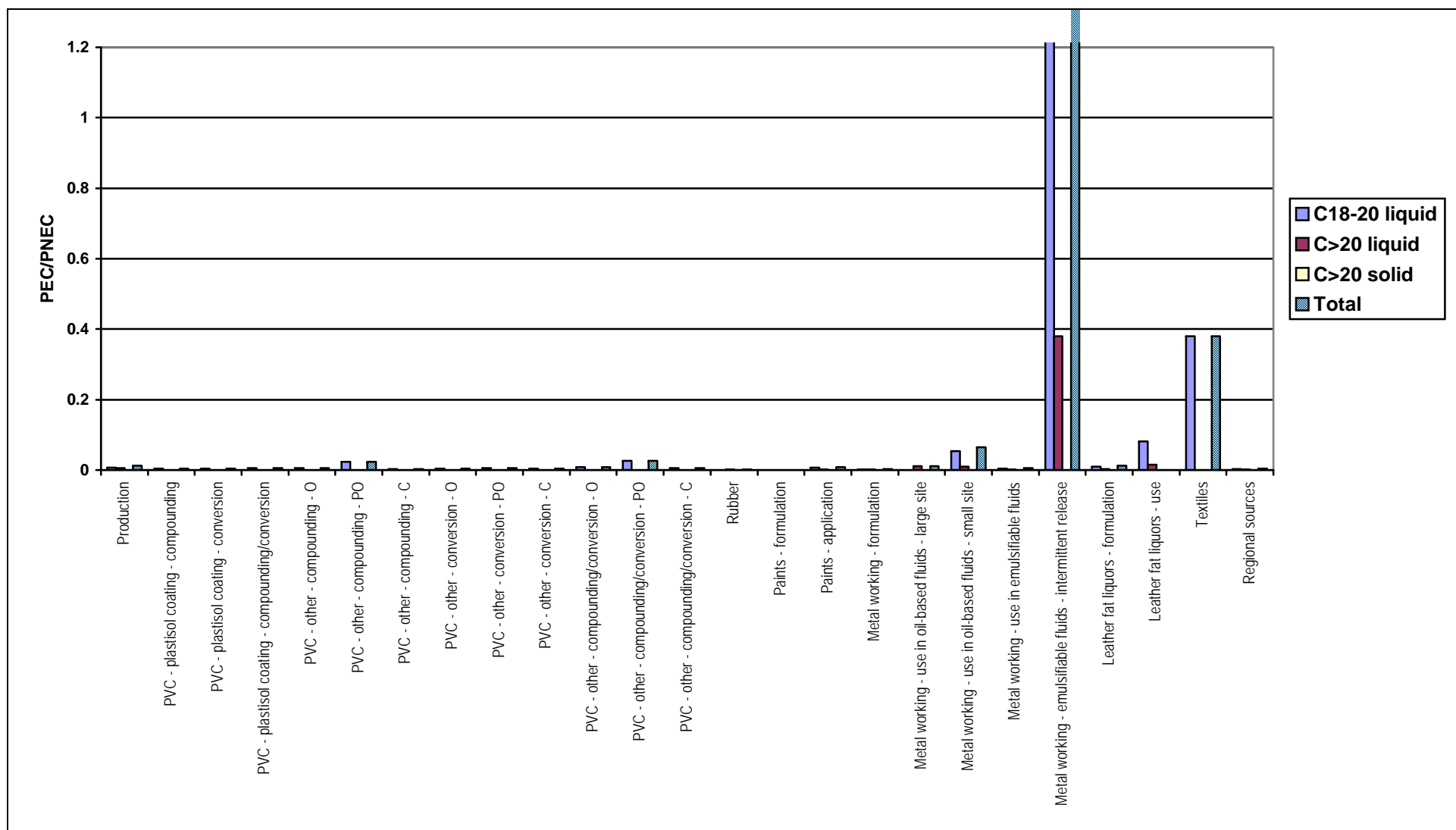


Figure 5.2 PEC/PNEC ratios for sediment

The TGD does not give any guidance for how this type of intermittent scenario should be treated in the risk characterisation for sediment. The PEC/PNEC ratios here have been derived based on the instantaneous concentration expected in sediment during an emission event (this assumes that equilibrium between the sediment and water is reached instantly), and also based on an average concentration over the year, taking into account the other emissions from the site. For the chlorinated paraffins considered, the PEC/PNEC ratio changes from >1 to <1 when the average PEC is used. The uncertainties in this scenario are discussed further in Section 5.1.4.

As discussed in Section 5.1.4, when metalworking lubricants containing up to 70 per cent chlorinated paraffin are considered, the PEC/PNEC ratio could be up to seven times higher than the calculation for a fluid with 10 per cent chlorinated paraffin content. In the use in oil-based fluids this increase would lead to a PEC/PNEC ratio for of 0.38 for C<sub>18-20</sub> liquid chlorinated paraffins and 0.070 for C<sub>>20</sub> liquid chlorinated paraffins. Therefore no risk would be expected even if the chlorinated paraffin content was as high as 70 per cent.

High concentrations of LCCPs are predicted to occur in the sediment compartment and so it is important to consider the risk characterisation for this compartment carefully. Recent tests on sediment organisms with medium-chain chlorinated paraffins showed that these were toxic to sediment organisms (the NOEC was 50 mg/kg wet weight), so the possibility exists that LCCPs may also be toxic to sediment organisms at concentrations similar to those predicted. Since the current PNECs for LCCPs are derived based on the equilibrium partitioning method, and the aquatic data on which they are based are rather uncertain, the whole assessment for the sediment compartment is uncertain. The most logical way forward for the assessment of sediment as a whole would be to investigate toxicity of LCCPs to sediment-organisms directly. However, given the generally low risk characterisation ratios found in the current assessment, such further testing is not considered to be a high priority.

#### **5.1.4 Uncertainties and possible refinements**

As with any "generic" risk assessment, there are uncertainties inherent in the approach taken. For LCCPs these uncertainties are compounded by the fact that the commercially produced substances contain many components; they are either difficult to test or fall outside the scope of simple standard testing methods. The derivation of the physico-chemical properties and other data necessary for the PEC calculations is therefore difficult.

In this assessment, a set of data has been chosen that is considered to be representative for three subgroups of LCCPs. These data necessarily rely on estimates and extrapolations from other data, and so in themselves are uncertain. Furthermore, given the nature of LCCP substances (low solubility, high log K<sub>ow</sub>, low vapour pressure), it is unlikely that actual further measurement of some of these properties is practical. The effect of variation in some of these physico-chemical properties on the environmental modelling has been investigated in Appendix E. However, there are still some areas where reliable information is lacking.

There is considerable uncertainty over the aquatic effects data for these substances; a conservative approach has therefore been taken to determine the PNECs used for surface water. As it is not possible to derive a reliable PNEC for the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins for surface water, this assessment takes a worst case screening approach. Even so, the resulting risk characterisation indicates that the PEC/PNEC is <1 for all scenarios considered.

Therefore, for the vast majority of uses, even though there are large uncertainties over the aquatic toxicity data, further testing on aquatic organisms does not appear to be warranted based on the results of this assessment. The sediment compartment appears to be much more relevant for these substances.

For this assessment, the PNECs for sediment have been estimated based on the equilibrium partitioning method. Recent tests on sediment organisms with medium-chain chlorinated paraffins showed that these were toxic to sediment organisms (a NOEC of 50 mg/kg wet weight was determined) and so the possibility exists that LCCPs may also be toxic to sediment organisms at similar concentrations.

However, the current PNECs for LCCPs are derived using the equilibrium partitioning method, but the aquatic data on which the calculations are based are rather uncertain, making uncertain the entire assessment for the sediment compartment. In addition, even if it is assumed that the  $C_{>20}$  liquid and  $C_{>20}$  solid chlorinated paraffins are not toxic to aquatic organisms at concentrations up to their water solubility, it does not necessarily follow that no toxicity would be expected to sediment-dwelling organisms because direct ingestion of sediment-bound substance could occur.

Investigation of the toxicity of LCCPs to sediment-organisms directly should therefore be considered in order to reduce some of this uncertainty. However, given the generally low risk characterisation ratios found in the current assessment, such further testing is not thought to be a high priority.

The actual emission estimates used in this assessment are also uncertain. For most scenarios considered, the best information available for specific industries has been used in preference to the default estimates. However, in many cases industry information was not available for LCCPs, but has been extrapolated from data for other substances. This approach necessarily introduces uncertainties into the estimates.

In addition, it is possible that LCCPs are imported into the EU. Figures on the actual imports are unknown, although an allowance for imports has been made in the way the emission estimates have been derived. Nevertheless, this lack of information introduces further uncertainties into the exposure assessment, particularly if the imported substance is used in applications not covered by the assessment.

For use in metal cutting/working fluids, the actual extent of use of LCCPs in water-based emulsions is unknown. Recent information from Euro Chlor has indicated that, as far as they are aware, there is no use in water-based emulsions, but the coverage of the survey is unclear. The available information indicates that LCCPs are used mainly in oil-based lubricants for deep drawing operations. Some of these oil types of lubricant may have LCCP contents higher than assumed in the PEC calculations, for example up to 70 per cent. Assuming the release of these high LCCP content fluids is the same as for the oil-based fluids in general, then the resulting PEC/PNEC ratio would be approximately seven times that obtained for a fluid with 10 per cent chlorinated paraffin content. Nevertheless, this higher PEC/PNEC ratio would still be  $<1$ .

For the intermittent release scenario for surface water, the PNEC is even more uncertain because the TGD recommends that the PNEC should be derived from acute data (the environmental exposure from this scenario will be very short-term), usually using an assessment factor of 100. However, it was not possible to determine the PNEC in this way as the substance involved showed little or no toxicity in acute tests, even when tested at concentrations well in excess of its water solubility; the PNEC for water for long-term exposure has been used instead. Despite this, the resulting risk characterisation ratio is  $<1$ , indicating a low risk.

For the intermittent release scenario for sediment, the TGD does not give any guidance for how this scenario should be treated in the risk characterisation. The PEC/PNEC ratios here have been derived:

- based on the instantaneous concentration expected in sediment during an emission event (this assumes that equilibrium between the sediment and water is reached instantly);
- based on an average concentration over the year, taking into account the other emissions from the site.

For the chlorinated paraffins considered, the PEC/PNEC ratio changes from  $>1$  to  $<1$  when the average PEC is used.

For the use of LCCPs in textiles, little information is currently available on the processes used, and the potential for emission to the environment. The current assessment is based on worst case default assumptions and so may grossly overestimate the actual emissions to the environment, and hence PECs. Further information on the emissions to the environment from this process would be useful to reduce the uncertainty with this scenario. However, no risks to the aquatic environment (water and sediment) were identified with the worst case approach taken.

Information is also lacking in the assessment of "waste remaining in the environment". Here there are no agreed methodologies available in the TGD for estimating PECs for this type of release. There are also uncertainties associated with the actual (bio)availability and environmental behaviour of the substance when released in this form (essentially as polymer particulates containing the substance).

### 5.1.5 Conclusions for the aquatic compartment

For surface water, the PEC/PNEC ratios are  $<1$  for all scenarios; it is concluded that LCCPs present a low risk to this compartment.

For sediment, the PEC/PNEC ratios are  $<1$  for all scenarios except for the intermittent release scenario of  $C_{18-20}$  liquid chlorinated paraffins from emulsion-based metal cutting/working fluids. The relevance of this scenario to the current use of LCCPs, and the current fluid disposal practices within the industry, is not clear. The assessment could be refined with:

- clarification of whether LCCPs are used in emulsion metal cutting/working fluids;
- clarification of the current disposal practices of emulsion metal cutting/working fluids containing LCCPs.

It should be noted, however, that the applicability of the equilibrium partitioning approach for these substances is uncertain, and toxic effects have been seen with other chlorinated paraffins at concentrations much lower than the PNECs assumed in this assessment. To reduce the uncertainty in the risk assessment for the sediment compartment, information on the actual toxicity to sediment-organisms should be considered. Ideally, these data should be obtained on a  $C_{18-20}$  liquid or  $C_{>20}$  liquid chlorinated paraffin product in the first instance. The results from toxicity tests with medium-chain chlorinated paraffins indicate that *Lumbriculus variegatus* or *Hyalella azteca* would be suitable test organisms. However, the results of the current assessment indicate that the need for such toxicity data should be a low priority at present.

## 5.2 Terrestrial compartment

### 5.2.1 Risk characterisation ratios

There are no toxicity studies available on plants, earthworms or other soil-dwelling organisms. The equilibrium partitioning method has been used to derive a value for  $PNEC_{soil}$  of 4,640 mg/kg wet weight for  $C_{18-20}$  liquid chlorinated paraffins and screening values,  $PNEC_{soil(screening)}$ , of 26,900 mg/kg wet weight for  $C_{>20}$  liquid chlorinated paraffins and >971,000 mg/kg wet weight for  $C_{>20}$  solid chlorinated paraffins. The TGD suggests that the PEC/PNEC ratio is increased by a factor of 10 for substances with  $\log Kow > 5$  to take into account direct ingestion of soil-bound substance. The resulting PEC/PNEC ratios obtained are shown in Table 5.3 and Figure 5.3.

The PEC/PNEC ratios are <1 for all scenarios considered. Therefore the risk to the soil compartment from production and use of LCCPs is low.

**Table 5.3 PEC/PNEC ratios for soil**

Scenario	Step	PEC/PNEC ratio			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Production	Generic	<1	<1	<1	<1
Use in PVC – plastisol coating	Compounding (O)	2.3×10 <sup>-3</sup>	b	b	2.3×10 <sup>-3</sup>
	Conversion (O)	2.3×10 <sup>-3</sup>	b	b	2.3×10 <sup>-3</sup>
	Compounding/conversion (O)	3.2×10 <sup>-3</sup>	b	b	3.2×10 <sup>-3</sup>
Use in PVC – extrusion/other	Compounding (O)	3.0×10 <sup>-3</sup>	b	b	3.0×10 <sup>-3</sup>
	Compounding (PO)	0.010	b	b	0.010
	Compounding (C)	2.1×10 <sup>-3</sup>	b	b	2.1×10 <sup>-3</sup>
	Conversion (O)	2.7×10 <sup>-3</sup>	b	b	2.7×10 <sup>-3</sup>
	Conversion (PO)	2.8×10 <sup>-3</sup>	b	b	2.8×10 <sup>-3</sup>
	Conversion (C)	2.6×10 <sup>-3</sup>	b	b	2.6×10 <sup>-3</sup>
	Compounding/conversion (O)	4.4×10 <sup>-3</sup>	b	b	4.4×10 <sup>-3</sup>
	Compounding/conversion (PO)	0.012	b	b	0.012
	Compounding/conversion (C)	3.4×10 <sup>-3</sup>	b	b	3.4×10 <sup>-3</sup>
Use in rubber	Compounding/conversion	b	3.4×10 <sup>-4</sup>	<9.1×10 <sup>-5</sup>	4.3×10 <sup>-4</sup>
Use in sealants	Formulation and use	<1	<1	b	<1
Use in paints	Formulation	<1	<1	<4.2×10 <sup>-7</sup>	<4.2×10 <sup>-7</sup>
	Industrial application	3.6×10 <sup>-3</sup>	4.7×10 <sup>-4</sup>	<2.0×10 <sup>-5</sup>	4.1×10 <sup>-3</sup>
	Domestic application	<1	<1	<1	<1
Use in metal cutting/working fluids	Formulation	1.4×10 <sup>-3</sup>	8.1×10 <sup>-5</sup>	b	1.5×10 <sup>-3</sup>
	Use in oil-based fluids (large site – 5% LCCP content)	b	2.2×10 <sup>-3</sup>	b	2.2×10 <sup>-3</sup>
	Use in oil-based fluids (large site – 10% LCCP content)	b	4.3×10 <sup>-3</sup>	b	4.3×10 <sup>-3</sup>
	Use in oil-based fluids (small site – 5% LCCP content)	0.013	2.0×10 <sup>-3</sup>	b	0.015
	Use in oil-based fluids (small site – 10% LCCP content)	0.024	3.9×10 <sup>-3</sup>	b	0.028
	Use in emulsifiable fluids	2.3×10 <sup>-3</sup>	2.4×10 <sup>-4</sup>	b	2.5×10 <sup>-3</sup>
	Use in emulsifiable fluids – intermittent release	0.10 <sup>a</sup>	0.018 <sup>a</sup>	b	0.12 <sup>a</sup>

Table 5.3 continued overleaf

**Table 5.3 continued**

Scenario	Step	PEC/PNEC ratio			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Use in leather fat liquors	Formulation	6.9×10 <sup>-3</sup>	5.6×10 <sup>-4</sup>	b	7.5×10 <sup>-3</sup>
	Use – complete processing of raw hides	0.035	5.9×10 <sup>-3</sup>	b	NA
Use in textile applications		0.16	b	b	0.16
Regional sources	Agricultural soil	9.1×10 <sup>-4</sup> – 1.2×10 <sup>-3</sup>	1.0×10 <sup>-3</sup>	<1.6×10 <sup>-7</sup> – <1.7×10 <sup>-7</sup>	1.9×10 <sup>-3</sup> – 2.2×10 <sup>-3</sup>
		Industrial/urban soil	0.024– 0.026	0.023– 0.025	<5.5×10 <sup>-5</sup> – <5.6×10 <sup>-5</sup>

Notes: <sup>a</sup> Assumes dilution of sewage sludge at waste water treatment plant before application to soil.  
 b = process makes no significant contribution to levels in water.  
 NA = not applicable.  
 O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).



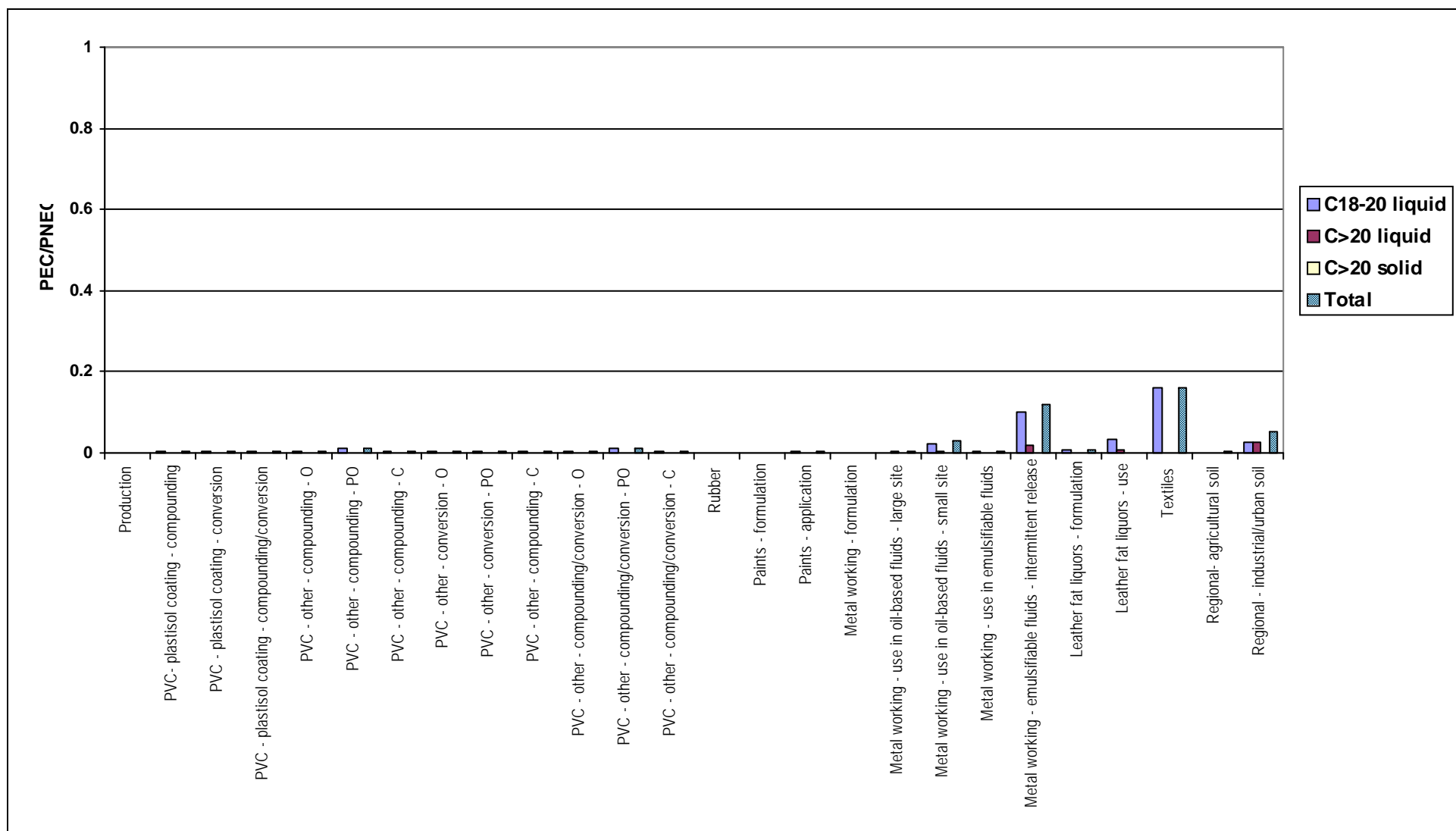


Figure 5.3 PEC/PNEC ratios for soil

## 5.2.2 Uncertainties and possible refinements

There are uncertainties over the emission estimates used for many of the scenarios considered in this assessment. These uncertainties are discussed in Section 5.1.4 in relation to the surface water and sediment compartments. The application to land of sludge generated during the treatment of waste water could be a major route to soil for LCCPs, so the uncertainties in the emissions to waste water are equally relevant here.

There are also uncertainties over the behaviour of LCCPs during waste water treatment (the fraction going to sludge) and the subsequent rate of biodegradation of LCCPs in soil to which the sludge is applied. Within the methodology used, the predicted behaviour during waste water treatment is governed mainly by the log Kow value and the Henry's Law constant. The effect on the environmental modelling made by variations to some of the key physico-chemical properties of LCCPs is explored in Appendix E. This work shows that the predicted concentrations in soil were relatively insensitive to the value of the physico-chemical properties used.

Appendix E also considers how the uncertainties in the biodegradation rate of LCCPs affect the PECs. The degradation rate was shown to be a key input parameter for the calculation of regional and (to a lesser extent) local concentrations. The degradation rate also has a major impact on the predicted concentrations in soil and any further concentrations derived from them (e.g. earthworms, root crops etc.). The current PEC/PNEC ratios essentially assume that no biodegradation occurs. If significant biodegradation of LCCPs does occur in the environment this activity would reduce the PEC/PNEC ratios (particularly at the regional level), even if the biodegradation rate is slow.

The industrial/urban soil scenarios result from long-term emissions of particulate matter containing LCCPs. There are some uncertainties in these estimates, particularly over the actual availability and persistence of the chlorinated paraffin over extended time periods. As discussed in Section 3.3.2.1, the length of time taken to reach steady state in the industrial/urban soil compartment is of the order of 1,000 years or more, which makes the predicted concentrations very uncertain. The predicted concentration can be calculated over a shorter timeframe. The concentration reached 100 years from now would be approximately 2 mg/kg wet weight for the C<sub>18-20</sub> liquid chlorinated paraffins, 14 mg/kg wet weight for the C<sub>>20</sub> liquid chlorinated paraffins and 0.5 mg/kg wet weight for the C<sub>>20</sub> solid chlorinated paraffins. The resulting PEC/PNEC ratios for industrial/urban soil would be  $4.3 \times 10^{-3}$ ,  $5.2 \times 10^{-3}$  and  $5.2 \times 10^{-6}$  for the three chlorinated paraffin types respectively, giving a total PEC/PNEC ratio of  $9.5 \times 10^{-3}$ .

It may be also possible to refine the PECs for industrial/urban soil scenarios by obtaining further exposure information or a more realistic biodegradation rate in soil for these substances. However, the effort required to obtain these values would be large and it is unlikely that the information would have a significant impact on the conclusions of the risk assessment.

Similar to the case with sediment, the PNEC for the soil compartment is uncertain, due to uncertainties in the underlying aquatic toxicity data and uncertainties in the applicability of the equilibrium partitioning method to LCCPs. Some of these uncertainties are already taken into account by the use of a conservative approach with regard to the assessment factors used etc. Recent tests on medium-chain chlorinated paraffins indicated that they were toxic to earthworms (*Eisenia fetida*), with a NOEC of 106 mg/kg wet weight. Thus, based on these data for other chlorinated paraffins, although it cannot be ruled out that LCCPs will be toxic to soil organisms, it is very unlikely that they will be toxic at

concentrations similar to those predicted in most local scenarios (<50 mg/kg wet weight, and generally between 1 and 10 mg/kg wet weight).

### 5.2.3 Conclusions for soil

The PEC/PNEC ratios are <1 for all scenarios considered. Therefore the risk to the soil compartment from production and use of LCCPs is low.

## 5.3 Atmosphere

### 5.3.1 Conclusions for the atmosphere

Neither biotic nor abiotic effects on the atmosphere are likely because of the limited atmospheric release and low volatility of LCCPs.

Long-range atmospheric transport and subsequent bioaccumulation in remote regions have been raised as a possible concern for chlorinated paraffins, particularly the short-chain ones. This issue is currently being discussed within the appropriate international fora, but no agreement has yet been reached.

The potential for long-range transport (and subsequent accumulation) of the LCCPs appears to be less than that for short-chain chlorinated paraffins. LCCPs generally have lower vapour pressures, are likely to adsorb more strongly to soil and sediment, and appear to be less bioaccumulative. However, the substances supplied in the market contain many components spanning a range of physico-chemical properties. Some components of the commercial products may have properties that may mean that long-range transport via the atmosphere is a possibility. This issue should be considered further in the appropriate international fora.

## 5.4 Non-compartment specific effects relevant for the food chain (secondary poisoning)

### 5.4.1 Risk characterisation ratios

PNECs for secondary poisoning by oral intake have been tentatively determined as 5 mg/kg food for the C<sub>18-20</sub> liquid chlorinated paraffins (screening value), 22 mg/kg food for the C<sub>>20</sub> liquid chlorinated paraffins and 22 mg/kg food for the C<sub>>20</sub> solid chlorinated paraffins. The estimated PEC/PNEC ratios for secondary poisoning are shown in Table 5.4 (via the fish food chain) and Table 5.5 (via the earthworm food chain) and in Figure 5.4 and Figure 5.5.

For the fish food chain, the PEC/PNEC ratios are all very low. Therefore it can be concluded that a risk of secondary poisoning via the fish food chain is low for LCCPs.

For the earthworm food chain, risk characterisation ratios >1 are obtained for the C<sub>18-20</sub> liquid chlorinated paraffins for two scenarios only (the use of LCCPs in emulsifiable metal cutting/working fluids where intermittent disposal to waste water is assumed, and the use in textiles). All other scenarios lead to risk characterisation ratios <1.

**Table 5.4 PEC/PNEC ratios for secondary poisoning via the fish food chain**

Scenario	Step	PEC/PNEC ratio – TGD method				PEC/PNEC ratio – alternate method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Production	Generic	2.4×10 <sup>-4</sup>	1.4×10 <sup>-5</sup>	6.8×10 <sup>-11</sup>	2.5×10 <sup>-4</sup>	4.8×10 <sup>-4</sup>	2.7×10 <sup>-4</sup>	6.8×10 <sup>-11</sup>	7.5×10 <sup>-4</sup>
Use in PVC – plastisol coating	Compounding (O)	9.2×10 <sup>-5</sup>	b	b	9.2×10 <sup>-5</sup>	1.8×10 <sup>-4</sup>	b	b	1.8×10 <sup>-4</sup>
	Conversion (O)	9.2×10 <sup>-5</sup>	b	b	9.2×10 <sup>-5</sup>	1.8×10 <sup>-4</sup>	b	b	1.8×10 <sup>-4</sup>
	Compounding/conversion (O)	9.8×10 <sup>-5</sup>	b	b	9.8×10 <sup>-5</sup>	2.0×10 <sup>-4</sup>	b	b	2.0×10 <sup>-4</sup>
Use in PVC – extrusion/other	Compounding (O)	9.6×10 <sup>-5</sup>	b	b	9.6×10 <sup>-5</sup>	1.9×10 <sup>-4</sup>	b	b	1.9×10 <sup>-4</sup>
	Compounding (PO)	1.5×10 <sup>-4</sup>	b	b	1.5×10 <sup>-4</sup>	3.0×10 <sup>-4</sup>	b	b	3.0×10 <sup>-4</sup>
	Compounding (C)	9.0×10 <sup>-5</sup>	b	b	9.0×10 <sup>-5</sup>	1.8×10 <sup>-4</sup>	b	b	1.8×10 <sup>-4</sup>
	Conversion (O)	9.4×10 <sup>-5</sup>	b	b	9.0×10 <sup>-5</sup>	1.9×10 <sup>-4</sup>	b	b	1.9×10 <sup>-4</sup>
	Conversion (PO)	9.6×10 <sup>-5</sup>	b	b	9.6×10 <sup>-5</sup>	1.9×10 <sup>-4</sup>	b	b	1.9×10 <sup>-4</sup>
	Conversion (C)	9.4×10 <sup>-5</sup>	b	b	9.4×10 <sup>-5</sup>	1.9×10 <sup>-4</sup>	b	b	1.9×10 <sup>-4</sup>
	Compounding/conversion (O)	1.1×10 <sup>-4</sup>	b	b	1.1×10 <sup>-4</sup>	2.2×10 <sup>-4</sup>	b	b	2.2×10 <sup>-4</sup>
	Compounding/conversion (PO)	1.6×10 <sup>-4</sup>	b	b	1.6×10 <sup>-4</sup>	3.2×10 <sup>-4</sup>	b	b	3.2×10 <sup>-4</sup>
	Compounding/conversion (C)	1.0×10 <sup>-4</sup>	b	b	1.0×10 <sup>-4</sup>	2.0×10 <sup>-4</sup>	b	b	2.0×10 <sup>-4</sup>
Use in rubber	Compounding/conversion	b	5.0×10 <sup>-6</sup>	2.0×10 <sup>-10</sup>	5.0×10 <sup>-6</sup>	b	1.0×10 <sup>-5</sup>	2.0×10 <sup>-10</sup>	1.0×10 <sup>-5</sup>
Use in sealants	Formulation and use	<1	<1	b	<1	<1	<1	b	<1
Use in paints	Formulation	<1	<1	5.0×10 <sup>-11</sup>	5.0×10 <sup>-11</sup>	<1	<1	5.0×10 <sup>-11</sup>	5.0×10 <sup>-11</sup>
	Industrial application	2.2×10 <sup>-3</sup>	5.9×10 <sup>-6</sup>	5.0×10 <sup>-10</sup>	2.2×10 <sup>-3</sup>	4.4×10 <sup>-4</sup>	1.2×10 <sup>-5</sup>	5.0×10 <sup>-10</sup>	4.5×10 <sup>-4</sup>
	Domestic application	<1 <sup>b</sup>	<1 <sup>b</sup>	<1 <sup>b</sup>	<1 <sup>b</sup>	<1 <sup>b</sup>	<1 <sup>b</sup>	<1 <sup>b</sup>	<1 <sup>b</sup>

Table 5.4 continued overleaf

**Table 5.4** continued

Scenario	Step	PEC/PNEC ratio – TGD method				PEC/PNEC ratio – alternate method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Use in metal cutting/working fluids	Formulation	8.6×10 <sup>-5</sup>	4.2×10 <sup>-6</sup>	b	9.0×10 <sup>-5</sup>	1.7×10 <sup>-4</sup>	8.2×10 <sup>-6</sup>	b	1.8×10 <sup>-4</sup>
	Use in oil-based fluids (large site – 5% LCCP content)	b	1.4×10 <sup>-5</sup>	b	1.4×10 <sup>-5</sup>	b	2.8×10 <sup>-5</sup>	b	2.8×10 <sup>-5</sup>
	Use in oil-based fluids (large site - 10% LCCP content)	b	2.4×10 <sup>-5</sup>	b	2.4×10 <sup>-5</sup>	b	5.0×10 <sup>-5</sup>	b	5.0×10 <sup>-5</sup>
	Use in oil-based fluids (small site – 5% LCCP content)	7.8×10 <sup>-4</sup>	1.3×10 <sup>-5</sup>	b	7.9×10 <sup>-4</sup>	1.6×10 <sup>-3</sup>	2.6×10 <sup>-5</sup>	b	1.6×10 <sup>-3</sup>
	Use in oil-based fluids (small site – 10% LCCP content)	1.5×10 <sup>-3</sup>	2.2×10 <sup>-5</sup>	b	1.5×10 <sup>-3</sup>	3.0×10 <sup>-3</sup>	4.5×10 <sup>-5</sup>	b	3.0×10 <sup>-3</sup>
	Use in emulsifiable fluids	1.4×10 <sup>-4</sup>	5.0×10 <sup>-6</sup>	b	1.5×10 <sup>-4</sup>	2.8×10 <sup>-4</sup>	1.0×10 <sup>-5</sup>	b	2.9×10 <sup>-4</sup>
	Use in emulsifiable fluids – intermittent release	4.8×10 <sup>-4 a</sup>	9.1×10 <sup>-6 a</sup>	b	4.9×10 <sup>-4 a</sup>	9.6×10 <sup>-4 a</sup>	1.8×10 <sup>-5 a</sup>	b	9.8×10 <sup>-4 a</sup>
Use in leather fat liquors	Formulation	1.6×10 <sup>-4</sup>	4.5×10 <sup>-6</sup>	b	1.6×10 <sup>-4</sup>	3.2×10 <sup>-4</sup>	9.1×10 <sup>-6</sup>	b	3.3×10 <sup>-4</sup>
	Use – complete processing of raw hides	7.8×10 <sup>-4</sup>	8.2×10 <sup>-6</sup>	b	NA	1.6×10 <sup>-3</sup>	1.6×10 <sup>-5</sup>	b	NA
Use in textile	Compounding	0.010	b	b	0.010	0.020	b	b	0.020

Notes: <sup>a</sup> Intermittent release scenario.

b = process makes no significant contribution to levels in water.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

NA = not applicable.

**Table 5.5 PEC/PNEC ratios for secondary poisoning via the earthworm food chain**

Scenario	Step	PEC/PNEC ratio – corrected TGD method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Production	Generic	<1	<1	<1	<1
Use in PVC – plastisol coating	Compounding (O)	0.048	b	b	0.048
	Conversion (O)	0.048	b	b	0.048
	Compounding/conversion (O)	0.059	b	b	0.059
Use in PVC – extrusion/other	Compounding (O)	0.057	b	b	0.057
	Compounding (PO)	0.16	b	b	0.16
	Compounding (C)	0.044	b	b	0.044
	Conversion (O)	0.054	b	b	0.054
	Conversion (PO)	0.054	b	b	0.054
	Conversion (C)	0.051	b	b	0.051
	Compounding/conversion (O)	0.074	b	b	0.074
	Compounding/conversion (PO)	0.18	b	b	0.18
	Compounding/conversion (C)	0.062	b	b	0.062
Use in rubber	Compounding/conversion	b	0.019	2.0×10 <sup>-3</sup>	0.021
Use in sealants	Formulation and use	<1	<1	b	<1
Use in paints	Formulation	<1	<1	1.3×10 <sup>-5</sup>	1.3×10 <sup>-5</sup>
	Industrial application	0.065	0.021	4.4×10 <sup>-4</sup>	0.086
	Domestic application	<1	<1	<1	<1

Table 5.5 continued overleaf

**Table 5.5** continued

Scenario	Step	PEC/PNEC ratio – corrected TGD method			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total
Use in metal cutting/working fluids	Formulation	0.034	0.015	b	0.049
	Use in oil-based fluids (large site – 5% LCCP content)	b	0.044	b	0.044
	Use in oil-based fluids (large site – 10% LCCP content)	b	0.074	b	0.074
	Use in oil-based fluids (small site – 5% LCCP content)	0.18	0.041	b	0.22
	Use in oil-based fluids (small site – 10% LCCP content)	0.33	0.069	b	0.40
	Use in emulsifiable fluids	0.048	0.017	b	0.065
	Use in emulsifiable fluids – intermittent release	1.4 <sup>a</sup>	0.25 <sup>a</sup>	b	1.7 <sup>a</sup>
Use in leather fat liquors	Formulation	0.11	0.022	b	0.13
	Use – complete processing of raw hides	0.48	0.094	b	NA
Use in textile		2.2	b	b	2.2

Notes: <sup>a</sup> Intermittent release scenario.

b = process makes no significant contribution to levels in water.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

NA = not applicable.

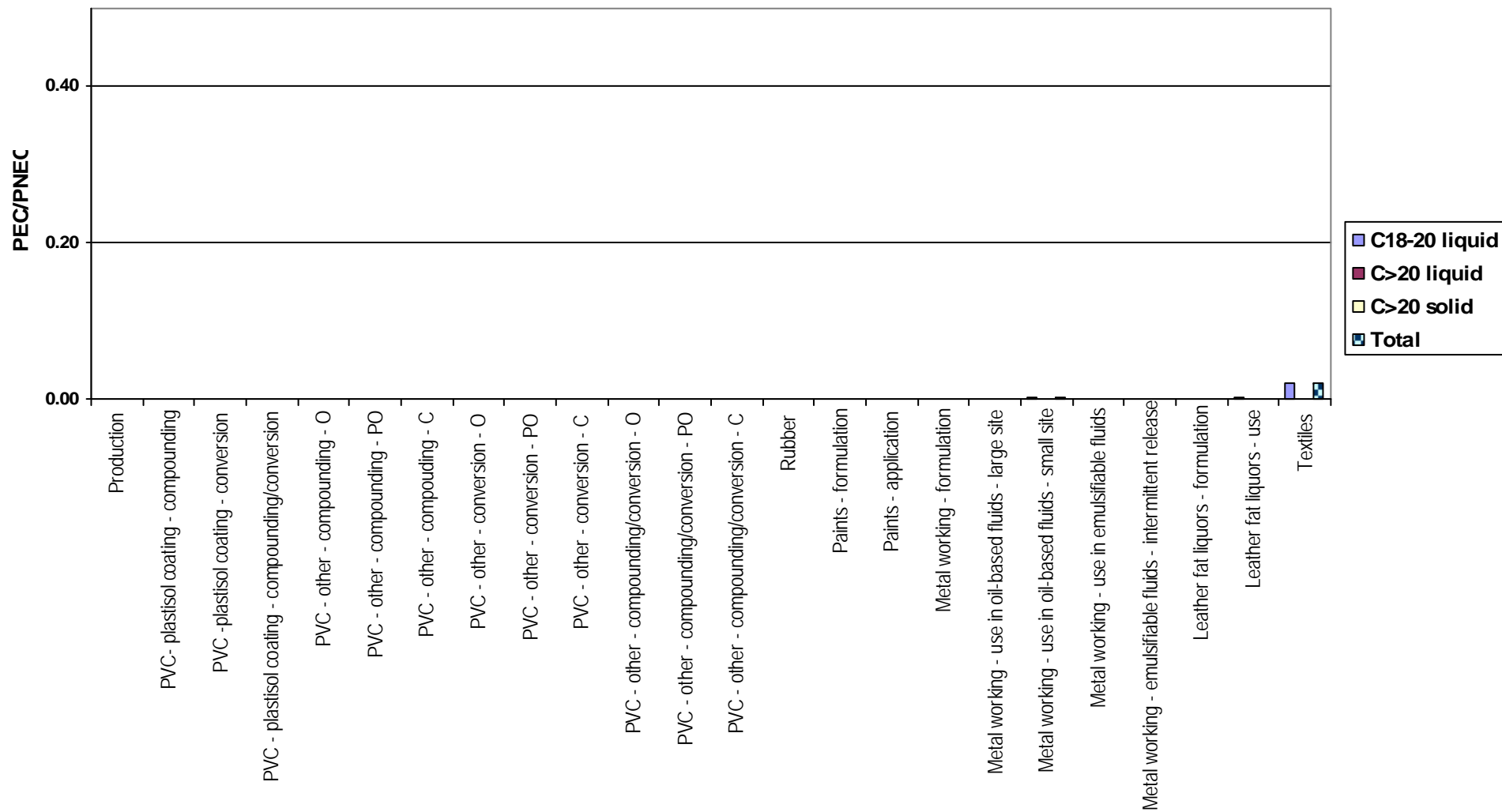


Figure 5.4 PEC/PNEC ratios for secondary poisoning by the fish food chain (alternate method)



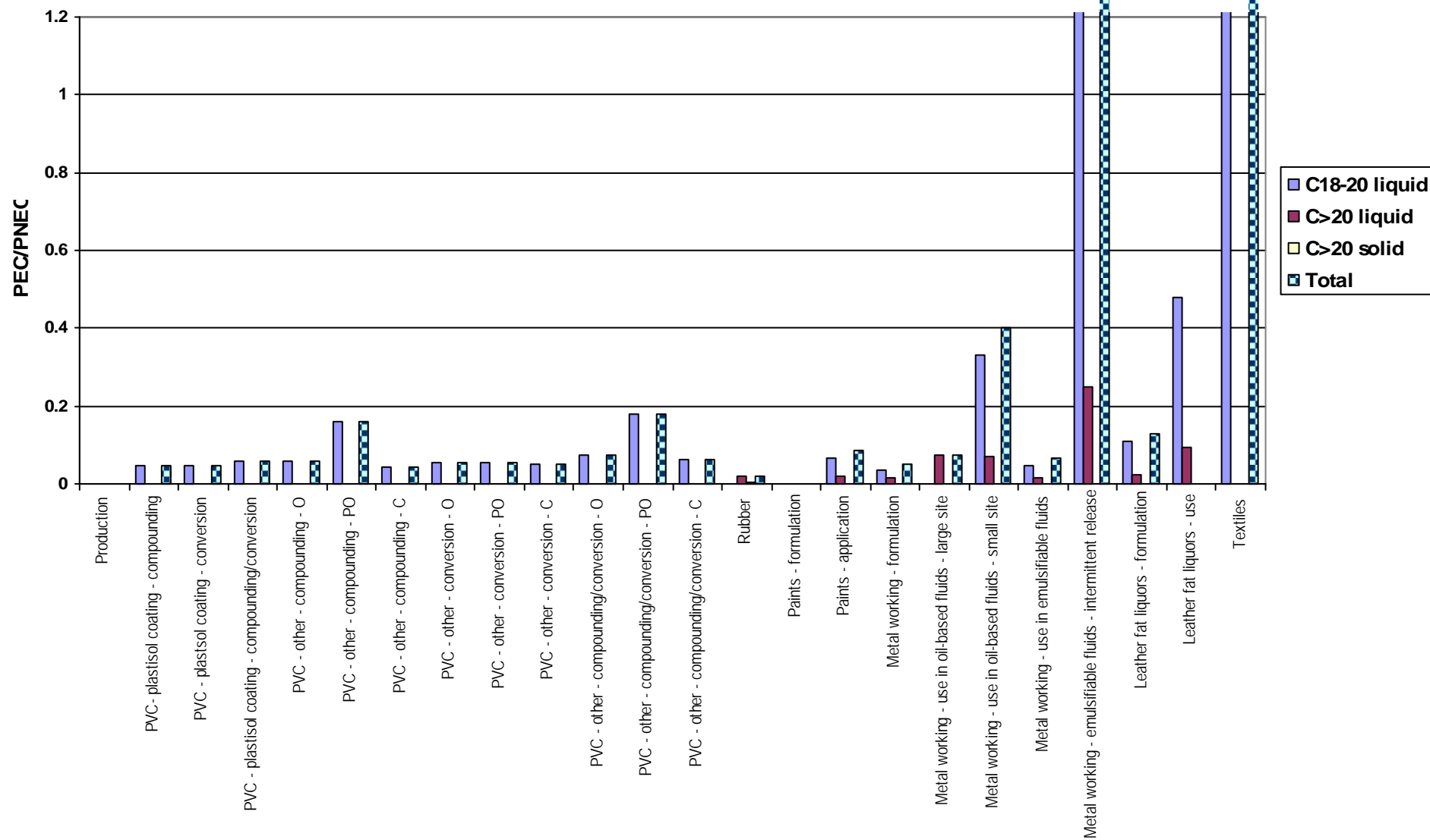


Figure 5.5 PEC/PNEC ratios for secondary poisoning by the earthworm food chain (corrected TGD method)

## 5.4.2 Uncertainties and possible refinements

The PECs for secondary poisoning depend on the predicted concentrations in surface water and soil. The uncertainties for these compartments – outlined in Section 5.1.4 and Section 5.2.2 – are also relevant here. In particular, the two scenarios that lead to a PEC/PNEC ratio >1 for earthworms (the intermittent release of LCCPs in metal cutting/working fluids and their use in textiles) also lead to a PEC/PNEC >1 for the sediment compartment. The application to land of sludge generated during the treatment of waste water could be a major route to soil for LCCPs, so the uncertainties in the emissions to waste water are equally relevant here as they are for sediment. Therefore, further exposure information would be useful to reduce the uncertainty in these two scenarios.

There are considerable uncertainties over the bioconcentration factors for LCCPs in fish and in earthworms. The current assessment is based on what are considered to be the best available estimates for the bioconcentration factor for fish and the bioaccumulation factor for earthworms from soil. The risk characterisation ratios for the fish food chain are very low so the uncertainties over the bioconcentration factor are probably not too significant in terms of the overall conclusions of the assessment. However, for the earthworm food chain, which has risk characterisation ratios above 1 in some scenarios, the uncertainty over the extent of uptake into earthworms is important to the overall conclusions as to whether a risk actually exists. The determination of an actual earthworm bioconcentration factor for LCCPs would therefore be worth considering.

There are also uncertainties over the PNECs used for secondary poisoning. In particular the PNEC for the C<sub>18-20</sub> liquid chlorinated paraffins is based on a conservative read-across approach from data on medium-chain chlorinated paraffins.

## 5.4.3 Conclusions for predators

The risk of secondary poisoning through the fish food chain appears to be low for all scenarios considered.

For the earthworm food chain, risk characterisation ratios >1 were obtained for the use of LCCPs in emulsion-based metal cutting/working fluids (intermittent release scenario) and textile applications. To make a decision on whether a risk actually exists the assessment could be refined with:

- clarification of whether LCCPs are used in emulsion metal cutting/working fluids;
- clarification of the current disposal practices of emulsion metal cutting/working fluids containing LCCPs;
- information on the emissions to the environment from textile processes using LCCPs.

Consideration could also be given to carrying out an earthworm bioaccumulation test with a C<sub>18-20</sub> liquid LCCP. However, the need for such testing is considered a low priority at present.

## 5.5 Marine compartment

### 5.5.1 Risk characterisation ratios

The PEC/PNEC ratios obtained for the marine compartment are summarised in Table 5.6 (marine water), Table 5.7 (marine sediment), Table 5.8 (marine predators) and Table 5.9 (marine top predators). The PEC/PNEC ratios for sediment have been increased by a factor of 10 to take account of the possibility of direct ingestion of sediment-bound substance.

The PEC/PNEC ratios are <1 for the majority of scenarios, indicating a low risk to the marine compartment. However PEC/PNEC ratios >1 are obtained for marine water and marine sediment for use in metal cutting/working fluids (intermittent release scenario) and for marine sediment for use in textiles.

**Table 5.6 PEC/PNEC ratios for marine water**

Scenario	Step	PEC/PNEC			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Production	Generic	4.2×10 <sup>-3</sup>	3.6×10 <sup>-3</sup>	2.1×10 <sup>-6</sup>	7.8×10 <sup>-3</sup>
Use in PVC – plastisol applications	Compounding (O)	1.8×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.8×10 <sup>-3</sup>
	Conversion (O)	1.8×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.8×10 <sup>-3</sup>
	Compounding/ conversion (O)	3.3×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.3×10 <sup>-3</sup>
Use in PVC – extrusion/ other	Compounding (O)	3.0×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.0×10 <sup>-3</sup>
	Compounding (PO)	0.015	NA <sup>a</sup>	NA <sup>a</sup>	0.015
	Compounding (C)	1.5×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.5×10 <sup>-3</sup>
	Conversion (O)	2.5×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.5×10 <sup>-3</sup>
	Conversion (PO)	2.7×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.7×10 <sup>-3</sup>
	Conversion (C)	2.3×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.3×10 <sup>-3</sup>
	Compounding/ conversion (O)	5.3×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	5.3×10 <sup>-3</sup>
	Compounding/ conversion (PO)	0.018	NA <sup>a</sup>	NA <sup>a</sup>	0.018
	Compounding/ conversion (C)	3.6×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.6×10 <sup>-3</sup>
Use in rubber	Compounding/ conversion	NA <sup>a</sup>	5.5×10 <sup>-4</sup>	1.6×10 <sup>-4</sup>	7.1×10 <sup>-4</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	8.9×10 <sup>-7</sup>	8.9×10 <sup>-7</sup>
	Industrial application	4.0×10 <sup>-3</sup>	7.6×10 <sup>-4</sup>	3.4×10 <sup>-5</sup>	4.8×10 <sup>-3</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

**Table 5.6 continued**

Scenario	Step	PEC/PNEC			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in metal cutting/working fluids	Formulation	2.1×10 <sup>-4</sup>	1.1×10 <sup>-4</sup>	NA <sup>a</sup>	3.2×10 <sup>-4</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	3.7×10 <sup>-3</sup> – 7.3×10 <sup>-3</sup>	NA <sup>a</sup>	3.7×10 <sup>-3</sup> – 7.3×10 <sup>-3</sup>
		Use in oil-based fluids (small)	0.019– 0.038	3.4×10 <sup>-3</sup> – 6.7×10 <sup>-3</sup>	NA <sup>a</sup>
	Use in emulsifiable fluids	1.8×10 <sup>-3</sup>	3.8×10 <sup>-3</sup>	NA <sup>a</sup>	5.6×10 <sup>-3</sup>
	Use in emulsifiable fluids – intermittent release	1.6	0.27	NA <sup>a</sup>	1.9
Use in leather fat liquors	Formulation	6.5×10 <sup>-3</sup>	1.2×10 <sup>-3</sup>	NA <sup>a</sup>	7.7×10 <sup>-3</sup>
	Use – complete processing of raw hides <sup>d</sup>	0.057	9.9×10 <sup>-3</sup>	NA <sup>a</sup>	NA
Use in textile applications		0.27	NA <sup>a</sup>	NA <sup>a</sup>	0.27
Regional sources		1.8×10 <sup>-4</sup>	1.1×10 <sup>-4</sup>	1.9×10 <sup>-7</sup>	2.9×10 <sup>-4</sup>

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in water.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

**Table 5.7 PEC/PNEC ratios for marine sediment**

Scenario	Step	PEC/PNEC			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Production	Generic	0.042 ( $\ll 1$ ) <sup>e</sup>	0.036 ( $\ll 1$ ) <sup>e</sup>	$2.1 \times 10^{-5}$ ( $\ll 1$ ) <sup>e</sup>	0.078 ( $\ll 1$ ) <sup>e</sup>
Use in PVC – plastisol applications	Compounding (O)	0.018	NA <sup>a</sup>	NA <sup>a</sup>	0.018
	Conversion (O)	0.018	NA <sup>a</sup>	NA <sup>a</sup>	0.018
	Compounding/ conversion (O)	0.033	NA <sup>a</sup>	NA <sup>a</sup>	0.033
Use in PVC – extrusion/ other	Compounding (O)	0.030	NA <sup>a</sup>	NA <sup>a</sup>	0.030
	Compounding (PO)	0.15	NA <sup>a</sup>	NA <sup>a</sup>	0.15
	Compounding (C)	0.015	NA <sup>a</sup>	NA <sup>a</sup>	0.015
	Conversion (O)	0.025	NA <sup>a</sup>	NA <sup>a</sup>	0.025
	Conversion (PO)	0.027	NA <sup>a</sup>	NA <sup>a</sup>	0.027
	Conversion (C)	0.023	NA <sup>a</sup>	NA <sup>a</sup>	0.023
	Compounding/ conversion (O)	0.053	NA <sup>a</sup>	NA <sup>a</sup>	0.053
	Compounding/ conversion (PO)	0.18	NA <sup>a</sup>	NA <sup>a</sup>	0.18
	Compounding/ conversion (C)	0.036	NA <sup>a</sup>	NA <sup>a</sup>	0.036
	Use in rubber	Compounding/ conversion	NA <sup>a</sup>	$5.5 \times 10^{-3}$	$1.6 \times 10^{-3}$
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	$8.9 \times 10^{-6}$	$8.9 \times 10^{-6}$
	Industrial application	0.040	$7.6 \times 10^{-3}$	$3.4 \times 10^{-4}$	0.048
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 5.7 continued overleaf

**Table 5.7 continued**

Scenario	Step	PEC/PNEC			
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in metal cutting/working fluids	Formulation	2.1×10 <sup>-3</sup>	1.1×10 <sup>-3</sup>	NA <sup>a</sup>	3.2×10 <sup>-3</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	0.037–0.073	NA <sup>a</sup>	0.037–0.073
	Use in oil-based fluids (small)	0.19–0.38	0.034–0.067	NA <sup>a</sup>	0.22–0.45
	Use in emulsifiable fluids	0.018	3.8×10 <sup>-3</sup>	NA <sup>a</sup>	0.022
	Use in emulsifiable fluids – intermittent release	16 or 0.11–0.28	2.7 or 0.019–0.047	NA <sup>a</sup>	19 or 0.13–0.33
Use in leather fat liquors	Formulation	0.065	0.012	NA <sup>a</sup>	0.077
	Use – complete processing of raw hides <sup>d</sup>	0.57	0.099	NA <sup>a</sup>	NA
Use in textile applications		2.7	NA <sup>a</sup>	NA <sup>a</sup>	2.7
Regional sources		3.7×10 <sup>-3</sup>	2.2×10 <sup>-3</sup>	3.9×10 <sup>-6</sup>	5.9×10 <sup>-3</sup>

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in sediment.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

<sup>e</sup> Calculation for a generic site. It is known that there is only one chlorinated paraffin production site that discharges into the sea after on-site treatment of the effluent. A confidential calculation for this site indicates that the PEC/PNEC ratios would be <<1.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

**Table 5.8 PEC/PNEC ratios for marine predators**

Scenario	Step	PEC/PNEC			
		C <sub>18-20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Production	Generic	2.4×10 <sup>-4</sup>	1.5×10 <sup>-5</sup>	5.0×10 <sup>-11</sup>	2.6×10 <sup>-4</sup>
Use in PVC – plastisol applications	Compounding (O)	3.2×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.2×10 <sup>-5</sup>
	Conversion (O)	3.2×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.2×10 <sup>-5</sup>
	Compounding/ conversion (O)	4.2×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	4.2×10 <sup>-5</sup>
Use in PVC – extrusion/ other	Compounding (O)	4.0×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	4.0×10 <sup>-5</sup>
	Compounding (PO)	1.1×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.1×10 <sup>-4</sup>
	Compounding (C)	3.0×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.0×10 <sup>-5</sup>
	Conversion (O)	3.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.6×10 <sup>-5</sup>
	Conversion (PO)	3.8×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.8×10 <sup>-5</sup>
	Conversion (C)	3.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.6×10 <sup>-5</sup>
	Compounding/ conversion (O)	5.2×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	5.2×10 <sup>-5</sup>
	Compounding/ conversion (PO)	1.2×10 <sup>-4</sup>	NA <sup>a</sup>	NA <sup>a</sup>	1.2×10 <sup>-4</sup>
	Compounding/ conversion (C)	4.2×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	4.2×10 <sup>-5</sup>
	Use in rubber	Compounding/ conversion	NA <sup>a</sup>	2.5×10 <sup>-6</sup>	2.3×10 <sup>-10</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	2.4×10 <sup>-11</sup>	2.4×10 <sup>-11</sup>
	Industrial application	2.2×10 <sup>-4</sup>	3.6×10 <sup>-6</sup>	6.8×10 <sup>-10</sup>	2.2×10 <sup>-4</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 5.8 continued overleaf

**Table 5.8 continued**

Scenario	Step	PEC/PNEC			
		C <sub>18-20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in metal cutting/working fluids	Formulation	2.4×10 <sup>-5</sup>	1.0×10 <sup>-6</sup>	NA <sup>a</sup>	2.4×10 <sup>-5</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	1.5×10 <sup>-5</sup> – 3.0×10 <sup>-5</sup>	NA <sup>a</sup>	1.5×10 <sup>-5</sup> – 3.0×10 <sup>-5</sup>
	Use in oil-based fluids (small)	1.0×10 <sup>-3</sup> – 2.0×10 <sup>-3</sup>	1.4×10 <sup>-5</sup> – 2.7×10 <sup>-5</sup>	NA <sup>a</sup>	1.0×10 <sup>-3</sup> – 2.0×10 <sup>-3</sup>
	Use in emulsifiable fluids	1.1×10 <sup>-4</sup>	2.1×10 <sup>-6</sup>	NA <sup>a</sup>	1.1×10 <sup>-4</sup>
	Use in emulsifiable fluids – intermittent release	5.8×10 <sup>-4</sup>	8.2×10 <sup>-6</sup>	NA <sup>a</sup>	5.9×10 <sup>-4</sup>
Use in leather fat liquors	Formulation	1.3×10 <sup>-4</sup>	1.7×10 <sup>-6</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
	Use – complete processing of raw hides <sup>d</sup>	1.0×10 <sup>-3</sup>	6.8×10 <sup>-6</sup>	NA <sup>a</sup>	NA
Use in textile applications		0.014	NA <sup>a</sup>	NA <sup>a</sup>	0.014

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in fish.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

<sup>e</sup> The PEC/PNECs for C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins would be around two times higher using the alternate method of calculation.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).



**Table 5.9 Predicted concentrations for marine top predators**

Scenario	Step	PEC <sub>local(marine top predators)</sub> (mg/kg wet wt.)			
		C <sub>18-20 liquid</sub> <sup>e</sup>	C <sub>&gt;20 liquid</sub> <sup>e</sup>	C <sub>&gt;20 solid</sub>	Total <sup>c</sup>
Production	Generic	6.4×10 <sup>-5</sup>	3.8×10 <sup>-6</sup>	1.8×10 <sup>-11</sup>	6.8×10 <sup>-5</sup>
Use in PVC – plastisol applications	Compounding (O)	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-5</sup>
	Conversion (O)	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-5</sup>
	Compounding/ conversion (O)	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-5</sup>
Use in PVC – extrusion/ other	Compounding (O)	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-5</sup>
	Compounding (PO)	4.0×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	4.0×10 <sup>-5</sup>
	Compounding (C)	2.4×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.4×10 <sup>-5</sup>
	Conversion (O)	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-5</sup>
	Conversion (PO)	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-5</sup>
	Conversion (C)	2.6×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.6×10 <sup>-5</sup>
	Compounding/ conversion (O)	3.0×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	3.0×10 <sup>-5</sup>
	Compounding/ conversion (PO)	4.4×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	4.4×10 <sup>-5</sup>
	Compounding/ conversion (C)	2.8×10 <sup>-5</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.8×10 <sup>-5</sup>
	Use in rubber	Compounding/ conversion	NA <sup>a</sup>	1.3×10 <sup>-6</sup>	5.5×10 <sup>-11</sup>
Use in sealants	Formulation and use	negligible <sup>b</sup>	negligible <sup>b</sup>	NA <sup>a</sup>	negligible <sup>b</sup>
Use in paints	Formulation	negligible <sup>b</sup>	negligible <sup>b</sup>	1.3×10 <sup>-11</sup>	1.3×10 <sup>-11</sup>
	Industrial application	6.2×10 <sup>-5</sup>	1.5×10 <sup>-6</sup>	1.5×10 <sup>-10</sup>	6.4×10 <sup>-5</sup>
	Domestic application	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>	negligible <sup>b</sup>

Table 5.9 continued overleaf

**Table 5.9 continued**

Scenario	Step	PEC <sub>local(marine top predators)</sub> (mg/kg wet wt.)			
		C <sub>18-20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> liquid <sup>e</sup>	C <sub>&gt;20</sub> solid	Total <sup>c</sup>
Use in metal cutting/working fluids	Formulation	2.4×10 <sup>-5</sup>	1.0×10 <sup>-6</sup>	NA <sup>a</sup>	2.5×10 <sup>-5</sup>
	Use in oil-based fluids (large)	NA <sup>a</sup>	3.9×10 <sup>-6</sup> – 6.8×10 <sup>-6</sup>	NA <sup>a</sup>	3.9×10 <sup>-6</sup> – 6.8×10 <sup>-6</sup>
		Use in oil-based fluids (small)	2.2×10 <sup>-4</sup> – 4.2×10 <sup>-4</sup>	3.6×10 <sup>-6</sup> – 6.4×10 <sup>-6</sup>	NA <sup>a</sup>
	Use in emulsifiable fluids	4.0×10 <sup>-5</sup>	1.3×10 <sup>-6</sup>	NA <sup>a</sup>	4.1×10 <sup>-5</sup>
	Use in emulsifiable fluids – intermittent release	1.3×10 <sup>-4</sup>	2.5×10 <sup>-6</sup>	NA <sup>a</sup>	1.3×10 <sup>-4</sup>
Use in leather fat liquors	Formulation	4.6×10 <sup>-5</sup>	1.2×10 <sup>-6</sup>	NA <sup>a</sup>	4.7×10 <sup>-5</sup>
	Use – complete processing of raw hides <sup>d</sup>	2.2×10 <sup>-4</sup>	2.2×10 <sup>-6</sup>	NA <sup>a</sup>	NA
Use in textile applications		2.8×10 <sup>-3</sup>	NA <sup>a</sup>	NA <sup>a</sup>	2.8×10 <sup>-3</sup>

Notes: <sup>a</sup> NA = not applicable; no significant use of the substance in this application.

<sup>b</sup> The process makes no significant contribution to the levels in fish.

<sup>c</sup> Total = total concentration assuming all types of chlorinated paraffin are released from a site.

<sup>d</sup> The calculation for complete processing of raw hides is considered to be the most realistic scenario.

<sup>e</sup> The PECs for C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins would be around two times higher using the alternate method of calculation.

O = open systems; PO = partially open systems; C = closed systems (as defined in OECD, 2004b).

## 5.5.2 Assessment against PBT criteria

The final part of the marine risk assessment procedure requires a screening of the properties of a substance to see if it is considered as a persistent (P), bioaccumulative (B) and toxic (T) substance.

### 5.5.2.1 Persistence

The persistence criteria laid down in the marine risk assessment guidance require a half-life >60 days in marine water or >180 days in marine sediment. For LCCPs, there are no tests available from which to estimate a reliable half-life for marine water or sediment. The available screening studies, although indicating that biodegradation does occur under some situations, indicate that LCCPs are unlikely to be readily biodegradable or inherently biodegradable. Therefore it can be assumed that LCCPs are potentially persistent or potentially very persistent under the criteria used.

### 5.5.2.2 Bioaccumulation

The criterion used in the marine risk assessment for bioaccumulation is a bioconcentration factor (BCF) >2,000 l/kg. There are no reliable experimental bioaccumulation factors available for LCCPs. In the main risk assessment report, BCFs of 1,092 l/kg for C<sub>18-20</sub> liquid chlorinated paraffins, 192 l/kg for C<sub>>20</sub> liquid chlorinated paraffins and <1 for C<sub>>20</sub> solid chlorinated paraffins were estimated from the log Kow values of 9.7, 10.3 and 17 respectively. These indicate that the bioaccumulation criterion is unlikely to be met for LCCPs.

The marine risk assessment guidance recommends that, when BCFs are estimated from log Kow, a linear structure-activity relationship should be used. This approach implies that all substances with a log Kow of >4.5 would meet the bioaccumulation criterion. Hence, the LCCPs would be considered as bioaccumulative under this definition.

The BCF values estimated above for LCCPs do not use the linear relationship, but use the equation from the TGD recommended for substances with log Kow >6. The values obtained using this relationship are broadly consistent with the trend found in the measured fish BCFs for other chlorinated paraffins. This finding shows that the actual BCF value decreases with increasing carbon chain length (measured fish BCF for short-chain chlorinated paraffins was 7,816 l/kg and the measured BCF for medium-chain chlorinated paraffins was 1,087 l/kg). Therefore based on the available data, the actual BCF for LCCPs would be expected to be lower than that measured for medium-chain chlorinated paraffins; it is therefore unlikely that the LCCPs would meet the bioaccumulation criterion based on the fish BCF.

The marine risk assessment methodology also allows other bioaccumulation data to be taken into account, but does not give specific criteria against which to judge whether the substance should be considered bioaccumulative or not. There are several dietary accumulation studies available for LCCPs. These show that LCCPs can be taken up by organisms (fish, mussels and mammals). In all cases the concentrations reached in the animals were less than those in the diet. This indicates that although uptake of the substance can occur via food, the levels should not increase through the food chain. Therefore, based on this interpretation of the data, LCCPs are not considered to be bioaccumulative under the definitions used in the draft marine risk assessment guidance.

### 5.5.2.3 Toxicity

The toxicity criterion used in the marine risk assessment guidance is a chronic NOEC <0.01 mg/l. The available data indicate that the chronic NOEC for LCCPs is 0.029 mg/l. This value was obtained from tests with *Daphnia magna* with a C<sub>18-20</sub> liquid chlorinated paraffin. Other data suggest that the C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins are not toxic to aquatic organisms at concentrations up to their water solubility limit.

Therefore, based on these data, LCCPs do not meet the toxicity criterion from the marine risk assessment guidance.

### 5.5.3 Uncertainties and possible refinements

In the PEC/PNEC assessment there are considerable uncertainties over both the PECs and PNECs. These uncertainties are similar to those discussed in Sections 5.1.4 and 5.2.2.

For the PBT assessment there are few reliable experimental data available that can be used to compare directly the P and B criteria. Based on the best estimates available, LCCPs are considered to potentially meet the P or vP criteria only.

It should be noted that there are currently some data gaps in the available long-term toxicity dataset for LCCPs. However, since the B criterion is not met, according to the draft risk assessment guidance, there is no need to carry out further testing to see if the T criterion is met.

### 5.5.4 Conclusions for the marine compartments

A marine risk assessment has been carried out for LCCPs using the draft methodology under development for inclusion in the TGD.

The provisional risk assessment carried out indicates a low risk to predators and top predators from the production and use of LCCPs but a risk to the marine environment from the intermittent release of LCCPs in emulsifiable metal cutting/working fluids (based on the current PEC/PNEC ratios for water and sediment). The use of LCCPs in textile applications may also pose a risk to the marine environment, based on the current PEC/PNEC ratios for sediment. It is possible to refine the PECs for these endpoints by obtaining further exposure information, in particular:

- clarification of whether LCCPs are used in emulsion metal cutting/working fluids;
- clarification of the current disposal practices of emulsion metal cutting/working fluids containing LCCPs;
- information on the emissions to the environment from textile processes using LCCPs.

It would also be possible to revise the PNEC for some of these endpoints by carrying out further long-term testing with aquatic organisms and/or sediment organisms, preferably marine species. However this type of testing would be very difficult to carry out for LCCPs and this should be considered a low priority.

For the persistent, bioaccumulative and toxic (PBT) criteria, LCCPs can be considered to be potentially persistent (P) or potentially very persistent (vP) based on the available

data. There are some uncertainties over the actual BCF value for LCCPs, but the available information indicates that this is likely to be <2,000 l/kg. It should also be noted that there are currently some data gaps in the available long-term toxicity dataset for LCCPs. However, since the B criterion is not met, according to the draft risk assessment guidance, there is no need to carry out further testing to see if the T criterion is met.

## 5.6 Man exposed via the environment

### 5.6.1 Risk characterisation ratios

For humans exposed via the environment, NOAELs and LOAELs have been determined or extrapolated for LCCPs. These are a NOAEL of 23 mg/kg/day for C<sub>18-20</sub> liquid chlorinated paraffins and a LOAEL of 100 mg/kg/day for both C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins (see Section 4.4.2). These are based on the most sensitive effects identified in repeated dose studies (liver or kidney toxicity).

Similar to the case with the derivation of the PNEC for secondary poisoning, it is suggested that the LOAEL values are divided by a factor of 3 to provide an estimate of the NOAEL for both C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins, and that the NOAEL for the C<sub>18-20</sub> liquid is divided by a factor of 2 to account for uncertainty resulting from the limited availability of toxicity data. Thus the NOAELs considered in this risk characterisation would be as follows:

C <sub>18-20</sub> liquid	NOAEL 12 mg/kg/day
C <sub>&gt;20</sub> liquid	NOAEL 33 mg/kg/day
C <sub>&gt;20</sub> solid	NOAEL 33 mg/kg/day

The predicted human exposure from environmental sources is summarised in Section 3.3.4. As discussed earlier, the applicability of the methods used to estimate the concentrations in the food chain for LCCPs is uncertain.

The estimated daily human intake from local sources is in the general range:

- $3.1 \times 10^{-6}$  mg/kg/day to 0.026 mg/kg/day for the C<sub>18-20</sub> liquid chlorinated paraffins;
- $8.5 \times 10^{-7}$  mg/kg/day to  $6.5 \times 10^{-3}$  mg/kg/day for the C<sub>>20</sub> liquid chlorinated paraffins;
- $3.4 \times 10^{-12}$  mg/kg/day to  $8.9 \times 10^{-4}$  mg/kg/day for the C<sub>>20</sub> solid chlorinated paraffins.

The margin of safety (MOS) between the above NOAELs and these exposure levels is:

- $461 - 3.9 \times 10^6$  for the C<sub>18-20</sub> liquid chlorinated paraffins;
- $5.1 \times 10^3 - 3.9 \times 10^7$  for the C<sub>>20</sub> liquid chlorinated paraffins;
- $3.7 \times 10^4 - 9.7 \times 10^{12}$  for the C<sub>>20</sub> solid chlorinated paraffins.

These MOS are very large for the C<sub>>20</sub> liquid chlorinated paraffins and the C<sub>>20</sub> solid chlorinated paraffins; it can be concluded therefore that there is no concern for local exposure in relation to repeated dose toxicity of these substances.

For the C<sub>18-20</sub> liquid chlorinated paraffins, the lowest MOS for local exposure is 461 (from use in textile applications); the MOS is  $\geq 1.8 \times 10^3$  for all other scenarios. These MOS are all high, indicating that there is little or no concern for local exposure in relation to repeated dose toxicity from these uses.

The value for human exposure for regional environmental sources predicted by EUSES is:

- $1.5 \times 10^{-4}$  mg/kg/day for the C<sub>18-20</sub> liquid products;
- $7.1 \times 10^{-4}$  mg/kg/day for the C<sub>>20</sub> liquid products;
- $4.2 \times 10^{-6}$  mg/kg/day for the C<sub>>20</sub> solid products.

The MOS between the above NOAELs and these exposure levels is:

- $8.0 \times 10^4$  for the C<sub>18-20</sub> liquid products;
- $4.7 \times 10^4$  for the C<sub>>20</sub> liquid products;
- $7.9 \times 10^6$  for the C<sub>>20</sub> solid products.

These MOS values are very high and therefore there is no concern for regional exposures in relation to repeated dose toxicity of LCCPs.

It should be taken into account here that there are considerable uncertainties in both the PECs and NOAELs considered in the assessment for exposure of man via the environment. It would be theoretically possible to obtain more reliable estimates of the likely exposure via the food chain for these substances by carrying out further testing to investigate the actual uptake into root crops, milk, meat and leaf crops. However, such testing would be difficult to carry out for these substance and, based on the approach above, such further testing is not currently warranted.

## 5.6.2 Uncertainties and possible refinements

There is considerable uncertainty in the PECs calculated for man via the environment. It may be possible to refine the PEC estimates by carrying out further investigations to measure the actual uptake from soil into root crops, from air into leaf crops and the subsequent transfer into meat and milk. However, such investigations would be extremely difficult to carry out and such refinement is not considered to be a priority at present.

It may also be possible to refine the PECs by obtaining further information on the release to the environment from the uses of LCCPs.

## 5.6.3 Conclusions for man exposed via the environment

The provisional risk assessment carried out indicates that the production and uses of the C<sub>18-20</sub> liquid, C<sub>>20</sub> liquid and C<sub>>20</sub> solid chlorinated paraffins are expected to present a low risk to man exposed via environmental routes.

## 5.7 Other issues

### 5.7.1 Presence of other chlorinated paraffin impurities in LCCPs

In Section 1.2.1, information was reported to indicate that the C<sub>18–20</sub> liquid chlorinated paraffins may contain a substantial proportion of C<sub>17</sub> chlorinated paraffins, and very small amounts of chlorinated paraffins of shorter chain lengths. The typical levels reported were 17 per cent C<sub>17</sub> and <1 per cent C<sub>16</sub>, although the range of the C<sub>17</sub> impurity was given as 10–20 per cent. The amounts of chlorinated paraffins with carbon chain lengths of C<sub>15</sub> or lower present in the C<sub>18–20</sub> liquid products would be negligibly small.

Since the C<sub>>20</sub> liquid and C<sub>>20</sub> chlorinated paraffins use a carbon feedstock that centres around C<sub>24</sub> or C<sub>25</sub>, these would not be expected to contain significant quantities of chlorinated paraffins with carbon chain lengths shorter than C<sub>20</sub>.

Based on the estimated regional and continental releases of C<sub>18–20</sub> liquid chlorinated paraffin, the amounts of C<sub>16–17</sub> chlorinated paraffin released are shown in Table 5.10.

**Table 5.10 Estimated amounts of C<sub>16–17</sub> chlorinated paraffin released to the environment**

Compartment	Regional release	Continental release
Air	1,160–1,616 kg/year	10,439–14,542 kg/year
Waste water	226–254 kg/year	2,033–2,288 kg/year
Surface water	213–378 kg/year	1,922–3,398 kg/year
Urban/industrial soil	351–808 kg/year	3,160–7,275 kg/year

These releases could add to the environmental burden of C<sub>16–17</sub> chlorinated paraffin that arises from medium-chain chlorinated paraffins, and are being considered further in the assessment of that substance.

In terms of the risk assessment of the LCCPs, the risk from the C<sub>16–17</sub> chlorinated paraffin impurities in the products should already be accounted for in the risk characterisation, since the assessment is based, in the main, on data obtained using the commercial product (which will contain the impurity). This will certainly be the case for secondary poisoning, where the PNEC is currently based on data on the medium-chain chlorinated paraffins in any case.

For surface water, the PNEC derived in the medium-chain chlorinated paraffins risk assessment is currently 1 µg/l (ECB, 2005a). This is slightly lower than the PNEC used here for the C<sub>18–20</sub> liquid products (PNEC 2.9 µg/l).

In the case of sediment and soil, the PNECs for C<sub>18–20</sub> liquid chlorinated paraffins used in this assessment (5,710 mg/kg wet weight and 4,640 mg/kg wet weight for sediment and soil, respectively) are considerably higher than those currently derived for medium-chain chlorinated paraffins (5 mg/kg wet weight and 10.6 mg/kg wet weight, respectively) based on actual toxicity tests on sediment and soil organisms.

In order to investigate the possible effects of the C<sub>16–17</sub> impurities further, PEC/PNEC ratios have been derived for this impurity assuming that it behaves in an identical

fashion in terms of environmental fate, behaviour and toxicity as the medium-chain chlorinated paraffins. The results of this analysis are given in Appendix G.

It should be noted that this approach assumes, in particular, that all the toxicity seen with the medium-chain chlorinated paraffins is due mainly to the C<sub>17</sub> component. This is not likely to be the case as there is a general trend that the chlorinated paraffins become less toxic and bioavailable with increasing carbon chain length. Thus, although this “worst case” approach can be used to identify situations where no risk exists, a PEC/PNEC >1 does not necessarily mean that an actual risk exists, rather that more information may be necessary to specifically address the effects of the impurities further.

This analysis indicated that possible risks to surface water, sediment and soil could occur from LCCPs in some applications of the substance. No risks from secondary poisoning from the fish food chain were identified, but a possible risk from all uses was found for the earthworm food chain. This indicates that the applicability of the PNEC derived for medium-chain chlorinated paraffins to the C<sub>16-17</sub> impurities present in the C<sub>18-20</sub> liquid chlorinated paraffins should be considered further.

### **5.7.2 Waste disposal**

Similar to chlorinated compounds in general, chlorinated paraffins can act as a source of chlorine during incineration processes. This chlorine can then lead to the formation of polychlorinated dioxins and furans – a well known problem associated with incineration.

In most cases, controls are already in place on incinerators to minimise the formation of these dioxins and furans, and so the presence of the chlorinated paraffins should not lead to increased emissions. However, other processes involving chlorinated paraffins may not be so well controlled. One specific example is when metal swarf from metal cutting is re-melted. In this case the swarf may contain metalworking/cutting fluids containing chlorinated paraffins which could theoretically contribute to the formation of chlorinated dioxins and furans in the process. There is insufficient information available on this issue to make an assessment of the significance this processes in terms of a risk for the environment.



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# Glossary Of Terms

<b>Term</b>	<b>Description</b>
Biochemical oxygen demand (BOD)	A measure of degradation potential..
Bioconcentration factor (BCF)	A measure of chemical uptake, being the ratio between the concentration in an organism and the concentration in an environmental compartment (usually water).
CAS number (no.)	An identifying code number assigned to chemicals by the Chemical Abstract Services. The CAS number is a generally recognised identification reference for a chemical; it is possible that a substance can have more than one such number.
Lowest observed adverse effect level (LOAEL)	The lowest concentration in a mammalian toxicity test that does gives rise to adverse effects (relative to a control).
Lowest observed effect concentration (LOEC)	The lowest concentration in a toxicity test that gives rise to adverse effects (relative to a control).
Median effective concentration (EC <sub>50</sub> )	The concentration in a toxicity test at which a particular effect is observed in half of the organisms exposed for a specified time.
Median lethal concentration/dose (LC/D <sub>50</sub> )	The concentration in a toxicity test that can be expected to cause death in half of the organisms exposed for a specified time.
No observed adverse effect level (NOAEL)	The highest concentration in a mammalian toxicity test that does not give rise to adverse effects (relative to a control).
No observed effect concentration (NOEC)	The highest concentration in a toxicity test that does not give rise to adverse effects (relative to a control).
Octanol-water partition coefficient (Kow)	This parameter gives an indication of the partitioning behaviour of a substance between water and lipid-containing materials such as cell membranes or organic matter in soils and sediments.
Readily biodegradable	Rapid environmental degradation to carbon dioxide and water, etc., as measured by laboratory screening tests involving micro-organisms

# Abbreviations

<b>Acronym</b>	<b>Description</b>
ABS	Acrylonitrile butadiene styrene copolymer
AChE	Acetylcholinesterase
AF	Assessment factor
ASTM	American Society for Testing and Materials
BACS	British Association for Chemical Specialities
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BMF	Biomagnification factor
BOD	Biochemical oxygen demand
bw	Body weight (also Bw, b.w.)
CAS	Chemical Abstract Services
CEFIC	European Chemical Industry Council
CEPAD	Conseil Européen des Phénols Alkylés et Derivés (the European Council for Alkylphenols and Derivatives): a trade association representing the major European producers of alkylphenols, and some of the users ( <a href="http://www.cefic.be/cepad/">http://www.cefic.be/cepad/</a> )
CMR	Carcinogenic, mutagenic and toxic to reproduction
CNS	Central nervous system
COD	Chemical oxygen demand
CSTEE	Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO)
Defra	Department of the Environment, Food and Rural Affairs
DETR	Department of the Environment, Transport and the Regions
DIN	Deutsche Industrie Norm (German norm)
dw	Dry weight
EAA	European Adjuvants Association

<b>Acronym</b>	<b>Description</b>
EC	European Communities
EC <sub>10</sub>	Effect concentration measured as 10% effect
EC <sub>50</sub>	Median effect concentration
ECB	European Chemicals Bureau
EC <sub>x</sub>	As EC <sub>50</sub> , but for x% effect; x usually being 0, 10, or 100
EDMAR	Endocrine disruption in the marine environment
EDTA	Endocrine disruption testing and assessment
EEC	European Economic Communities
EINECS	European Inventory of Existing Commercial Chemical Substances – this lists all chemical substances that were supplied to the market prior to 18th September 1981
EN	European Norm
EOSCA	European Oilfield Speciality Chemicals Association
EPA	Environmental Protection Agency (USA)
EQS	Environmental quality standard
ESD	Emission Scenario Document
ESIS	European Chemical Substances Information System
ESR	The Existing Substances Regulation – Council Regulation (EEC) 793/93 on the evaluation and control of the risks of ‘existing’ substances
EU	European Union
EU-15	The 15 European Union Member States prior to May 2004
EUSES	European Union System for the Evaluation of Substances (software tool in support of the TGD on risk assessment)
FAF	Food accumulation factor
GLP	Good laboratory practice
GSI	Gonadosomatic index
HLC	Henry’s Law constant
HPLC	High pressure liquid chromatography
HPV	High production volume (supply > 1000 tonnes/year)

<b>Acronym</b>	<b>Description</b>
HPVC	High production volume chemical (supply > 1000 tonnes/year)
HSDB	Hazardous Substances Data Bank
HSI	Hepatosomatic index
IC	Industrial category
IC <sub>50</sub>	Median immobilisation concentration or median inhibitory concentration
IPC	Integrated pollution control
IPCS	International Programme on Chemical Safety
IPPC	Integrated Pollution Prevention and Control (EC Directive 96/61/EEC)
ISO	International Organisation for Standardisation
IUCLID	International Uniform Chemical Information Database: contains data collected under the Existing Substances Regulation (ESR)
IUPAC	International Union for Pure and Applied Chemistry
K <sub>oc</sub>	Organic carbon normalised distribution coefficient
K <sub>ow</sub>	Octanol-water partition coefficient
K <sub>p</sub>	Solids-water partition coefficient
K <sub>plant-water</sub>	Partition coefficient between plant tissues and water
K <sub>susp-water</sub>	Partition coefficient between suspended sediment and water
K <sub>soil-water</sub>	Partition coefficient between soil and water
L(E)C <sub>50</sub>	Median lethal (effect) concentration
LD <sub>50</sub>	Median lethal dose
LDPE	Low density polyethylene
LOAEL	Lowest observed adverse effect level
LOEC	Lowest observed effect concentration
LOEL	Lowest observed effect level
log K <sub>ow</sub>	Log of the octanol-water partition coefficient (K <sub>ow</sub> )
LPV	Low production volume (supply 10-1,000 tonnes/year)
LPVC	Low production volume chemical (supply 10-1,000 tonnes/year)

<b>Acronym</b>	<b>Description</b>
LQ	Quantification limit
MBS	Methyl methacrylate butadiene styrene terpolymer
MITI	Ministry of International Trade and Industry, Japan
MOS	Margin of safety
N	Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
n.t.p.	Normal temperature and pressure
NO(A)EL	No observed (adverse) effect level
NOEC	No observed effect concentration
OECD	Organisation for Economic Cooperation and Development
OSI	Ovarian somatic index
OSPAR	Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic, <a href="http://www.ospar.org">http://www.ospar.org</a>
P	Persistent
PBT	Persistent, bioaccumulative and toxic
PEC	Predicted environmental concentration
pH	Logarithm (to the base 10) of the hydrogen ion concentration [H <sup>+</sup> ]
pKa	Logarithm (to the base 10) of the acid dissociation constant
PNEC	Predicted no effect concentration
PP	Polypropylene
ppb	Parts per billion
ppm	Parts per million
PVC	Polyvinyl chloride
(Q)SAR	(Quantitative) structure-activity relationship
RBA	Relative binding affinity
RCR	Risk characterisation ratio
SEPA	Scottish Environmental Protection Agency

<b>Acronym</b>	<b>Description</b>
SETAC	Society of Environmental Toxicology And Chemistry
SIAR	SIDS Initial Assessment Report, OECD
SIDS	Screening Information Dataset, OECD
SMILES	Simplified Molecular Input Line Entry System – the SMILES code is a chemical notation system used to represent a molecular structure by a linear string of symbols; it is a simple way of entering chemical structural information into a computer programme
SRC	Syracuse Research Corporation
STP	Sewage treatment plant
STW	Sewage treatment works
TG	Test guideline
TGD	Technical Guidance Document
UBA	Umweltbundesamt (Federal Environment Protection Agency in Austria and Germany)
UGPLI	Urogenital pupilla length index
US EPA	Environmental Protection Agency, USA
UV	Ultraviolet region of the electromagnetic spectrum
vB	Very bioaccumulative
vP	Very persistent
vPvB	Very persistent and very bioaccumulative
WAF	Water accommodated fraction
w/v	Weight per volume ratio
w/w	Weight per weight ratio
wt	Weight
wwt	Wet weight
WWTP	Wastewater treatment plant

# Appendix A EUSES modelling

This appendix contains reference to copies of the EUSES printout files for long-chain chlorinated paraffins (LCCPs). The EUSES modelling has been carried out separately for the three main types of LCCP considered in the assessment. The EUSES printout for C<sub>18-20</sub> liquid chlorinated paraffins, C<sub>>20</sub> liquid chlorinated, C<sub>>20</sub> solid chlorinated paraffins are available from the Environment Agency. Please contact - e-mail: [ukesrenv@environment-agency.gov.uk](mailto:ukesrenv@environment-agency.gov.uk)

## A1 C<sub>18-20</sub> liquid chlorinated paraffins

The results from the following scenarios from the main report are included in the printout.

<u>EUSES Printout</u>	<u>Scenario</u>
USE PATTERN 1 production	Production generic production site
USE PATTERN 2 formulation industrial use private use	Use in PVC – plastisol coating compounding site – open system conversion site – open system combined compounding/conversion site – open system
USE PATTERN 3 formulation industrial use private use	Use in PVC – extrusion/other – open system compounding site – open system conversion site – open system combined compounding/conversion site – open system
USE PATTERN 4 formulation industrial use private use	Use in PVC – extrusion/other – partially open system compounding site – partially open system conversion site – partially open system combined compounding/conversion site – partially open system
USE PATTERN 5 formulation industrial use private use	Use in PVC – extrusion other – closed system compounding site – closed system conversion site – closed system combined compounding/conversion site – closed system
USE PATTERN 6 formulation industrial use	Use in paints and varnishes formulation site industrial application of paints
USE PATTERN 7 formulation industrial use private use service life waste treatment	Use in metal cutting/working fluids formulation site use in oil-based fluids (small site; 5% LCCP content) use in oil-based fluids (small site; 10% LCCP content) use in emulsifiable fluids use in emulsifiable fluids – intermittent release



USE PATTERN 8 formulation industrial use private use waste treatment	Use in leather fat liquors formulation site (default calculation) use – complete processing of raw hides use – processing of “wet blue” formulation site (industry-specific calculation)
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USE PATTERN 9 industrial use	Use in textiles textile treatment site
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The EUSES file for C<sub>18-20</sub> liquid chlorinated paraffins is available from the Environment Agency. Please contact - e-mail: [ukesrenv@environment-agency.gov.uk](mailto:ukesrenv@environment-agency.gov.uk)

## A2 C<sub>>20</sub> liquid chlorinated paraffins

The results for the following scenarios from the main report are included in the printout:

<u>EUSES Printout</u>	<u>Scenario</u>
USE PATTERN 1 production	Production generic production site
USE PATTERN 2 Industrial use	Use in rubber combined compounding/conversion site
USE PATTERN 3 formulation industrial use	Use in paints and varnishes formulation site industrial application of paints
USE PATTERN 4 formulation industrial use private use service life waste treatment	Use in metal cutting/working fluids – oil based formulation site use in oil-based fluids (large site; 5% LCCP content) use in oil-based fluids (large site; 10% LCCP content) use in oil-based fluids (small site; 5% LCCP content) use in oil-based fluids (small site; 10% LCCP content)
USE PATTERN 5 industrial use waste treatment	Use in metal cutting/working fluids – water based use in emulsifiable fluids use in emulsifiable fluids – intermittent release
USE PATTERN 6 formulation industrial use private use waste treatment	Use in leather fat liquors formulation site (default calculation) use – complete processing of raw hides use – processing of “wet blue” formulation site (industry-specific calculation)

The EUSES file for C<sub>>20</sub> liquid chlorinated paraffins is available from the Environment Agency. Please contact - e-mail: [ukesrenv@environment-agency.gov.uk](mailto:ukesrenv@environment-agency.gov.uk).

## A3 C<sub>>20</sub> solid chlorinated paraffins

The results from the following scenarios from the main report are included in the printout.

<u>EUSES Printout</u>	<u>Scenario</u>
USE PATTERN 1 production	Production generic production site
USE PATTERN 2 industrial use	Use in rubber combined compounding/conversion site
USE PATTERN 3 formulation industrial use	Use in paints and varnishes formulation site industrial application of paints

The EUSES file for C<sub>>20</sub> solid chlorinated paraffins is available from the Environment Agency. Please contact - e-mail: [ukesrenv@environment-agency.gov.uk](mailto:ukesrenv@environment-agency.gov.uk)

# Appendix B Estimated vapour pressure of LCCPs

The vapour pressure has been estimated for LCCPs using the following equation derived for short-chain chlorinated paraffins:

$$\log(\text{vapour pressure}) = -(0.353 \times \text{no. of C atoms}) - (0.645 \times \text{no. of Cl atoms}) + 4.462$$

where vapour pressure is in Pa at 25°C.

Taken from: Drouillard K G, Tomy G T, Muir D C G and Friesen K J *Volatility of chlorinated n-alkanes (C10-C12): Vapour pressures and Henry's Law constants*. Environmental Toxicology and Chemistry, 17, 1998, 1252-1260.

**Table B1** Estimated vapour pressure for LCCPs (C<sub>18</sub>–C<sub>30</sub>)

No of carbons	No of chlorines	No of hydrogens	Molecular weight (g/mole)	Chlorine content (by weight)	Estimated vapour pressure (Pa)
18	1	37	288.5	12.3%	2.90E-03
18	2	36	323	22.0%	6.58E-04
18	3	35	357.5	29.8%	1.49E-04
18	4	34	392	36.2%	3.37E-05
18	5	33	426.5	41.6%	7.64E-06
18	6	32	461	46.2%	1.73E-06
18	7	31	495.5	50.2%	3.92E-07
18	8	30	530	53.6%	8.87E-08
18	9	29	564.5	56.6%	2.01E-08
18	10	28	599	59.3%	4.55E-09
18	11	27	633.5	61.6%	1.03E-09
18	12	26	668	63.8%	2.33E-10
18	13	25	702.5	65.7%	5.28E-11
18	14	24	737	67.4%	1.20E-11
18	15	23	771.5	69.0%	2.71E-12
18	16	22	806	70.5%	6.14E-13
18	17	21	840.5	71.8%	1.39E-13
19	1	39	302.5	11.7%	1.29E-03
19	2	38	337	21.1%	2.92E-04
19	3	37	371.5	28.7%	6.61E-05
19	4	36	406	35.0%	1.50E-05
19	5	35	440.5	40.3%	3.39E-06
19	6	34	475	44.8%	7.67E-07
19	7	33	509.5	48.8%	1.74E-07
19	8	32	544	52.2%	3.94E-08
19	9	31	578.5	55.2%	8.91E-09
19	10	30	613	57.9%	2.02E-09
19	11	29	647.5	60.3%	4.57E-10
19	12	28	682	62.5%	1.04E-10
19	13	27	716.5	64.4%	2.34E-11
19	14	26	751	66.2%	5.31E-12

No of carbons	No of chlorines	No of hydrogens	Molecular weight (g/mole)	Chlorine content (by weight)	Estimated vapour pressure (Pa)
19	15	25	785.5	67.8%	1.20E-12
19	16	24	820	69.3%	2.72E-13
19	17	23	854.5	70.6%	6.17E-14
19	18	22	889	71.9%	1.40E-14
20	1	41	316.5	11.2%	5.71E-04
20	2	40	351	20.2%	1.29E-04
20	3	39	385.5	27.6%	2.93E-05
20	4	38	420	33.8%	6.64E-06
20	5	37	454.5	39.1%	1.50E-06
20	6	36	489	43.6%	3.40E-07
20	7	35	523.5	47.5%	7.71E-08
20	8	34	558	50.9%	1.75E-08
20	9	33	592.5	53.9%	3.95E-09
20	10	32	627	56.6%	8.95E-10
20	11	31	661.5	59.0%	2.03E-10
20	12	30	696	61.2%	4.59E-11
20	13	29	730.5	63.2%	1.04E-11
20	14	28	765	65.0%	2.36E-12
20	15	27	799.5	66.6%	5.33E-13
20	16	26	834	68.1%	1.21E-13
20	17	25	868.5	69.5%	2.74E-14
20	18	24	903	70.8%	6.19E-15
20	19	23	937.5	71.9%	1.40E-15
20	20	22	972	73.0%	3.18E-16
21	1	43	330.5	10.7%	2.54E-04
21	2	42	365	19.5%	5.74E-05
21	3	41	399.5	26.7%	1.30E-05
21	4	40	434	32.7%	2.94E-06
21	5	39	468.5	37.9%	6.67E-07
21	6	38	503	42.3%	1.51E-07
21	7	37	537.5	46.2%	3.42E-08
21	8	36	572	49.7%	7.74E-09
21	9	35	606.5	52.7%	1.75E-09
21	10	34	641	55.4%	3.97E-10
21	11	33	675.5	57.8%	8.99E-11
21	12	32	710	60.0%	2.04E-11
21	13	31	744.5	62.0%	4.61E-12
21	14	30	779	63.8%	1.04E-12
21	15	29	813.5	65.5%	2.37E-13
21	16	28	848	67.0%	5.36E-14
21	17	27	882.5	68.4%	1.21E-14
21	18	26	917	69.7%	2.75E-15
21	19	25	951.5	70.9%	6.22E-16
21	20	24	986	72.0%	1.41E-16
21	21	23	1020.5	73.1%	3.19E-17
22	1	45	344.5	10.3%	1.12E-04
22	2	44	379	18.7%	2.55E-05
22	3	43	413.5	25.8%	5.77E-06
22	4	42	448	31.7%	1.31E-06
22	5	41	482.5	36.8%	2.96E-07
22	6	40	517	41.2%	6.70E-08

No of carbons	No of chlorines	No of hydrogens	Molecular weight (g/mole)	Chlorine content (by weight)	Estimated vapour pressure (Pa)
22	7	39	551.5	45.1%	1.52E-08
22	8	38	586	48.5%	3.44E-09
22	9	37	620.5	51.5%	7.78E-10
22	10	36	655	54.2%	1.76E-10
22	11	35	689.5	56.6%	3.99E-11
22	12	34	724	58.8%	9.04E-12
22	13	33	758.5	60.8%	2.05E-12
22	14	32	793	62.7%	4.63E-13
22	15	31	827.5	64.4%	1.05E-13
22	16	30	862	65.9%	2.38E-14
22	17	29	896.5	67.3%	5.38E-15
22	18	28	931	68.6%	1.22E-15
22	19	27	965.5	69.9%	2.76E-16
22	20	26	1000	71.0%	6.25E-17
22	21	25	1034.5	72.1%	1.42E-17
22	22	24	1069	73.1%	3.21E-18
23	1	47	358.5	9.9%	4.99E-05
23	2	46	393	18.1%	1.13E-05
23	3	45	427.5	24.9%	2.56E-06
23	4	44	462	30.7%	5.79E-07
23	5	43	496.5	35.8%	1.31E-07
23	6	42	531	40.1%	2.97E-08
23	7	41	565.5	43.9%	6.73E-09
23	8	40	600	47.3%	1.52E-09
23	9	39	634.5	50.4%	3.45E-10
23	10	38	669	53.1%	7.82E-11
23	11	37	703.5	55.5%	1.77E-11
23	12	36	738	57.7%	4.01E-12
23	13	35	772.5	59.7%	9.08E-13
23	14	34	807	61.6%	2.06E-13
23	15	33	841.5	63.3%	4.66E-14
23	16	32	876	64.8%	1.05E-14
23	17	31	910.5	66.3%	2.39E-15
23	18	30	945	67.6%	5.41E-16
23	19	29	979.5	68.9%	1.22E-16
23	20	28	1014	70.0%	2.77E-17
23	21	27	1048.5	71.1%	6.28E-18
23	22	26	1083	72.1%	1.42E-18
23	23	25	1117.5	73.1%	3.22E-19
24	1	49	372.5	9.5%	2.21E-05
24	2	48	407	17.4%	5.01E-06
24	3	47	441.5	24.1%	1.14E-06
24	4	46	476	29.8%	2.57E-07
24	5	45	510.5	34.8%	5.82E-08
24	6	44	545	39.1%	1.32E-08
24	7	43	579.5	42.9%	2.99E-09
24	8	42	614	46.3%	6.76E-10
24	9	41	648.5	49.3%	1.53E-10
24	10	40	683	52.0%	3.47E-11
24	11	39	717.5	54.4%	7.85E-12
24	12	38	752	56.6%	1.78E-12

No of carbons	No of chlorines	No of hydrogens	Molecular weight (g/mole)	Chlorine content (by weight)	Estimated vapour pressure (Pa)
24	13	37	786.5	58.7%	4.03E-13
24	14	36	821	60.5%	9.12E-14
24	15	35	855.5	62.2%	2.07E-14
24	16	34	890	63.8%	4.68E-15
24	17	33	924.5	65.3%	1.06E-15
24	18	32	959	66.6%	2.40E-16
24	19	31	993.5	67.9%	5.43E-17
24	20	30	1028	69.1%	1.23E-17
24	21	29	1062.5	70.2%	2.79E-18
24	22	28	1097	71.2%	6.31E-19
24	23	27	1131.5	72.2%	1.43E-19
24	24	26	1166	73.1%	3.24E-20
25	1	51	386.5	9.2%	9.82E-06
25	2	50	421	16.9%	2.22E-06
25	3	49	455.5	23.4%	5.04E-07
25	4	48	490	29.0%	1.14E-07
25	5	47	524.5	33.8%	2.58E-08
25	6	46	559	38.1%	5.85E-09
25	7	45	593.5	41.9%	1.32E-09
25	8	44	628	45.2%	3.00E-10
25	9	43	662.5	48.2%	6.79E-11
25	10	42	697	50.9%	1.54E-11
25	11	41	731.5	53.4%	3.48E-12
25	12	40	766	55.6%	7.89E-13
25	13	39	800.5	57.7%	1.79E-13
25	14	38	835	59.5%	4.05E-14
25	15	37	869.5	61.2%	9.16E-15
25	16	36	904	62.8%	2.07E-15
25	17	35	938.5	64.3%	4.70E-16
25	18	34	973	65.7%	1.06E-16
25	19	33	1007.5	66.9%	2.41E-17
25	20	32	1042	68.1%	5.46E-18
25	21	31	1076.5	69.3%	1.24E-18
25	22	30	1111	70.3%	2.80E-19
25	23	29	1145.5	71.3%	6.34E-20
25	24	28	1180	72.2%	1.44E-20
25	25	27	1214.5	73.1%	3.25E-21
26	1	53	400.5	8.9%	4.36E-06
26	2	52	435	16.3%	9.86E-07
26	3	51	469.5	22.7%	2.23E-07
26	4	50	504	28.2%	5.06E-08
26	5	49	538.5	33.0%	1.15E-08
26	6	48	573	37.2%	2.59E-09
26	7	47	607.5	40.9%	5.87E-10
26	8	46	642	44.2%	1.33E-10
26	9	45	676.5	47.2%	3.01E-11
26	10	44	711	49.9%	6.82E-12
26	11	43	745.5	52.4%	1.55E-12
26	12	42	780	54.6%	3.50E-13
26	13	41	814.5	56.7%	7.93E-14
26	14	40	849	58.5%	1.79E-14

No of carbons	No of chlorines	No of hydrogens	Molecular weight (g/mole)	Chorine content (by weight)	Estimated vapour pressure (Pa)
26	15	39	883.5	60.3%	4.06E-15
26	16	38	918	61.9%	9.20E-16
26	17	37	952.5	63.4%	2.08E-16
26	18	36	987	64.7%	4.72E-17
26	19	35	1021.5	66.0%	1.07E-17
26	20	34	1056	67.2%	2.42E-18
26	21	33	1090.5	68.4%	5.48E-19
26	22	32	1125	69.4%	1.24E-19
26	23	31	1159.5	70.4%	2.81E-20
26	24	30	1194	71.4%	6.37E-21
26	25	29	1228.5	72.2%	1.44E-21
26	26	28	1263	73.1%	3.27E-22
27	1	55	414.5	8.6%	1.93E-06
27	2	54	449	15.8%	4.38E-07
27	3	53	483.5	22.0%	9.91E-08
27	4	52	518	27.4%	2.24E-08
27	5	51	552.5	32.1%	5.08E-09
27	6	50	587	36.3%	1.15E-09
27	7	49	621.5	40.0%	2.61E-10
27	8	48	656	43.3%	5.90E-11
27	9	47	690.5	46.3%	1.34E-11
27	10	46	725	49.0%	3.03E-12
27	11	45	759.5	51.4%	6.85E-13
27	12	44	794	53.7%	1.55E-13
27	13	43	828.5	55.7%	3.52E-14
27	14	42	863	57.6%	7.96E-15
27	15	41	897.5	59.3%	1.80E-15
27	16	40	932	60.9%	4.08E-16
27	17	39	966.5	62.4%	9.25E-17
27	18	38	1001	63.8%	2.09E-17
27	19	37	1035.5	65.1%	4.74E-18
27	20	36	1070	66.4%	1.07E-18
27	21	35	1104.5	67.5%	2.43E-19
27	22	34	1139	68.6%	5.51E-20
27	23	33	1173.5	69.6%	1.25E-20
27	24	32	1208	70.5%	2.82E-21
27	25	31	1242.5	71.4%	6.40E-22
27	26	30	1277	72.3%	1.45E-22
27	27	29	1311.5	73.1%	3.28E-23
28	1	57	428.5	8.3%	8.57E-07
28	2	56	463	15.3%	1.94E-07
28	3	55	497.5	21.4%	4.40E-08
28	4	54	532	26.7%	9.95E-09
28	5	53	566.5	31.3%	2.25E-09
28	6	52	601	35.4%	5.11E-10
28	7	51	635.5	39.1%	1.16E-10
28	8	50	670	42.4%	2.62E-11
28	9	49	704.5	45.4%	5.93E-12
28	10	48	739	48.0%	1.34E-12
28	11	47	773.5	50.5%	3.04E-13
28	12	46	808	52.7%	6.89E-14

No of carbons	No of chlorines	No of hydrogens	Molecular weight (g/mole)	Chlorine content (by weight)	Estimated vapour pressure (Pa)
28	13	45	842.5	54.8%	1.56E-14
28	14	44	877	56.7%	3.53E-15
28	15	43	911.5	58.4%	8.00E-16
28	16	42	946	60.0%	1.81E-16
28	17	41	980.5	61.6%	4.10E-17
28	18	40	1015	63.0%	9.29E-18
28	19	39	1049.5	64.3%	2.10E-18
28	20	38	1084	65.5%	4.76E-19
28	21	37	1118.5	66.7%	1.08E-19
28	22	36	1153	67.7%	2.44E-20
28	23	35	1187.5	68.8%	5.53E-21
28	24	34	1222	69.7%	1.25E-21
28	25	33	1256.5	70.6%	2.84E-22
28	26	32	1291	71.5%	6.43E-23
28	27	31	1325.5	72.3%	1.46E-23
28	28	30	1360	73.1%	3.30E-24
29	1	59	442.5	8.0%	3.80E-07
29	2	58	477	14.9%	8.61E-08
29	3	57	511.5	20.8%	1.95E-08
29	4	56	546	26.0%	4.42E-09
29	5	55	580.5	30.6%	1.00E-09
29	6	54	615	34.6%	2.26E-10
29	7	53	649.5	38.3%	5.13E-11
29	8	52	684	41.5%	1.16E-11
29	9	51	718.5	44.5%	2.63E-12
29	10	50	753	47.1%	5.96E-13
29	11	49	787.5	49.6%	1.35E-13
29	12	48	822	51.8%	3.05E-14
29	13	47	856.5	53.9%	6.92E-15
29	14	46	891	55.8%	1.57E-15
29	15	45	925.5	57.5%	3.55E-16
29	16	44	960	59.2%	8.04E-17
29	17	43	994.5	60.7%	1.82E-17
29	18	42	1029	62.1%	4.12E-18
29	19	41	1063.5	63.4%	9.33E-19
29	20	40	1098	64.7%	2.11E-19
29	21	39	1132.5	65.8%	4.79E-20
29	22	38	1167	66.9%	1.08E-20
29	23	37	1201.5	68.0%	2.45E-21
29	24	36	1236	68.9%	5.56E-22
29	25	35	1270.5	69.9%	1.26E-22
29	26	34	1305	70.7%	2.85E-23
29	27	33	1339.5	71.6%	6.46E-24
29	28	32	1374	72.3%	1.46E-24
29	29	31	1408.5	73.1%	3.31E-25
30	1	61	456.5	7.8%	1.69E-07
30	2	60	491	14.5%	3.82E-08
30	3	59	525.5	20.3%	8.65E-09
30	4	58	560	25.4%	1.96E-09
30	5	57	594.5	29.9%	4.44E-10
30	6	56	629	33.9%	1.00E-10



No of carbons	No of chlorines	No of hydrogens	Molecular weight (g/mole)	Chlorine content (by weight)	Estimated vapour pressure (Pa)
30	7	55	663.5	37.5%	2.28E-11
30	8	54	698	40.7%	5.15E-12
30	9	53	732.5	43.6%	1.17E-12
30	10	52	767	46.3%	2.64E-13
30	11	51	801.5	48.7%	5.98E-14
30	12	50	836	51.0%	1.36E-14
30	13	49	870.5	53.0%	3.07E-15
30	14	48	905	54.9%	6.95E-16
30	15	47	939.5	56.7%	1.57E-16
30	16	46	974	58.3%	3.56E-17
30	17	45	1008.5	59.8%	8.07E-18
30	18	44	1043	61.3%	1.83E-18
30	19	43	1077.5	62.6%	4.14E-19
30	20	42	1112	63.8%	9.38E-20
30	21	41	1146.5	65.0%	2.12E-20
30	22	40	1181	66.1%	4.81E-21
30	23	39	1215.5	67.2%	1.09E-21
30	24	38	1250	68.2%	2.47E-22
30	25	37	1284.5	69.1%	5.58E-23
30	26	36	1319	70.0%	1.26E-23
30	27	35	1353.5	70.8%	2.86E-24
30	28	34	1388	71.6%	6.49E-25
30	29	33	1422.5	72.4%	1.47E-25
30	30	32	1457	73.1%	3.33E-26

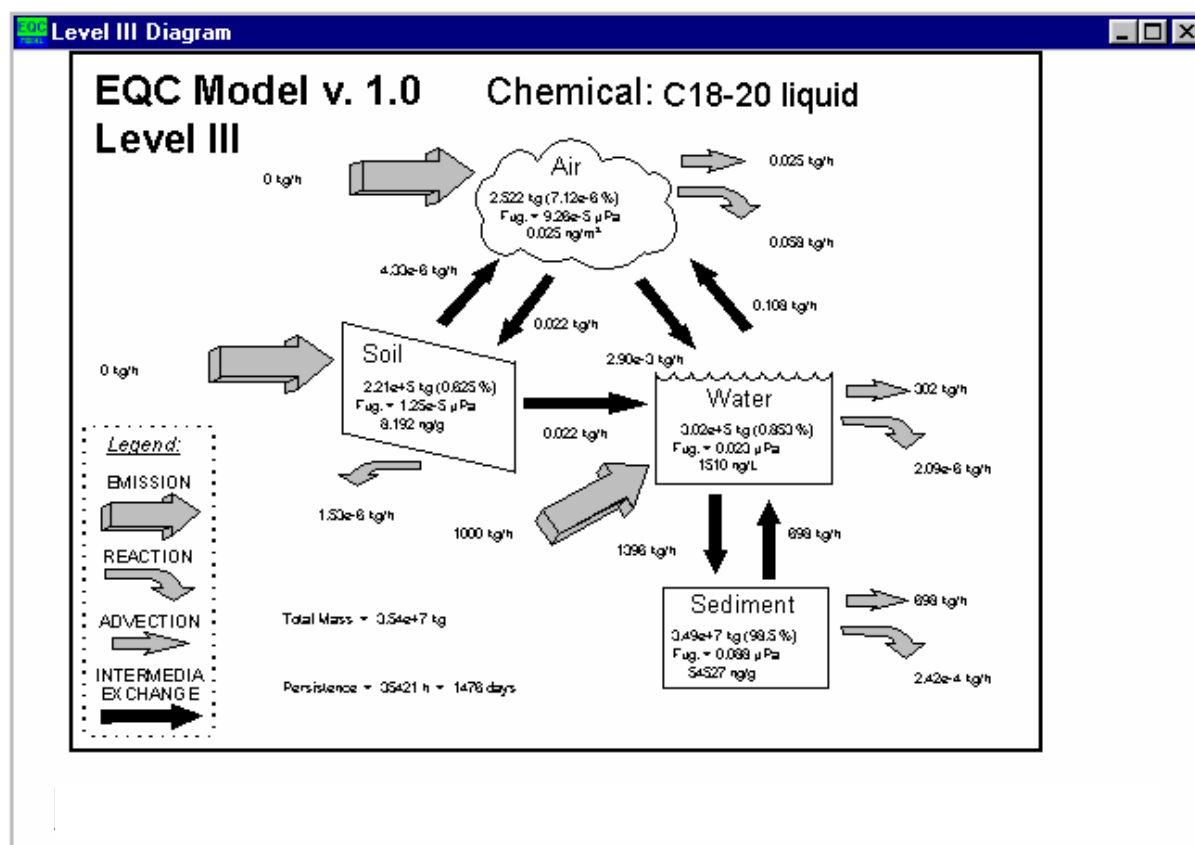
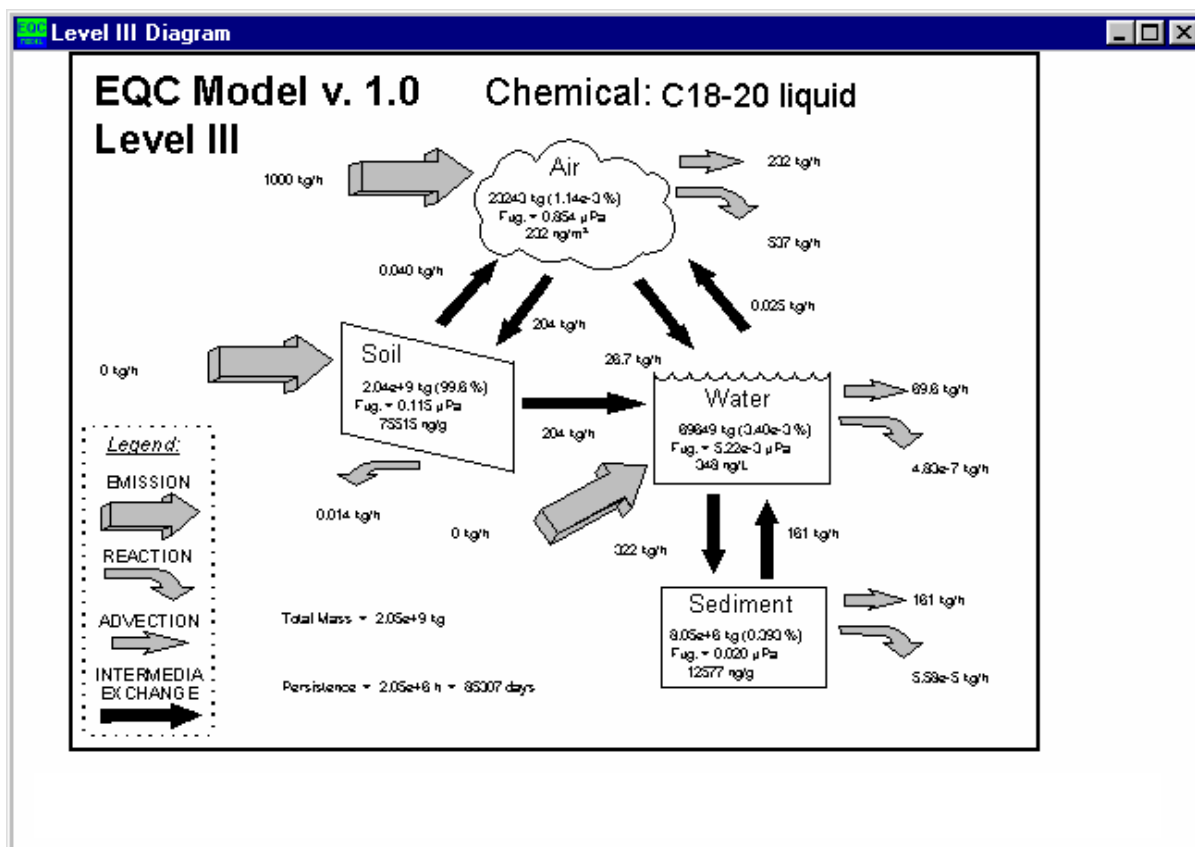
# Appendix C Generic level III fugacity modelling

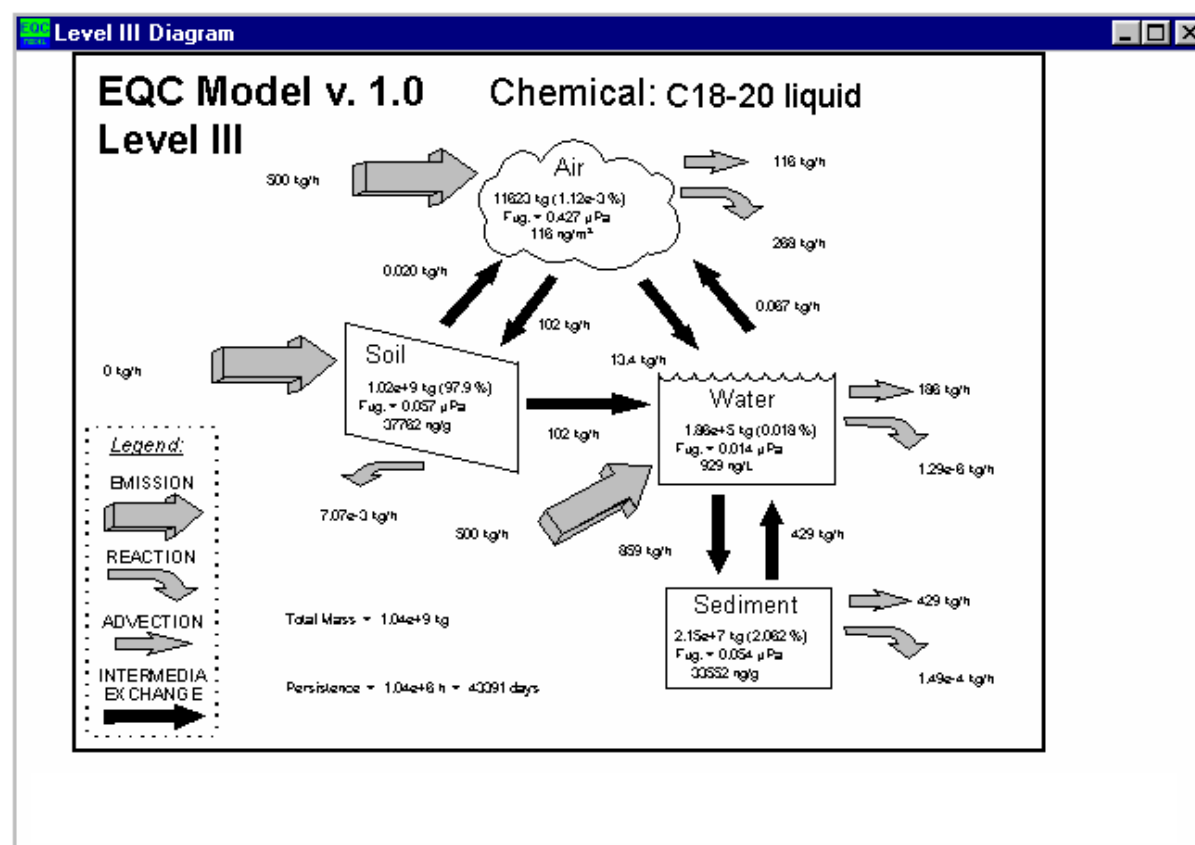
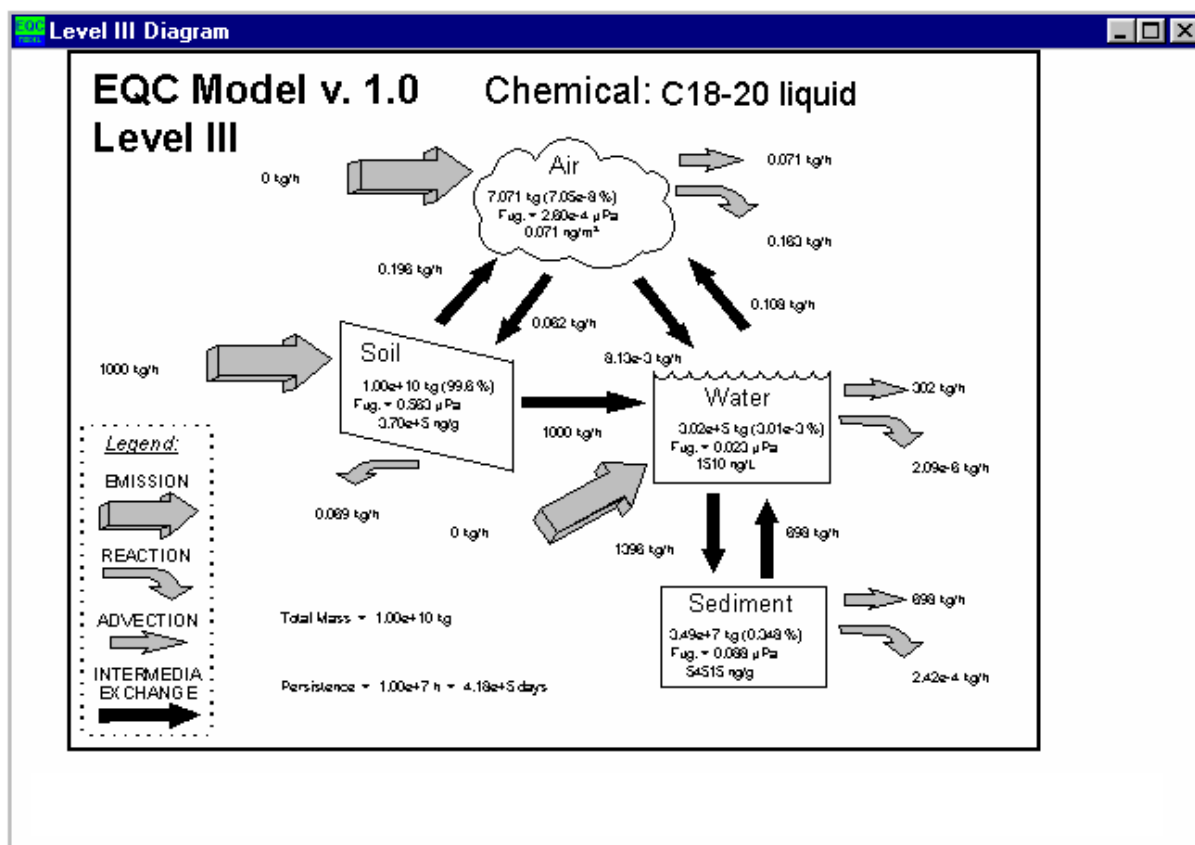
The potential environmental distribution of LCCPs has been studied using a generic level III fugacity model. The level III model used was a four compartment model (EQC Model version 1.01, May 1997) similar to that recommended for use within the OECD HPV program. The model was run using the default settings in the model and the chemical specific input data shown in Table C1.

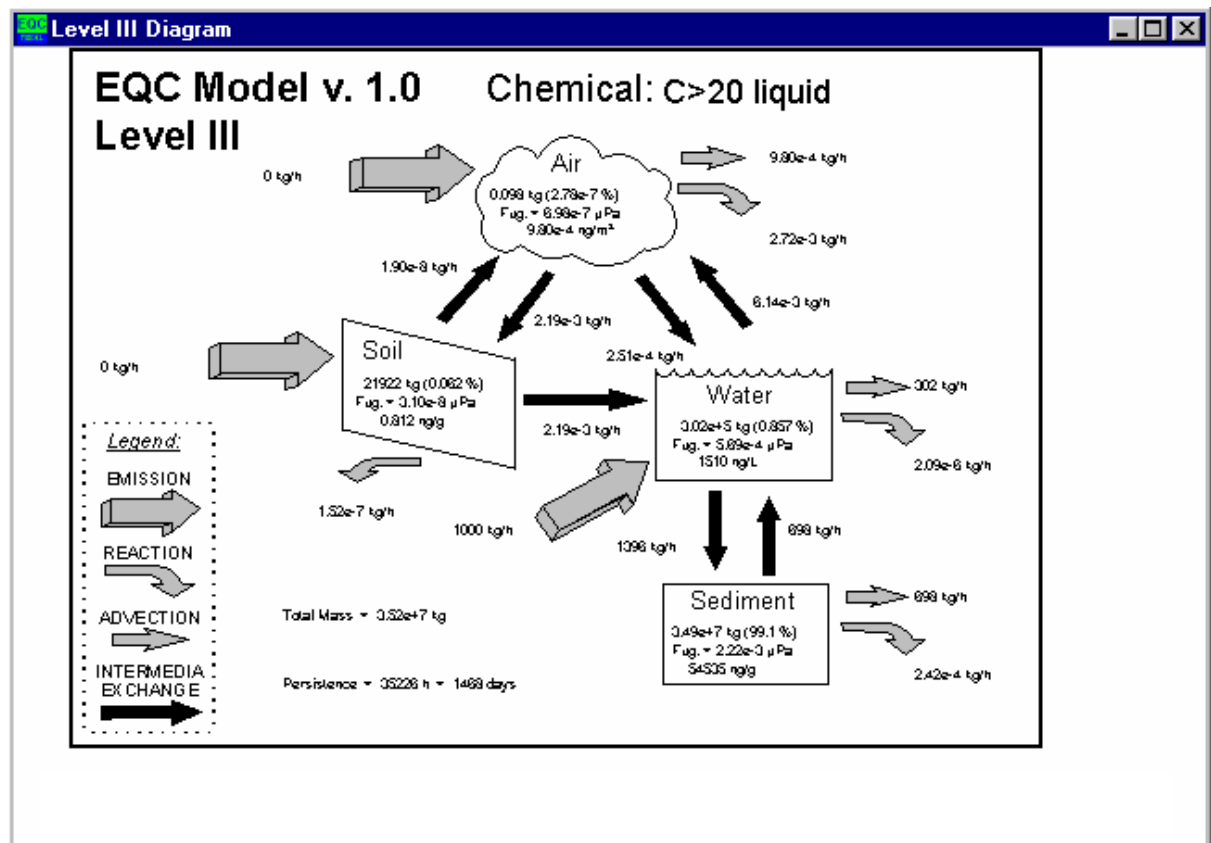
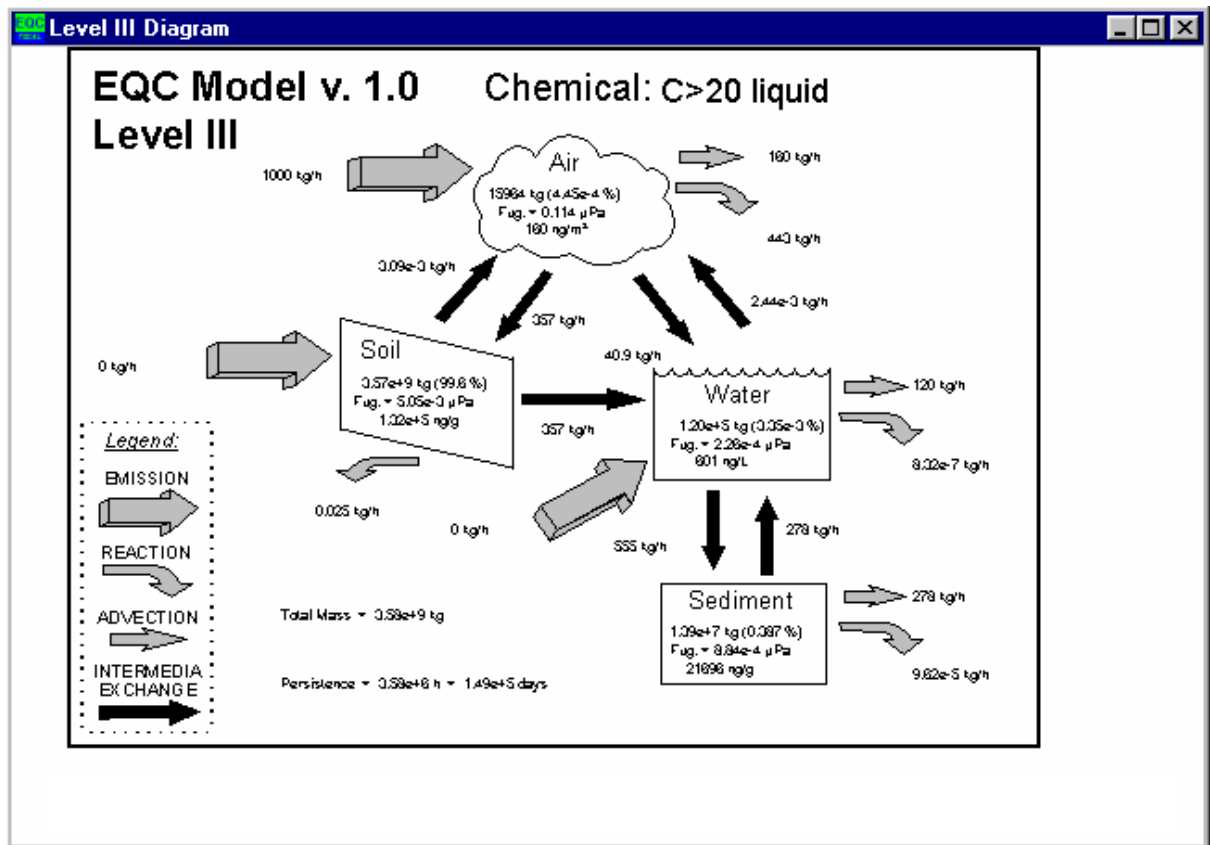
**Table C1 Properties of LCCPs used in fugacity modelling**

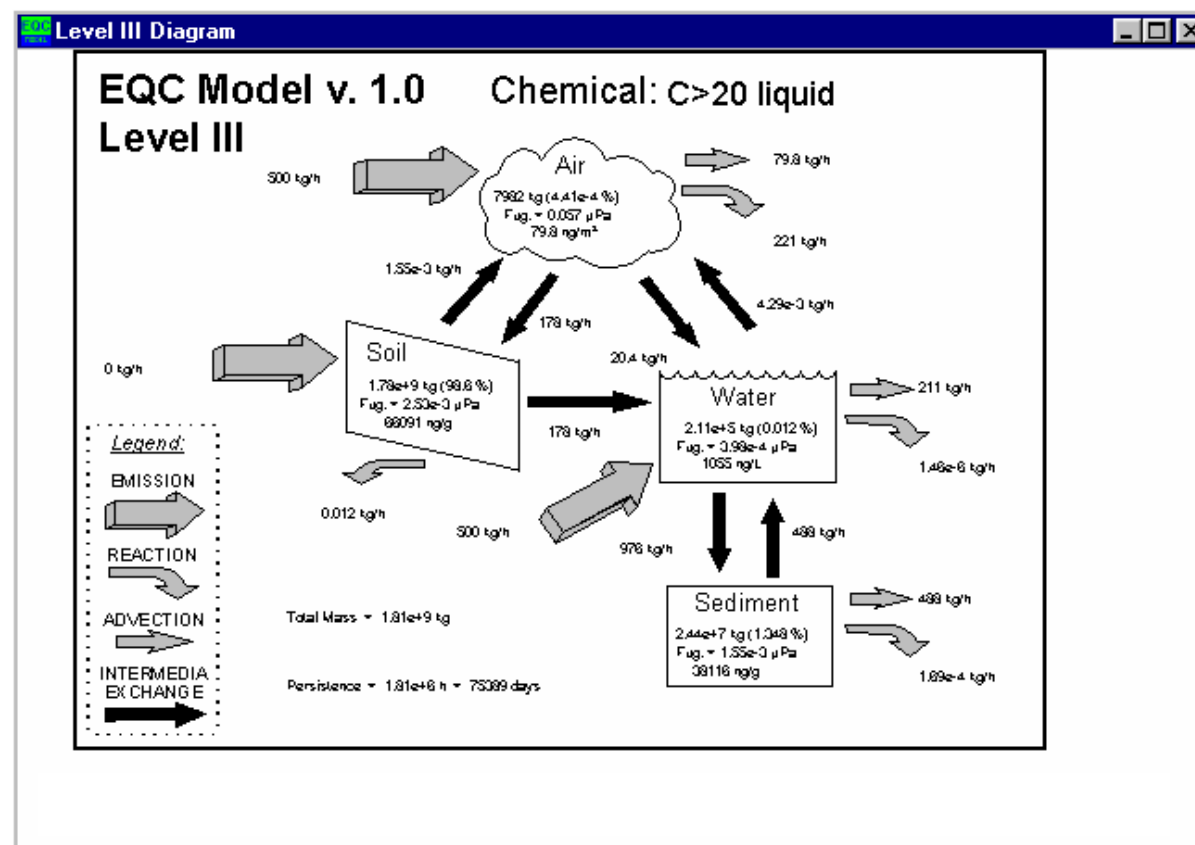
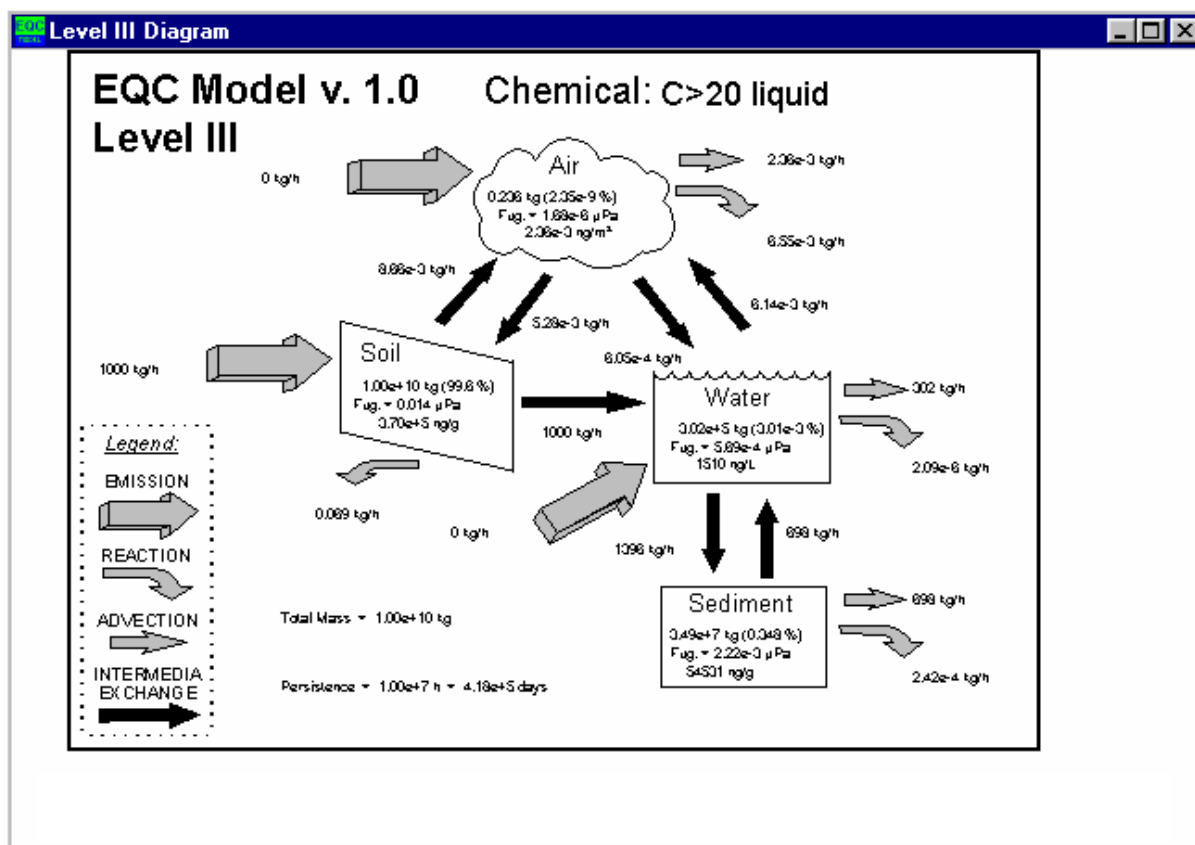
Property	Value		
	<b>C<sub>18-20</sub> liquid chlorinated paraffin</b>	<b>C<sub>&gt;20</sub> liquid chlorinated paraffin</b>	<b>C<sub>&gt;20</sub> solid chlorinated paraffin</b>
Molecular weight	456 g/mole (corresponding to C <sub>19</sub> , 50% wt. Cl)	600 g/mole (corresponding to C <sub>24</sub> , 52% wt. Cl)	960 g/mole (corresponding to C <sub>24</sub> , 70% wt. Cl)
Water solubility	5 µg/l	5 µg/l	5 µg/l
Vapour pressure	2.5×10 <sup>-4</sup> Pa	2.5×10 <sup>-5</sup> Pa	1.5×10 <sup>-14</sup> Pa
Log Kow	9.7	10.3	17
Degradation half-life in air	30 hours	25 hours	110 hours
Degradation half-life in other media	very large (e.g. 1×10 <sup>11</sup> hours)	very large (e.g. 1×10 <sup>11</sup> hours)	very large (e.g. 1×10 <sup>11</sup> hours)

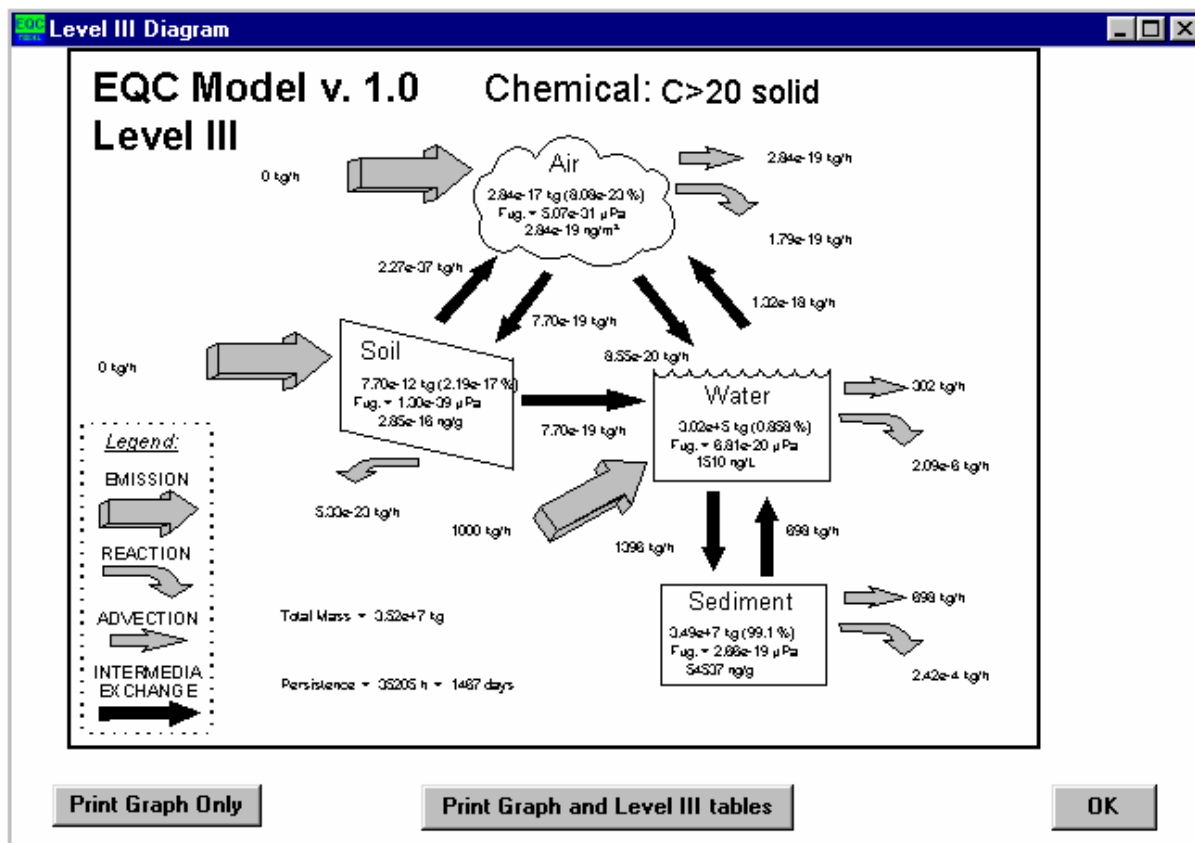
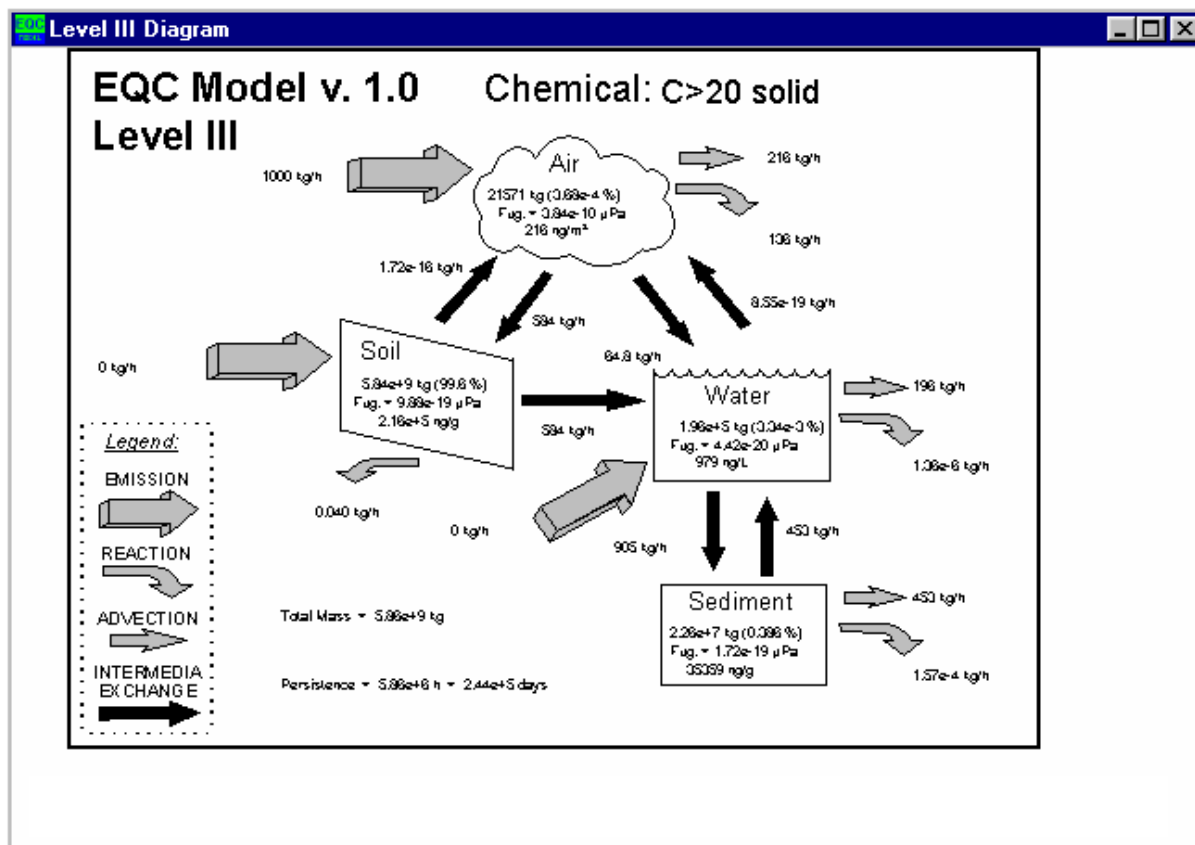
The level III model was run four times for each group of LCCPs, with a nominal release rate of 1,000 kg/hour initially entering the air, soil or water compartments in different proportions. The following diagrams show the predicted environmental distributions.

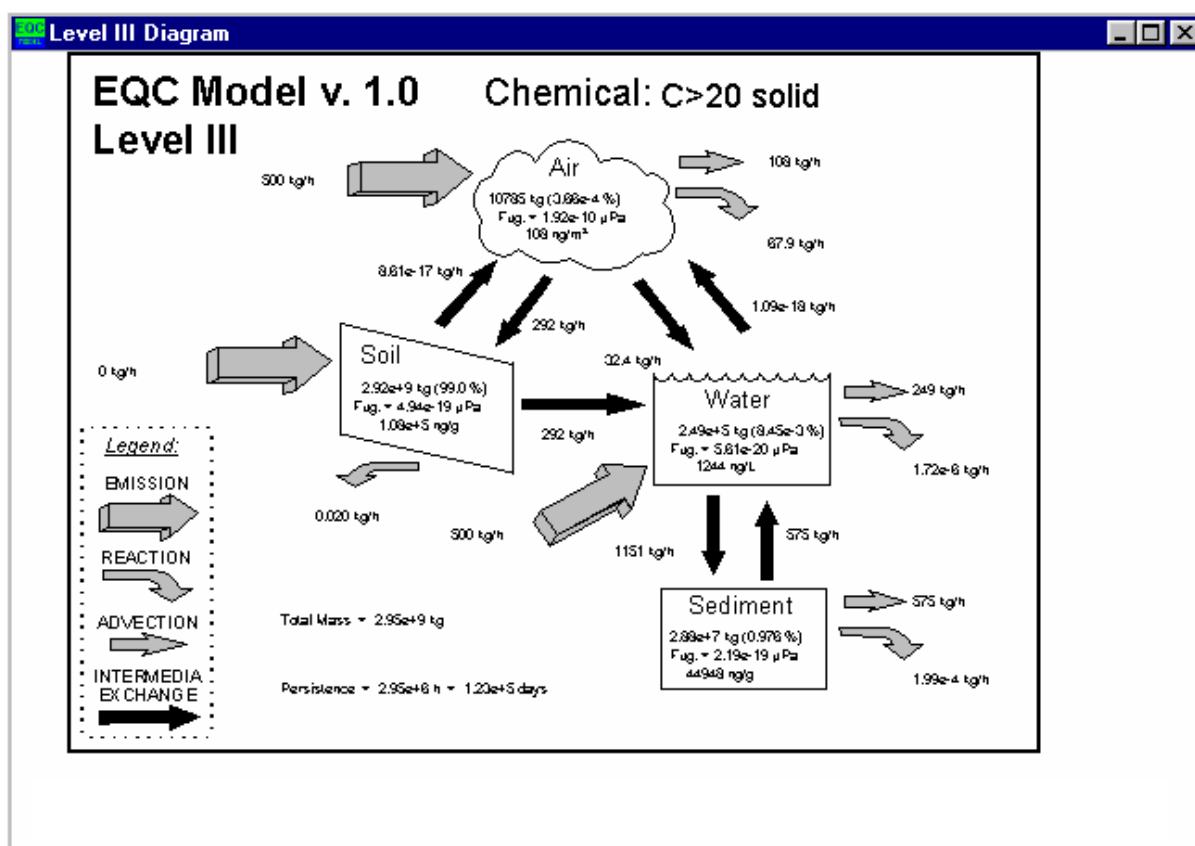
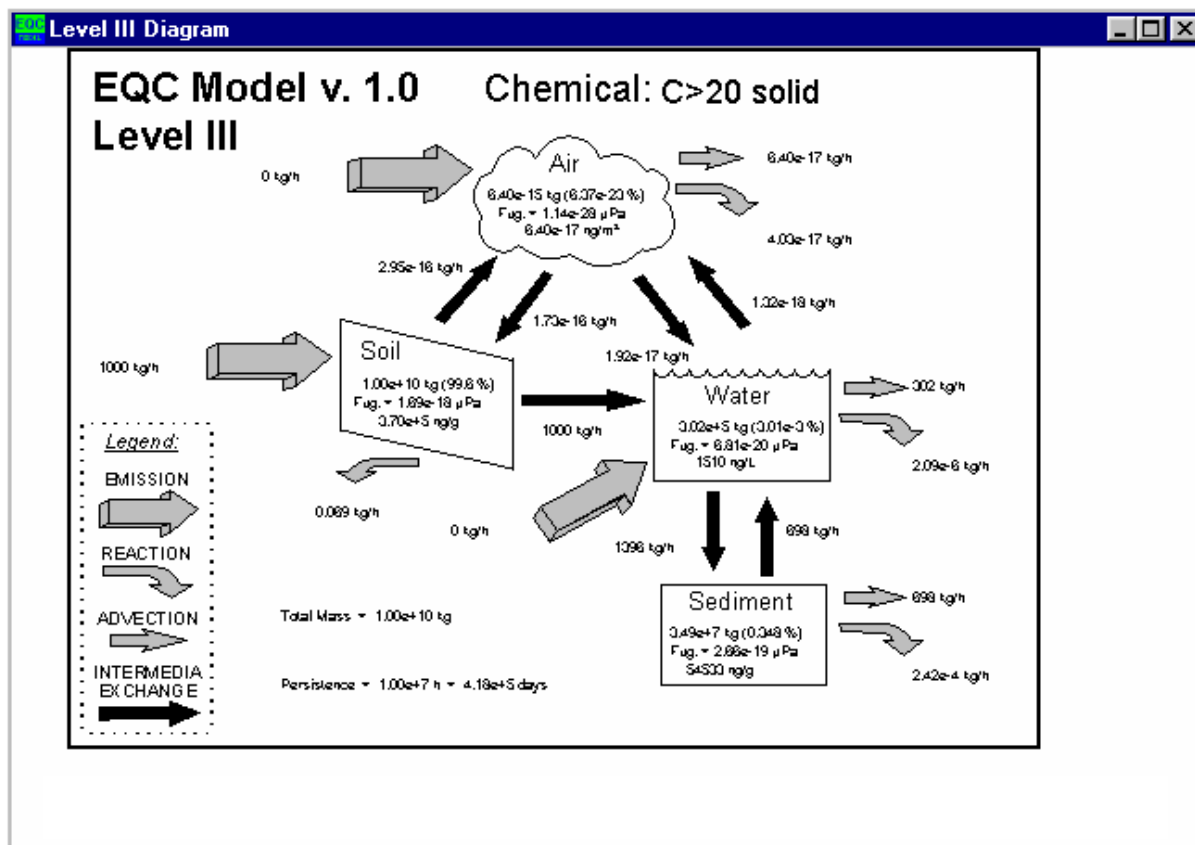














# Appendix D Analytical methods used to determine LCCP in environmental media

Several studies have been undertaken to measure the levels of chlorinated paraffins in water and sediment. However, the analyses are complicated by the fact that there are a wide range of possible chlorinated paraffins (of different carbon chain length, degrees of chlorination and position of the chlorine atoms along the carbon chain) present in any given commercial product. Thus, care has to be taken when comparing the results of one survey with those of another, since different reference compounds may have been used and hence different chemical species may have been measured. The main analytical methods used for determining the concentrations of LCCPs in environmental samples are discussed in the following paragraphs. The methods have been referred to by the author names that appear in the sections on environmental levels in the main part of the report. The results from all the methods used are dependent to some extent on the substance(s) used as reference.

## **Campbell and McConnell, 1980**

This method combines solvent extraction/partition, column chromatography and finally TLC with argentation. Quantitation is by visual comparison of the intensity of the TLC 'spot' with those from standards. The intensity of the spot is chlorine dependent and so, in order to err on the high side of the possible concentration, low chlorine content paraffin e.g. 42–45% wt Cl, is used as reference for calibration. The method is relatively insensitive to chemical structure and can reportedly distinguish between C<sub>10-20</sub> chlorinated paraffins and C<sub>20-30</sub> chlorinated paraffins. This method, therefore, is likely to quantify all LCCPs present in a sample, but may overestimate the concentration, particularly of the C<sub>18-20</sub> chlorinated paraffins, due to interferences with other types of chlorinated paraffin.

## **Murray *et al.*, 1987a and 1987b**

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 LCCPs are 496–506 and 512–517 amu. The commercial product, Paroil 142 (C<sub>20-30</sub>, 40–50% Cl), was used as reference material. This method is reasonably specific for LCCPs with carbon chain lengths >C<sub>20</sub>, but will only identify the components which give rise to ions in the mass spectrometer in the ranges scanned.

## **Jansson *et al.*, 1993**

This method is based on GC-MS with NCI. The method does not appear to distinguish between chlorinated paraffins of different chain length and uses Dechlorane as an internal standard and several unspecified commercial chlorinated paraffin products as reference compounds. The method can probably be considered to give an approximation of the concentration of total (i.e. short-, medium and long-chain length) chlorinated paraffins present in a sample.

### **Environment Agency Japan, 1991**

Very few experimental details are given. The technique is probably based on a GC-MS method, 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.

### **Greenpeace, 1995**

This method uses on-column reduction of the chlorinated paraffin to the parent hydrocarbon, followed by GC-MS quantification of the parent hydrocarbon. A range of alkanes between C<sub>10</sub> and C<sub>24</sub> were used as external standards and an average chlorine content of 50 per cent was assumed for the chlorinated paraffins to allow quantification. This approach may slightly underestimate the chlorinated paraffin concentration if high chlorine content material is present. The method could apparently distinguish between individual chlorinated paraffins with different carbon chain lengths and should unambiguously identify the presence of LCCPs (C<sub>18</sub> to C<sub>24</sub>), provided any interfering n-paraffins are removed from the sample prior to analysis.

### **Rieger and Ballschmiter, 1995**

Sample clean-up using a silica-gel column was employed. The commercial product Hordaflex LC 60 (C<sub>10-13</sub>, 62% Cl) was used as a calibration standard (as only peaks corresponding to C<sub>10-13</sub> chlorinated paraffins were detected). Analysis was carried out using GC-ECD (electron capture detector) and GC-MS with negative chemical ionisation. The following masses were monitored in the analysis for LCCPs: m/z = 494, 496 and 498 (C<sub>18</sub>H<sub>31</sub>Cl<sub>7</sub>); 508, 510 and 512 (C<sub>19</sub>H<sub>33</sub>Cl<sub>7</sub>). The method is similar to that used by Murray *et al.* (1987a and b).

### **van Zeijl, 1997**

The chlorinated paraffin-containing extracts were fractionated using high performance liquid chromatography (HPLC) with gel permeation columns. The analysis was then carried out on the chlorinated paraffin fractions using GC-MS with electron capture negative ionisation. The following negative ion clusters were monitored in the analyses: m/z -35 and -37 (corresponding to Cl<sup>-</sup>); m/z -70 and -72 (corresponding to Cl<sub>2</sub><sup>-</sup>) and m/z -71 and -73 (corresponding to HCl<sub>2</sub><sup>-</sup>). There are few details of the compounds used for analytical standards. A range of technical products appears to have been studied and the product whose mass spectra resembled that of the sample most closely appears to have been used for quantification. This substance appears to have been a C<sub>22-26</sub>, 42% wt. Cl product as the majority of the chlorinated paraffins found were thought to be LCCPs. The report indicates that the choice of the reference compound was important as the detector responses were found to vary by about one order of magnitude between the various products studies.

### **Rotard, 1998 and Kemmlein, 2002**

The analysis was carried out by dechlorination of the chlorinated paraffins in the injector of the gas chromatograph (the injector contained a palladium catalyst and a mixture of hydrogen and helium was used as carrier gas), followed by analysis of the n-paraffins formed by mass-spectrometry detector. Quantification was achieved using n-alkane standards from C<sub>10</sub> to C<sub>29</sub>. A 50 per cent chlorine content was assumed to convert the n-alkane concentrations measured to a concentration of chlorinated paraffin.

The samples were extracted using n-hexane. After removal of lipids (where appropriate), the extracts were concentrated and chromatographed over superactive basic aluminium oxide with cyclopentane and then cyclopentane/ethylformate (3:7

mixture). The second fraction was collected, concentrated and subject to analysis. It is not clear if the sample clean-up method used removed potential interferences from n-alkanes prior to the analysis.

### **Froescheis, 1997**

Few details of the method used are currently available.

### **Summary**

As can be seen from the above discussion, there are potential problems with all the methods used. Most of the methods are likely to provide a rough estimate of the concentration of LCCP, although some methods may not detect all the LCCPs present in a sample. The choice of the standard/reference compound used for quantification is important in these analysis, because if the composition of the reference compound is significantly different from that of the substance in the environment, then substantial errors could be introduced into the analysis and mis-identification of the type of chlorinated paraffin present could occur. Thus the analytical methods should all be treated as giving only approximate concentrations in environmental samples.

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# Appendix E Effects of uncertainty in the physico-chemical properties, degradation rate and emissions on the modelling of LCCPs

## E1 Physico-chemical properties

LCCPs are complex mixtures. This presents some problems over the values of physico-chemical properties to be chosen for the environmental modelling of these substances. In order to simplify the environmental modelling in the main risk assessment report, a set of physical and chemical properties were chosen as being representative of each of the three main groups of LCCPs.

However, for the majority of the physico-chemical properties relevant for the environmental modelling, a range of values has been determined, representing the complex nature of the products. This appendix considers the effect that varying some of the key physico-chemical properties (within the range measured) has on the predicted environmental concentration. In order to do this simply, the EUSES model was run several times using the release estimates for one hypothetical local scenario (Paints – formulation – default calculation); this scenario was chosen as an example because it had releases to both air and waste water, and is a relevant scenario for each of the three main groups of LCCPs considered. The model was also run for the total regional and continental releases.

Note: this analysis has been carried out using EUSES 1.0 and an earlier estimate for the local, the regional and continental release (based on usage information from 1999). The results are not, therefore, comparable with the regional and continental releases currently used in the main risk assessment).

The physico-chemical properties for LCCPs are discussed in Chapter 1 of the main risk assessment report. The values used in the main report as input data for the various example calculations are shown in Table E1. The values chosen reflect the range of values measured or estimated for LCCPs.

For this exercise most of the necessary partition coefficients – the organic carbon-water partition coefficient ( $K_{oc}$ ), the bioconcentration factors for fish, and the accumulation factor earthworms – were estimated from the log  $K_{ow}$  using the default methods in EUSES 1.0. All calculations assumed that 93 per cent of LCCPs were removed from the waste water treatment plant due to adsorption onto sewage sludge. Table E2 gives the resulting PECs from this approach.

Table E3 outlines the PEC/PNEC ratios obtained for surface water, sediment, soil and secondary poisoning, using the various physico-chemical properties. For the soil and sediment endpoints, both the PEC and PNEC depend on the value used for the organic carbon-water partition coefficient, and hence log  $K_{ow}$ . It should be noted that for this analysis the PNEC in water was set to 0.29  $\mu\text{g/l}$  for all three types of LCCPs and the PNEC for secondary was set to 0.5 mg/kg food, 100 mg/kg food and 600

mg/kg food for  $C_{18-20}$ ,  $C_{>20 \text{ liquid}}$  and  $C_{>20 \text{ solid}}$  LCCPs, respectively (this reflects the PNECs in an earlier draft of the assessment).

**Table E1 Input data for EUSES model for the various scenarios considered**

Model Input	Value used in EUSES calculation														
	Main assessment			A			B			C			D		
	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
Molecular weight (g/mole)	500	600	960	500	600	960	500	600	960	500	600	960	500	600	960
Water solubility (µg/l)	5	5	5	5	5	5	0.5	0.5	0.5	0.05	0.05	0.05	0.005	0.005	0.005
Vapour pressure (Pa)	2.5 × 10 <sup>-4</sup>	2.5 × 10 <sup>-5</sup>	1.5 × 10 <sup>-14</sup>	5 × 10 <sup>-4</sup>	5 × 10 <sup>-5</sup>	5 × 10 <sup>-14</sup>	5 × 10 <sup>-5</sup>	5 × 10 <sup>-7</sup>	5 × 10 <sup>-16</sup>	5 × 10 <sup>-6</sup>	5 × 10 <sup>-9</sup>	5 × 10 <sup>-18</sup>	5 × 10 <sup>-7</sup>	5 × 10 <sup>-11</sup>	5 × 10 <sup>-20</sup>
Henrys Law constant (Pa.m <sup>3</sup> .mole <sup>-1</sup> )	16	15	1 × 10 <sup>-6</sup>	200	200	1 × 10 <sup>-5</sup>	1	1	1 × 10 <sup>-7</sup>	0.1	0.1	1 × 10 <sup>-8</sup>	0.01	0.01	1 × 10 <sup>-9</sup>
Log Kow	9.7	10.3	17	7.5	7.5	14	8.5	8.5	15	10.5	9.5	18	11.5	12	19
Koc <sup>a</sup> (l/kg)	9.06 × 10 <sup>7</sup>	2.77 × 10 <sup>8</sup>	>1 × 10 <sup>10</sup>	1.5 × 10 <sup>6</sup>	1.5 × 10 <sup>6</sup>	2.8 × 10 <sup>11</sup>	9.7 × 10 <sup>6</sup>	9.7 × 10 <sup>6</sup>	1.8 × 10 <sup>12</sup>	4.0 × 10 <sup>8</sup>	6.2 × 10 <sup>7</sup>	4.8 × 10 <sup>14</sup>	2.6 × 10 <sup>9</sup>	6.6 × 10 <sup>9</sup>	>3.1 × 10 <sup>15</sup>
Fish BCF <sup>a</sup> (l/kg)	1,096	192	<1	3.80 × 10 <sup>4</sup>	3.80 × 10 <sup>4</sup>	<1	1.32 × 10 <sup>4</sup>	1.32 × 10 <sup>4</sup>	<1	100	1,820	<1	2.2	<1	<1
PNEC <sub>water</sub> (µg/l)	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29
PNEC <sub>sediment</sub> (mg/kg wet wt.) <sup>b</sup>	572	1,748	63,043	9.5	9.5	1.7 × 10 <sup>6</sup>	61.2	61.2	1.1 × 10 <sup>7</sup>	2,523	392	3.0 × 10 <sup>9</sup>	16,391	41,609	>1 × 10 <sup>10</sup>
PNEC <sub>soil</sub> (mg/kg wet wt.) <sup>b</sup>	464	1,418	51,176	7.5	7.5	1.4 × 10 <sup>6</sup>	49.7	49.7	9.3 × 10 <sup>6</sup>	2,046	318	2.5 × 10 <sup>9</sup>	13,304	33,776	>1 × 10 <sup>10</sup>
PNEC <sub>secondary poisoning</sub> (mg/kg food)	0.5	100	600	0.5	100	600	0.5	100	600	0.5	100	600	0.5	100	600

Note <sup>a</sup> Koc and BCF estimated from log Kow.

<sup>b</sup> PNECs for sediment and soil calculated by the equilibrium partitioning method – dependent on Koc value.

**Table E2 Resulting concentrations for the various scenarios considered**

Endpoint	Value estimated in EUSES calculation														
	Main assessment			A			B			C			D		
	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
<b>Local concentrations (Paint – formulation site)</b>															
Surface water (µg/l)	3.1 ×10 <sup>-3</sup>	1.7 ×10 <sup>-3</sup>	5.0 ×10 <sup>-5</sup>	0.12	0.15	1.8 ×10 <sup>-6</sup>	0.028	0.046	2.8 ×10 <sup>-7</sup>	7.2 ×10 <sup>-4</sup>	7.5 ×10 <sup>-3</sup>	1.0 ×10 <sup>-9</sup>	1.1 ×10 <sup>-4</sup>	7.1 ×10 <sup>-5</sup>	1.6 ×10 <sup>-10</sup>
Sediment (mg/kg wet wt.)	6.2	10.2	10.8	4.0	4.8	10.8	5.9	9.8	10.8	6.3	10.2	10.8	6.3	10.2	10.8
Agricultural soil (mg/kg wet wt.)	2.1	2.1	3.6	1.9	2.2	3.6	2.4	2.2	3.6	2.6	2.1	3.6	2.6	2.1	3.6
Air (during emission episode) (mg/m <sup>3</sup> )	1.0 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	2.1 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	2.1 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	2.1 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	2.1 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	1.0 ×10 <sup>-5</sup>	2.1 ×10 <sup>-5</sup>
Fish (for secondary poisoning) (mg/kg wet wt.)	1.6 ×10 <sup>-3</sup>	2.2 ×10 <sup>-4</sup>	2.0 ×10 <sup>-8</sup>	2.0	3.0	7.5 ×10 <sup>-10</sup>	0.18	0.42	1.2 ×10 <sup>-10</sup>	1.6 ×10 <sup>-4</sup>	9.3 ×10 <sup>-3</sup>	4.3 ×10 <sup>-13</sup>	1.2 ×10 <sup>-7</sup>	4.8 ×10 <sup>-8</sup>	6.7 ×10 <sup>-14</sup>
Earthworms (for secondary poisoning) (mg/kg wet wt.)	0.13	0.19	0.0013	5.0	11.8	4.9 ×10 <sup>-5</sup>	1.3	5.3	7.6 ×10 <sup>-6</sup>	0.034	0.77	2.8 ×10 <sup>-8</sup>	5.4 ×10 <sup>-3</sup>	0.0078	4.3 ×10 <sup>-9</sup>
<b>Predicted regional concentrations</b>															
Surface water (µg/l)	3.1 ×10 <sup>-4</sup>	7.7 ×10 <sup>-4</sup>	6.3 ×10 <sup>-7</sup>	0.0035	0.030	2.3 ×10 <sup>-8</sup>	0.0031	0.022	3.5 ×10 <sup>-9</sup>	8.1 ×10 <sup>-5</sup>	0.0034	1.3 ×10 <sup>-11</sup>	1.3 ×10 <sup>-5</sup>	3.2 ×10 <sup>-5</sup>	2.0 ×10 <sup>-12</sup>
Sediment (mg/kg wet wt.)	1.1	8.2	0.24	0.20	1.7	0.24	1.2	8.0	0.24	1.3	8.2	0.24	1.3	8.3	0.24
Agricultural soil (mg/kg wet wt.)	1.1	12.2	0.15	0.21	2.7	0.15	1.2	12.1	0.15	1.3	12.2	0.15	1.3	12.3	0.15
Air (mg/m <sup>3</sup> )	3.6 ×10 <sup>-7</sup>	1.2 ×10 <sup>-7</sup>	6.2 ×10 <sup>-10</sup>	6.8 ×10 <sup>-7</sup>	2.2 ×10 <sup>-6</sup>	6.2 ×10 <sup>-10</sup>	3.3 ×10 <sup>-7</sup>	1.3 ×10 <sup>-7</sup>	6.2 ×10 <sup>-10</sup>	3.0 ×10 <sup>-7</sup>	1.1 ×10 <sup>-7</sup>	6.2 ×10 <sup>-10</sup>	3.0 ×10 <sup>-7</sup>	1.1 ×10 <sup>-7</sup>	6.2 ×10 <sup>-10</sup>



**Table E3 Resulting PEC/PNEC ratios for the various scenarios considered**

Endpoint	PEC/PNEC ratio														
	Main assessment			A			B			C			D		
	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
<b>Local concentrations (Paints– formulation site)</b>															
Surface water (µg/l)	0.010	5.9× 10 <sup>-3</sup>	1.7 ×10 <sup>-4</sup>	0.41	0.51	6.2× 10 <sup>-6</sup>	0.096	0.16	9.7× 10 <sup>-7</sup>	2.5× 10 <sup>-3</sup>	0.026	3.4× 10 <sup>-9</sup>	3.8× 10 <sup>-4</sup>	2.4× 10 <sup>-4</sup>	5.5× 10 <sup>-10</sup>
Sediment (mg/kg wet wt.)	0.10	0.058	1.7× 10 <sup>-3</sup>	4.1	5.1	6.2× 10 <sup>-5</sup>	0.96	1.6	9.8× 10 <sup>-6</sup>	0.025	0.26	3.6× 10 <sup>-8</sup>	3.8× 10 <sup>-3</sup>	2.5× 10 <sup>-3</sup>	<1.1× 10 <sup>-8</sup>
Agricultural soil (30 days average) (mg/kg wet wt.)	0.045	0.015	7.0× 10 <sup>-4</sup>	2.5	2.5	2.6× 10 <sup>-5</sup>	0.48	0.44	3.9× 10 <sup>-6</sup>	0.013	0.066	1.4× 10 <sup>-8</sup>	2.0× 10 <sup>-3</sup>	6.2× 10 <sup>-4</sup>	<3.6× 10 <sup>-9</sup>
Fish (for secondary poisoning) (mg/kg wet wt.)	3.2× 10 <sup>-3</sup>	2.2× 10 <sup>-6</sup>	3.3× 10 <sup>-11</sup>	4.0	0.030	1.3× 10 <sup>-12</sup>	0.36	4.2× 10 <sup>-3</sup>	2.0× 10 <sup>-13</sup>	3.2× 10 <sup>-4</sup>	9.3× 10 <sup>-5</sup>	7.2× 10 <sup>-16</sup>	2.4× 10 <sup>-7</sup>	4.8× 10 <sup>-10</sup>	1.1× 10 <sup>-16</sup>
Earthworms (for secondary poisoning) (mg/kg wet wt.)	0.26	1.9× 10 <sup>-3</sup>	2.2× 10 <sup>-6</sup>	10.0	0.12	8.2× 10 <sup>-8</sup>	2.6	0.0530	1.3× 10 <sup>-8</sup>	0.068	7.7× 10 <sup>-3</sup>	4.7× 10 <sup>-11</sup>	0.011	7.8× 10 <sup>-5</sup>	7.2× 10 <sup>-12</sup>
<b>Predicted regional concentrations</b>															
Surface water (µg/l)	1.1× 10 <sup>-3</sup>	2.7× 10 <sup>-3</sup>	2.1× 10 <sup>-6</sup>	0.012	0.10	7.9× 10 <sup>-8</sup>	0.011	0.076	1.2× 10 <sup>-8</sup>	2.8× 10 <sup>-4</sup>	0.012	4.5× 10 <sup>-11</sup>	4.5× 10 <sup>-5</sup>	1.1× 10 <sup>-4</sup>	6.9× 10 <sup>-12</sup>
Sediment (mg/kg wet wt.)	0.019	0.047	3.8× 10 <sup>-5</sup>	0.21	1.8	1.4× 10 <sup>-6</sup>	0.20	1.3	2.2× 10 <sup>-7</sup>	5.1× 10 <sup>-3</sup>	0.21	8.0× 10 <sup>-10</sup>	7.9× 10 <sup>-4</sup>	2.0× 10 <sup>-3</sup>	<2.4× 10 <sup>-10</sup>
Agricultural soil (mg/kg wet wt.)	0.024	0.086	2.9× 10 <sup>-5</sup>	0.28	3.6	1.1× 10 <sup>-6</sup>	0.24	2.4	1.6× 10 <sup>-7</sup>	6.4× 10 <sup>-3</sup>	0.38	6.0× 10 <sup>-10</sup>	9.8× 10 <sup>-4</sup>	3.6× 10 <sup>-3</sup>	<1.5× 10 <sup>-10</sup>

The shaded areas in Table E3 indicate where a change in the conclusions of the main report would occur (i.e. a change of PEC/PNEC ratio from <1 to >1) as a result of choosing different values for the physico-chemical properties.

For surface water, the local PECs vary markedly with the log Kow value, and hence Koc value. The PEC reduces as the Koc value increases due to the increased adsorption of the substance onto suspended sediment. However, the PEC/PNEC ratios are all <1 in the examples seen; the same conclusion would be reached whichever log Kow value was used.

For sediment and soil, the actual PECs are relatively insensitive to the value of the physico-chemical properties used (Table E2), varying only by a factor of two in the local calculations. However, the results of the analysis show that the PNEC, and hence PEC/PNEC ratio is highly dependant on the log Kow value (and hence Koc value).

The PNEC for soil and sediment assumes that the toxicity through the soil or sediment pore water can be described adequately by the available aquatic toxicity data. The resulting PEC/PNEC ratio is increased by a factor of 10 to take into account the possibility of direct ingestion of the sediment. The uncertainty for sediment and soil appears to lie on the PNEC side of the risk characterisation, rather than the estimation of physico-chemical properties. Actual sediment toxicity data for C<sub>18-20</sub> liquid and C<sub>>20</sub> liquid chlorinated paraffins may be needed before this uncertainty can be removed.

For air, the local concentrations predicted are very insensitive to the values of the physico-chemical properties chosen. The regional air concentrations show some variation, but have a similar magnitude in all of the example calculations.

For secondary poisoning, the PECs and hence PEC/PNEC ratios vary markedly with the log Kow value. This is because the fish and earthworm bioconcentration factors that are used in the secondary poisoning calculations are estimated from log Kow. No reliable bioconcentration factors are currently available for LCCPs.

## **E2 Degradation rate**

Since LCCPs are not readily biodegradable, the appropriate default rate constants for degradation in surface water ( $6.93 \times 10^{-7} \text{ day}^{-1}$ ), soil ( $6.93 \times 10^{-7} \text{ day}^{-1}$ ) and sediment ( $6.93 \times 10^{-8} \text{ day}^{-1}$ ) were used in the EUSES modelling in the main report. These correspond to degradation half-lives of the order of 2,740 years in soil and surface water, and 27,400 years in bulk sediment.

There is some experimental evidence that LCCPs may undergo biodegradation in the environment but it is not possible to derive appropriate degradation rate constants from this data. However it is likely that LCCPs are less persistent in the environment than is indicated by these default degradation half-lives. Therefore the sensitivity of the calculations to these degradation rates was investigated.

In this analysis the physico-chemical properties used were those outlined in the main report and the regional releases were taken to be the following values (from an earlier draft of the risk assessment report):

	C <sub>18-20</sub> , liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
Air	8,945 kg/year	3,491 kg/year	14.6 kg/year
Surface water (via wwtp)	1,405 kg/year	18,165 kg/year	221kg/year
Surface water (direct)	2,074 kg/year	17,550 kg/year	46 kg/year
Industrial/urban soil	4,343 kg/year	29,412 kg/year	1,10kg/year

The EUSES model was run several times with different values for the degradation rate constants. The results are shown in Table E4.

As can be seen from the data presented in Table E4, the regional soil concentration is particularly sensitive to the value of the chosen degradation rate.

**Table E4** Effects of varying the biodegradation half-life on predicted regional concentrations

Biodegradation rate constant		Half-life		PEC <sub>regional</sub>											
Surface water, soil	Bulk sediment	Surface water, soil	Bulk sediment	Surface water (µg/l)			Sediment (mg/kg wet wt.)			Agricultural soil (mg/kg wet wt.)			Urban/industrial soil (mg/kg wet wt.)		
				C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
6.93 × 10 <sup>-7</sup>	6.93 × 10 <sup>-8</sup>	2,740 years	27,400 years	2.95 × 10 <sup>-4</sup>	7.24 × 10 <sup>-4</sup>	5.8 × 10 <sup>-7</sup>	1.03	7.72	0.223	1.00	11.5	0.14	15.3	101	3.8
6.93 × 10 <sup>-6</sup>	6.93 × 10 <sup>-7</sup>	274 years	2,740 years	1.54 × 10 <sup>-4</sup>	4.00 × 10 <sup>-4</sup>	3.1 × 10 <sup>-7</sup>	0.54	4.26	0.117	0.15	1.73	0.021	4.22	27.7	1.03
6.93 × 10 <sup>-5</sup>	6.93 × 10 <sup>-6</sup>	27.4 years	274 years	1.09 × 10 <sup>-4</sup>	3.03 × 10 <sup>-4</sup>	2.2 × 10 <sup>-7</sup>	0.38	3.22	0.083	0.016	0.183	2.2 × 10 <sup>-3</sup>	0.511	3.35	0.125
6.93 × 10 <sup>-4</sup>	6.93 × 10 <sup>-5</sup>	2.74 years	27.4 years	8.97 × 10 <sup>-5</sup>	2.52 × 10 <sup>-4</sup>	1.8 × 10 <sup>-7</sup>	0.304	2.61	0.066	0.0016	0.018	2.2 × 10 <sup>-4</sup>	0.052	0.342	0.013
1.90 × 10 <sup>-3</sup>	1.90 × 10 <sup>-4</sup>	1 year	10 years	7.18 × 10 <sup>-5</sup>	2.02 × 10 <sup>-4</sup>	1.4 × 10 <sup>-7</sup>	0.23	2.00	0.051	5.87 × 10 <sup>-4</sup>	6.7 × 10 <sup>-3</sup>	8.1 × 10 <sup>-5</sup>	0.019	0.125	4.7 × 10 <sup>-3</sup>
6.93 × 10 <sup>-3</sup>	6.93 × 10 <sup>-3</sup>	100 days	2.74 years	4.32 × 10 <sup>-5</sup>	1.21 × 10 <sup>-4</sup>	8.5 × 10 <sup>-8</sup>	0.118	1.01	0.026	1.61 × 10 <sup>-4</sup>	1.8 × 10 <sup>-3</sup>	2.2 × 10 <sup>-5</sup>	5.2 × 10 <sup>-3</sup>	0.034	1.3 × 10 <sup>-3</sup>
0.0139	1.93 × 10 <sup>-3</sup>	50 days	1.37 years	3.11 × 10 <sup>-5</sup>	8.73 × 10 <sup>-5</sup>	6.1 × 10 <sup>-8</sup>	0.070	0.597	0.015	8.02 × 10 <sup>-5</sup>	9.15 × 10 <sup>-4</sup>	1.1 × 10 <sup>-5</sup>	2.6 × 10 <sup>-3</sup>	0.017	6.4 × 10 <sup>-4</sup>
0.0231	2.31 × 10 <sup>-3</sup>	30 days	300 days	2.48 × 10 <sup>-5</sup>	6.96 × 10 <sup>-5</sup>	4.9 × 10 <sup>-8</sup>	0.045	0.386	0.0098	4.83 × 10 <sup>-5</sup>	5.51 × 10 <sup>-4</sup>	6.7 × 10 <sup>-6</sup>	1.6 × 10 <sup>-3</sup>	0.010	3.8 × 10 <sup>-4</sup>

# Appendix F Estimation of waste remaining in the environment and further consideration of diffusive emissions from articles

## F1 Introduction

This appendix considers an alternative approach to that given in the main risk assessment report to estimate the possible diffusive emissions of LCCPs from products over their lifetimes. The basis of the approach taken here is outlined in the November 1999 and May 2000 draft EU Risk Assessment Reports for di-(2-ethylhexyl) phthalate (DEHP), for which Sweden is the rapporteur country. The method was used in the 2005 final EU Risk Assessment Report for medium-chain chlorinated paraffins for which the United Kingdom is the rapporteur country. The approach considers both losses of the substance itself over the lifetime of products containing the substance and also the production of any waste containing the substance that may be released to the environment over the lifecycle. The approach is relatively crude but may provide "order of magnitude" estimates for the releases of LCCPs. No specific guidance is currently given in the Technical Guidance Document (TGD) for estimating these types of releases, but it is understood that an approach similar to that taken here will be incorporated into a future revision of the TGD.

DEHP is the major plasticiser used in PVC, and accounts for around 51 per cent of the total phthalate plasticiser in use. In some calculations in this appendix it is assumed that the use pattern of PVC containing LCCPs is similar to that of PVC containing DEHP. This assumption is reasonable as LCCPs in PVC are mainly used as secondary plasticisers alongside the primary plasticisers (phthalates such as DEHP).

The relative market share of PVC containing LCCPs is needed before the data given in the DEHP report can be used. This value can be estimated roughly from key data (the information on DEHP is taken from the May 2000 draft of the risk assessment for that substance), especially:

- quantity of DEHP used in PVC (and other polymers) in the EU is 462,000 tonnes/year;
- typical DEHP content of PVC = 30 per cent;
- estimated quantity of PVC containing DEHP produced in the EU is given as  $1.54 \times 10^6$  tonnes/year.

As DEHP accounts for around 51 per cent of the phthalate plasticiser usage in PVC, the total amount of phthalate-plasticised PVC produced in the EU can be estimated at approximately  $3 \times 10^6$  tonnes/year.

Based on an estimate of the amount of PVC containing LCCPs produced in the EU, LCCPs could be present in around 0.11–0.17 per cent ( $C_{18-20}$  liquid) of the total plasticised PVC produced in the EU. A figure of 0.17 per cent for  $C_{18-20}$  liquid chlorinated paraffins will be considered in the following sections as a worst case.

As indicated in the main report, C<sub>18-20</sub> liquid chlorinated paraffins are the main type of LCCP currently used in PVC. However, it is known that relatively small amounts of C<sub>>20</sub> liquid chlorinated paraffins have been used in PVC applications in the recent past and so PVC containing this type of LCCP is still likely to be in service in the EU. Therefore it is appropriate to also consider the emissions of this type of chlorinated paraffin from PVC in use.

The estimated emissions for the C<sub>>20</sub> liquid chlorinated paraffins given in the following sections are based on an assumption that they were present in a maximum of around 0.008 per cent of the total PVC manufactured in the EU in the late 1990s.

In the draft DEHP risk assessment, the uses of flexible PVC were split between indoor and outdoor uses, with 78 per cent of the flexible PVC used in indoor applications and 22 per cent used in outdoor applications. This split will also be assumed to be applicable for PVC containing LCCPs here.

It should be noted that the actual amounts of LCCPs used in the various PVC applications considered are much less well defined than is the case for DEHP. The assumptions made about the amounts and use of LCCPs in these applications introduce further uncertainty into the emissions estimated.

## **F2 Estimated emissions from volatilisation from PVC**

In the EU Risk Assessment Report for medium-chain chlorinated paraffins, an emission figure to air for medium-chain chlorinated paraffins of  $5 \times 10^{-4}$  µg/m<sup>2</sup>/s was determined for volatilisation from PVC over 21 days. Assuming this emission rate remains constant with time, this emission figure is equivalent to 15.8 mg/m<sup>2</sup>/year. The equivalent emission figure derived for DEHP in the draft Risk Assessment of that substance was 9.5 mg/m<sup>2</sup>/year. No equivalent data are available for LCCPs.

However, in the main risk assessment report it was indicated that the C<sub>18-20</sub> liquid chlorinated paraffins were around 2.5 times less volatile than DEHP (which is itself slightly less volatile than some medium-chain chlorinated paraffins); an estimated emission figure of 3.8 mg/m<sup>2</sup>/year will be used for the C<sub>18-20</sub> liquid chlorinated paraffins. The equivalent assumption made for the C<sub>>20</sub> liquid chlorinated paraffins is that they are five times less volatile than DEHP, giving an emission factor of 1.9 mg/m<sup>2</sup>/year.

This factor is used here to estimate releases to the environment taking into account the surface area of products in a similar way to that carried out for DEHP, from which much of the available emission data was originally derived.

### **F2.1 Indoor applications**

#### *F2.1.1 PVC flooring*

In the draft DEHP risk assessment, the total annual production of PVC flooring in the EU was taken as  $2.3 \times 10^8$  m<sup>2</sup>/year, with a lifetime of 20 years. If it is assumed that C<sub>18-20</sub> liquid chlorinated paraffins are present in 0.17 per cent of the flooring, the amount of flooring containing C<sub>18-20</sub> liquid chlorinated paraffins produced in the EU is  $3.9 \times 10^5$  m<sup>2</sup>/year and the total amount present in the EU is  $7.8 \times 10^6$  m<sup>2</sup> assuming a 20 year life-span.

Using the emission factor estimated above for on the total area of flooring estimated to contain C<sub>18-20</sub> liquid chlorinated paraffins present in the EU gives an estimated air emission of 30 kg/year of C<sub>18-20</sub> liquid chlorinated paraffins from this source (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 0.70 kg/year).

It is thought that around 50–60 per cent of cushion vinyl flooring is coated with polyurethane in order to improve the wear resistance and stain resistance of the product. This coating will obviously affect the potential for volatilisation of LCCPs from the product but no information is available on this. Assuming such a coating reduces the emissions by a factor of 10 and is applied to 50 per cent of flooring, then the estimated emissions would be reduced to 17 kg/year for C<sub>18–20</sub> liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 0.39 kg/year).

#### *F2.1.2 Vinyl wall covering*

In the draft DEHP risk assessment the total annual production of vinyl wall covering in the EU was taken as  $4 \times 10^8$  m<sup>2</sup>/year, with a lifetime of seven years. The total amount of vinyl wall covering present in the EU at any one time is therefore  $2.8 \times 10^9$  m<sup>2</sup>. Assuming that C<sub>18–20</sub> liquid paraffins are present in 0.17 per cent of the wall covering, the total amount of wall covering containing LCCPs present in the EU is  $4.8 \times 10^6$  m<sup>2</sup>.

Using the emission factor above, gives an estimated air emission of 18 kg/year for the C<sub>18–20</sub> liquid chlorinated paraffins from this source (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 0.43 kg/year).

#### *F2.1.3 Coated products, film and sheet*

In the draft DEHP risk assessment the relevant statistics for the production of coated products, film and sheet (e.g. upholstery, packaging, stationary products, luggage, clothing etc.) containing phthalate plasticisers could not be obtained. Instead the worst case assumption of 40 tonnes/year for total phthalate emissions from these products, as determined by the European Council for Plasticisers and Intermediates (ECPI, 1996), was used as the basis of the release estimate. This estimate was based on a product lifetime of seven years.

If it is assumed that C<sub>18–20</sub> liquid chlorinated paraffins are present in 0.17 per cent of these products and that the emission rate is 2.5 times lower than that of the phthalates present, then an air emission of 27 kg/year for C<sub>18–20</sub> liquid chlorinated paraffins can be estimated from this source (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 0.64 kg/year).

#### *F2.1.4 Cable*

In the draft DEHP risk assessment report the relevant statistics for the production of cable containing phthalate plasticisers could not be obtained. Instead the worst case assumption of 50 tonnes/year for total phthalate emissions from these products, as determined by the European Council for Plasticisers and Intermediates (ECPI, 1996), was used as the basis of the release estimate.

As was the case with coated products, film and sheet, if it is assumed that C<sub>18–20</sub> liquid chlorinated paraffins are present in 0.17 per cent of these products and that the emission rate is 2.5 times lower than that of the phthalates present, then an air emission of 34 kg/year for C<sub>18–20</sub> liquid chlorinated paraffins can be estimated from this source (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 0.80 kg/year).

#### *F2.1.5 Hose and profile*

In the draft DEHP risk assessment report the relevant statistics for the production of hose and profile containing phthalate plasticisers could not be obtained. Instead it was assumed that, as the surface to volume ratio and lifetime were similar to PVC flooring, the overall releases of DEHP would be similar to flooring. The ratio of DEHP used in flooring:profile/hose (74,708 tonnes/year:55,911 tonnes/year or 1.34:1) was used to scale the estimated emissions from PVC flooring to give an estimate from this use.

If it is assumed that LCCPs are present in PVC flooring and hoses/profile in a similar ratio to that found for DEHP (i.e. 1.34:1) the releases to air from this application can be estimated using the above scaling factor on the estimated releases of LCCPs from PVC flooring. Thus the estimated release to air of LCCPs from this source is 22 kg/year of C<sub>18-20</sub> liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 0.52 kg/year).

## **F2.2 Outdoor applications**

The draft risk assessment report on DEHP provided estimated figures for the surface areas for various outdoor PVC products produced each year containing DEHP and that may emit DEHP. These estimates are shown in Table F1, along with the estimated lifetimes of the products. These figures were estimated from the known DEHP yearly consumption in these applications and applying a “surface correction factor” to convert the consumption figures to an “annual surface area produced” figure. Since DEHP accounts of around 51 per cent of the total phthalate plasticiser use in PVC, the surface area of all flexible (phthalate plasticised) PVC produced each year in these applications will be around twice the values given.



**Table F1 Estimated DEHP emitting surface area and lifetime of outdoor PVC products containing DEHP**

PVC product	Annual emitting surface area (based on DEHP annual production)	Lifetime
Car undercoating	3,703,700 m <sup>2</sup> /year	12 years
Roofing material	529,100 m <sup>2</sup> /year	20 years
Coil coating	26,455,000 m <sup>2</sup> /year	10 years
Fabric coating	22,222,200 m <sup>2</sup> /year	10 years
Cable and wires (above ground)	2,116,400 m <sup>2</sup> /year	30 years
Cable and wires (buried)	8,465,600 m <sup>2</sup> /year	30 years
Hoses and profiles	1,587,300 m <sup>2</sup> /year	10 years
Shoe soles	3,174,600 m <sup>2</sup> /year	5 years

Assuming C<sub>18-20</sub> liquid chlorinated paraffins occur in around 0.17 per cent of all plasticised PVC used in the above applications, and using an emission rate of 3.8 mg/m<sup>2</sup>/year, emission to air estimates can be obtained for LCCPs over the lifetime of the PVC products (Table F2). The equivalent emissions for C<sub>>20</sub> liquid chlorinated paraffins are also shown.

**Table F2 Estimated LCCP emission for outdoor PVC products**

PVC product	LCCP emission	
	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid
Car undercoating	{0.57 kg/year} <sup>a</sup>	{0.014 kg/year} <sup>a</sup>
Roofing material	0.14 kg/year	0.003 kg/year
Coil coating	3.4 kg/year	0.080 kg/year
Fabric coating	2.9 kg/year	0.068 kg/year
Cable and wires (above ground)	0.81 kg/year	0.019 kg/year
Cable and wires (buried – emissions will be to soil compartment)	3.3 kg/year	0.077 kg/year
Hoses and profiles	0.21 kg/year	0.005 kg/year
Shoe soles	0.21 kg/year	0.005 kg/year

Notes: <sup>a</sup> Chlorinated paraffins are not thought to be used in car undercoating – calculation given only as an example.

Emission = 2 × annual surface area produced based on:

DEHP × lifetime × fraction of PVC containing LCCP × emission rate (mg/year).

### F3 Estimated emissions from LCCPs leaching from PVC

In these estimates it is assumed that LCCPs have a similar potential for leaching from PVC as DEHP as a worst case (see main risk assessment report).

#### F3.1 Indoor applications

##### F3.1.1 Washing clothing with PVC printing

It is not known if LCCPs are used in this application. In the draft risk assessment report for DEHP a total EU release of DEHP from this application was estimated at 99 tonnes/year (range 18–180 tonnes/year), based on measurements of phthalate loss carried out in Denmark. If it is assumed that LCCPs are used in this application, then a release of 327 kg/year of C<sub>18–20</sub> liquid chlorinated paraffins can be estimated based on the relative amounts of PVC containing DEHP and LCCPs estimated earlier (i.e. C<sub>18–20</sub> chlorinated paraffins may be present in up to 0.17 per cent of the total plasticised PVC or up to 0.33 per cent of the PVC containing DEHP); the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 15 kg/year). There is a large uncertainty in this figure due to uncertainties in the release rate and the relative amounts of LCCPs used in this application (if they are used at all).

### *F3.1.2 Washing PVC flooring*

An emission figure for DEHP of 5 µg/dm<sup>2</sup> (=500 µg/m<sup>2</sup>) per cleaning event (10 day interval) was reported in the draft DEHP risk assessment, based on experimental data from Sweden. The study was designed only to determine the leaching loss and did not include any loss due to abraded particulates.

In the draft DEHP risk assessment report the total annual production of PVC flooring in the EU was taken as 2.3×10<sup>8</sup> m<sup>2</sup>/year, with a lifetime of 20 years. If it is assumed that C<sub>18–20</sub> liquid chlorinated paraffins are present in 0.17 per cent of the flooring, the total amount of flooring containing C<sub>18–20</sub> liquid chlorinated paraffins present in the EU is 7.8×10<sup>6</sup> m<sup>2</sup>. Using the above emission figure and assuming cleaning of the flooring once per week, the estimated emission of LCCP is 203 kg/year for C<sub>18–20</sub> liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 9.6 kg/year).

It is thought that around 50–60 per cent of cushion vinyl flooring is coated with polyurethane in order to improve the wear resistance and stain resistance of the product. This coating will obviously affect the potential for leaching of LCCPs from the product, but no information is available at this time. If it is assumed that this coating reduces the leaching loss by a factor of 10 and is applied to 50 per cent of the flooring, then the estimated emissions would be 102 kg/year for C<sub>18–20</sub> for liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 5.3 kg/year).

The draft DEHP risk assessment report also considered abrasion loss from PVC flooring. The assessment used data from standard tests for abrasion loss that indicated about 0.1–0.15 mm (average 0.125 mm) of the surface will be worn away over the lifetime of the flooring. Assuming the flooring is typically 2 mm thick, this abrasion loss corresponds to a loss rate of around 6.25 per cent over the lifetime of the PVC flooring or 0.31 per cent/year. This loss was assumed to occur on all PVC flooring where walking occurred frequently and this was estimated to be around 50 per cent of the total PVC area.

Earlier, it was estimated that around 7.8×10<sup>6</sup> m<sup>2</sup> of PVC-flooring could contain C<sub>18–20</sub> liquid chlorinated paraffins. Assuming an initial thickness of 0.002 m (2 mm) and a representative density of around 1,200–1,300 kg/m<sup>3</sup> for plasticised PVC (from the draft risk assessment of DEHP), the amount of PVC containing C<sub>18–20</sub> liquid chlorinated paraffins in flooring can be roughly estimated as 20,280 tonnes (C<sub>18–20</sub> liquid) at any one time (assuming a 20 year lifetime). If the abrasion rate is 0.31 per cent/year, and 50 per cent of the available flooring is subject to abrasion, then the amount of PVC abraded as particulates is 31.4 tonnes/year. The LCCP could be present at 10 per cent in these particulates, i.e. 3,140 kg/year of C<sub>18–20</sub> liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 148 kg/year).

Again, it also needs to be taken into account that around 50–60 per cent of cushion vinyl flooring is coated with polyurethane which will reduce the wear rate of the product, and hence emission of LCCP. No information is available on this, but if it is assumed that such a coating reduces the emission rate of LCCPs by a factor of 10 and is applied to 50 per cent of flooring, then the estimated particulate emissions would be reduced to 1,730 kg/year for C<sub>18–20</sub> liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 81 kg/year).

These particulates are likely to end up in waste water (by washing) or landfill (by cleaning methods not involving water). In the May 2000 draft of the DEHP risk assessment, it was assumed that 50 per cent of these emissions would end up in waste water. This would amount to around 865–1,570 kg/year of C<sub>18–20</sub> liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 41–74 kg/year).

### F3.2 Outdoor applications

The annual releases of plasticiser from roofing materials have been estimated from studies carried out by Pastruska *et al.* (1988) and Pastruska and Just (1990). These gave overall loss figures (includes volatilisation, leaching and degradation) of phthalates from the roofing material of 0.15 per cent/year for open air exposures and 0.35 per cent/year for a surface covered with gravel.

In the draft risk assessment report for DEHP these figures were converted into surface area emission figures for DEHP of 1.98 g/m<sup>2</sup>/year for uncovered surfaces and 4.62 g/m<sup>2</sup>/year for gravel-covered surfaces. These figures were assumed to represent the leaching loss from the PVC, and were expected to be distributed 50 per cent to surface water and 50 per cent to soil.

Using a similar methodology as used for DEHP, the following surface area emission figures can be estimated for LCCPs using the above data.

1 m <sup>2</sup> of roofing material (1.5 mm thickness)	= 1.5×10 <sup>6</sup> mm <sup>3</sup> volume
Density of PVC (unplasticised)	= 1.406 mg/mm <sup>3</sup>
Density of DEHP	= 0.985 mg/mm <sup>3</sup>
Density of LCCP	= 1.3 mg/mm <sup>3</sup>
Overall density of plasticised PVC (10 per cent LCCP and 35 per cent DEHP)	= 1.248 mg/mm <sup>3</sup>
1 m <sup>2</sup> of roofing material (1.5 mm thickness)	= 1,872 g
Amount of LCCP present in 1 m <sup>2</sup> roofing material	= 10 per cent = 187.2 g/m <sup>2</sup>
Annual emission rate	= 0.15 per cent/year or or = 0.35 per cent year
Surface area emission factor for LCCP	= 0.28 g/m <sup>2</sup> /year or = 0.65 g/m <sup>2</sup> /year

These calculations assume that the LCCPs are as equally susceptible to removal (leaching) as DEHP. Processes other than leaching (e.g. biodegradation) could have occurred in these experiments with phthalates, which may not be applicable to LCCPs, resulting in an overestimate of the leaching loss.

Assuming the C<sub>18–20</sub> liquid chlorinated paraffins occur in around 0.17 per cent respectively of all plasticised PVC used in the outdoor applications outlined in Section F2.2, and using an emission rate of 0.65 g/m<sup>2</sup>/year for gravel-covered surfaces and 0.28 g/m<sup>2</sup>/year for open surfaces, estimated leaching losses can be obtained over the lifetime of the PVC products (Table F3). The equivalent emissions for C<sub>>20</sub> liquid chlorinated paraffins are also shown.

**Table F3 Estimated LCCP leaching losses from outdoor PVC products**

PVC product	Emission factor	Estimated leaching loss	
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid
Car undercoating	{0.28 g/m <sup>2</sup> /year} <sup>a</sup>	{42 kg/year} <sup>a</sup>	{2.0 kg/year} <sup>a</sup>
Roofing material	0.65 g/m <sup>2</sup> /year	23 kg/year	1.1 kg/year
Coil coating	0.28 g/m <sup>2</sup> /year	251 kg/year	12 kg/year
Fabric coating	0.28 g/m <sup>2</sup> /year	212 kg/year	10 kg/year
Cable and wires (above ground)	0.28 g/m <sup>2</sup> /year	60 kg/year	2.8kg/year
Cable and wires (buried) emissions will be to soil compartment)	0.65 g/m <sup>2</sup> /year	(560 kg/year	26 kg/year
Hoses and profiles	0.28 g/m <sup>2</sup> /year	15 kg/year	0.71 kg/year
Shoe soles	0.65 g/m <sup>2</sup> /year	35 kg/year	1.7 kg/year

Note: <sup>a</sup> Chlorinated paraffins are not thought to be used in car undercoating – calculation given only as an example.  
Emission = 2 × annual surface area produced based on:  
DEHP × lifetime × fraction of PVC containing LCCP × emission factor (g/year).

In addition, a figure of 47 tonnes/year of DEHP was estimated to be released to waste water during the washing of car underbodies in the draft risk assessment for DEHP. The “scaled” emission for LCCPs (taking into account the relative amounts used in PVC applications) would be around 160 kg/year of C<sub>18-20</sub> liquid chlorinated paraffins (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 7.1 kg/year). However, it is thought that chlorinated paraffins do not have a significant use in car undercoating.

## F4 Emissions during waste disposal

### F4.1 Car shredding

As well as PVC-coated underbodies (which are unlikely to contain chlorinated paraffins), cars may contain other PVC articles (e.g. cable or wiring) that may contain LCCPs. The draft risk assessment report on DEHP includes an emission scenario for this endpoint and this information has been used here to estimate the worst case emissions of chlorinated paraffins during the process as follows:

Amount of PVC per car	= 16 kg
Percentage of PVC that is plasticised	= 35 per cent
Amount of plasticised PVC/car	= 5.4 kg
Maximum amount of chlorinated paraffin/car (assuming 10 per cent content in PVC)	= 0.54 kg
Total number of cars processed in EU	= 10,600,000/year
Total amount of chlorinated paraffins present	= 5,724 tonnes/year
Number of shredder sites in EU	= 252
Average amount of chlorinated paraffin processed	= 22.7 tonnes/year/site
Number of days of operation	= 300
Emission factor to air	= 0.05 per cent
Local release of chlorinated paraffins to air	= 11.4 kg/year
	= 0.038 kg/day
Total EU release of chlorinated paraffins to air	= 2.86 tonnes/year

The main type of chlorinated paraffin used in PVC is medium-chain chlorinated paraffin. LCCPs account for only a small fraction of the total chlorinated paraffin usage in PVC (estimated at around 0.5 per cent for C<sub>18-20</sub> liquid chlorinated paraffins in the late 1990s). Therefore, the estimated air emissions of C<sub>18-20</sub> liquid chlorinated paraffins from this source would be expected to be 1.9×10<sup>-4</sup> kg/day at a local site and 14 kg/year in the EU as a whole (the equivalent emission for the C<sub>>20</sub> liquid chlorinated paraffins would be 1.5×10<sup>-5</sup> kg/day at a local site and 1.1 kg/year in the EU as a whole).

#### **F4.2 Incineration of municipal waste**

No information is available on levels of LCCPs in the exhaust gases from municipal waste incinerators and so it is not possible to estimate a release from this source. The conditions present during municipal waste incineration would be expected to effectively destroy any LCCPs present.

#### **F4.3 Municipal landfill**

No information is available on the amounts of LCCPs subject to leaching from municipal landfills. In the draft risk assessment of DEHP it was estimated that around 15 tonnes/year of DEHP could leach from landfills to waste water in the EU. If it is assumed that LCCPs have a similar potential to leach as DEHP then the amount of LCCPs leached could be estimated to be around 51 kg/year of C<sub>18-20</sub> liquid chlorinated paraffins, based on scaling the DEHP figure to the relative total volumes of DEHP and LCCPs used in PVC applications in the EU (the equivalent emission for C<sub>>20</sub> liquid chlorinated paraffins is 2.3 kg/year).

#### **F4.4 Waste remaining in the environment**

Waste remaining in the environment can be considered to be particles of polymer product (e.g. PVC, paint, sealant etc.) which contain the LCCP. These particles are primarily released to the urban/industrial soil compartment, but they may also end up in sediment or air. End-products with outdoor uses are most likely to be sources of this waste. The release can occur both over the lifetime of the product (due to weathering, wear etc.) and at disposal (particularly where articles are dismantled or subjected to other mechanical processes).

In the draft DEHP risk assessment, waste remaining in the environment was identified to be produced from a number of outdoor applications of PVC, i.e.:

- car undercoating;
- roofing material;
- coil coating;
- fabric coating;
- cables and wires;
- hoses and profiles;
- shoe soles.

Furthermore, it was stated that 22 per cent of the DEHP in PVC was used in these outdoor applications. The actual breakdown of the use of LCCPs between these different sources is not known and so it will be assumed that around 22 per cent of the LCCP is also used in PVC for outdoor applications.

In addition, LCCPs are also used in rubber products, textile products, outdoor paints and building sealants which also need to be considered as possible sources of waste remaining in the environment. The use in leather fat liquors and metalworking/cutting fluids are not considered to contribute significantly to these types of release. Table F4 outlines the relevant tonnages for the applications considered.

The emission factors used for these types of losses in the draft DEHP risk assessment were around 2–10 per cent over the lifetime of the product, with the higher factor being applied to articles subject to high wear rates (such as car underbodies and shoe soles), and two per cent during disposal operations. The assumptions behind the derivation of these factors were not given in the report. These releases were thought to occur mainly to urban/industrial soil. A similar approach is taken here as a worst case, using similar factors as used for DEHP. Only outdoor applications are considered to contribute significantly to the waste over the lifetime of the articles. However, for some of the applications (e.g. sealants, textiles, paints) the actual fraction used in outdoor applications is uncertain and so it has been assumed that all of the LCCPs are used in outdoor applications as a worst case.

This approach assumes that:

- the quantity of articles/products containing LCCPs disposed of each year is equal to the quantity of new articles/products containing LCCPs produced each year;
- the emissions factors estimate the total release over the entire service life of the product/article (i.e. for high wear articles, 10 per cent of the product is worn away as particles/dust over the lifetime of the product).

For use in rubber products, sealants/adhesives and paints, a particulate emission factor of two per cent over the technical lifetime of the product and two per cent at disposal is used (in the May 2000 draft of the DEHP assessment a figure of five per cent over the technical lifetime and five per cent at disposal was used for paints and sealants, so these values are also considered). However, for PVC applications, there may be some high wear products produced (e.g. shoe soles) and so a higher particulate emission factor may be appropriate to some of these applications.

Since the actual breakdown of the use of LCCPs between these various PVC end-uses is currently unknown, an emission factor of six per cent over the lifetime of the technical product was used (average of the low and high wear factors), with two per cent emission at disposal. The calculations also take into account the LCCPs estimated to be lost via volatilisation and leaching over the lifetime in order to avoid double counting of these emissions.

The emissions are likely to be mainly to soil. In the draft DEHP assessment it was assumed that 75 per cent of the emission would be to industrial/urban soil and 0.1 per cent to air, with the remainder occurring to surface water (sediment). The same split of the emissions will be used here in the absence of any further information. The emissions are summarised in Table F4.

There are many uncertainties inherent in these emission estimates. Further, since this “waste” is essentially polymeric particles (e.g. rubber, polymer, sealant, paint) containing the LCCP, it is not known if this is “available” in the environment and therefore whether organisms are at any risk to exposure.

In addition to these particulate releases, an estimated 865–1,570 kg/year of C<sub>18–20</sub> liquid chlorinated paraffins (and 41–74 kg/year C<sub>>20</sub> liquid chlorinated paraffins) may be

emitted to waste water (and 865–1,570 kg/year of C<sub>18–20</sub> liquid chlorinated paraffins and 41–74 kg/year of C<sub>>20</sub> liquid chlorinated paraffin to landfill/disposal) as particulates for PVC flooring as a result of wear and subsequent washing (see Section F3.1.2).

**Table F4 Estimation of waste remaining in the environment**

		Uses considered for waste remaining in environment								
		PVC		Rubber		Sealants/adhesives		Paints		
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid <sup>a</sup>	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
Amount of LCCP emitted as waste remaining in the environment over technical lifetime of product (kg/year)		6,900	300	83,452	4,140	5,000– 5,162	10,140– 10,460	30,660– 32,220	27,180– 27,400	5,550
Amount of LCCP emitted as waste remaining in the environment at disposal (kg/year)		2,270	94	81,782	4,060	4,900– 5,060	9,940– 10,260	30,020– 31,600-	26,640– 26,860	5,440
Total amount of LCCP as waste remaining in the environment (kg/year)		9,170	394	165,234	8,200	9,900– 10,222	20,080– 20,720	60,680– 63,820	53,820– 54,260	10,990
Distribution of emission	urban soil	75%	75%	75%	75%	75%		75%	75%	75%
	surface water	24.9%	24.9%	24.9%	24.9%	24.9%		24.9%	24.9%	24.9%
	air	0.1%	0.1%	0.1%	0.1%	0.1%		0.1%	0.1%	0.1%
Total amount of LCCP as waste remaining in the environment to: (kg/year)	urban soil	6,878	296	123,926	6,150	7,425– 7,667	15,060– 15,540	45,510- 43,800	40,365– 40,695	8,243
	surface water	2,283	98	41,143	2,042	2,465– 2,545	5,000– 5,159	15,110- 14,542	13,401– 13,511	2,737
	air	9	0.4	165	8	10	20	61	53–54	11

Note: <sup>a</sup> Calculation based on past use in this application.



## F5 Summary of emissions estimated

Table F5 summarises the emissions estimated here for diffusive losses of LCCPs during the lifetime of PVC products and during the disposal of articles. Table F6 summarises the emissions of LCCPs as particulates (waste remaining in the environment) over the lifecycle of products.

**Table F5 Summary of diffusive losses of LCCPs from PVC during product lifetimes and disposal**

Lifestage		Emission of LCCP (kg/year)			
		Volatility losses to air		Leaching loss to water and soil	
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid
Product lifetime	flooring (i)	17–30	0.39–0.70	102–203 <sup>b</sup>	5.3–9.6 <sup>b</sup>
	wall covering (i)	18	0.43		
	coated products, film and sheet (i)	27	0.64	327 <sup>a,b</sup>	15 <sup>a,b</sup>
	cable (i)	34	0.80		
	hose and profile (i)	22	0.52		
	roofing material (o)	0.14	0.003	23 <sup>c</sup>	1.1 <sup>c</sup>
	coil coating (o)	3.4	0.080	251 <sup>c</sup>	12 <sup>c</sup>
	fabric coating (o)	2.9	0.068	212 <sup>c</sup>	10 <sup>c</sup>
	cable (o)	0.81	0.019	60 <sup>c</sup>	2.8 <sup>c</sup>
		(+3.3 to deep soil)	(+0.077 to deep soil)	(+560 to deep soil)	(26 to deep soil)
	hoses and profile (o)	0.21	0.005	15 <sup>c</sup>	0.71 <sup>c</sup>
	shoe soles	0.21	0.005	35 <sup>c</sup>	1.7 <sup>c</sup>
Total from PVC over product lifetime to	air	126–139	3.0–3.3		
	waste water			429–530	20–25
	surface water			298	14
	urban/industrial soil			298	14
	deep soil	3.3	0.077	560	2
Waste disposal	car shredding	14	1.1		
	incineration	small	small		
	municipal landfill			51 <sup>b</sup>	2.3 <sup>b</sup>
Total from PVC at disposal		14	1.1	51	2.3
		(to air)	(to air)	(to waste water)	(to waste water)

Notes: <sup>a</sup> Estimated for washing clothing with PVC printing – it is not known if LCCPs are used in this application.

<sup>b</sup> Losses primarily to wastewater.

<sup>c</sup> Losses to soil and water (assumed to be split 50:50 between surface water and industrial/urban soil).

i = indoor application; o = outdoor application.

**Table F6 Summary of waste remaining in the environment during product lifetimes and disposal**

Lifestage		Emission of long-chain chlorinated paraffin as particulates (kg/year)											
		Air			Surface water			Waste water			Urban/industrial soil		
		C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid	C <sub>18-20</sub> liquid	C <sub>&gt;20</sub> liquid	C <sub>&gt;20</sub> solid
Product lifetime	PVC	7	0.3		1,718	75		865– 1,570 <sup>a</sup>	41– 74 <sup>a</sup>		5,175	225	
	Rubber		83	4		20,780	1,031					62,589	3,105
	Sealants/adhesives	5	10		1,245– 1,285	2,525– 2,605					3,750– 3,872	7,605– 7,845	
	Paints	31–32	27	6	7,634– 8,023	6,768– 6,823	1,382				22,995– 24,165	20,385– 20,550	4,163
Waste disposal	PVC	2	0.09		565	23					1,703	71	
	Rubber		81	4		20,364	1,011					61,337	3,045
	Sealants/adhesives	5	10		1,220– 1,260	2,475– 2,555					3,675– 3,795	7,455– 7,695	
	Paints	31–32	27	5	7,475– 7,868	6,633– 6,688	1,355				22,515– 23,700	19,980– 20,145	4,080
Total		81–83	238	19	19,857– 20,719	59,643– 59,913	4,779	865– 1,570	41–74		59,813– 62,410	179,647– 180,457	14,393

Note: <sup>a</sup> Emission to waste water from washing PVC-flooring. A similar amount estimated to end up in landfill.

In order to generate these figures, a large number of “worst case” assumptions have had to be made. This leads to a large uncertainty in the figures obtained, and the approach taken may grossly overestimate the actual releases. In particular, the information on leaching losses from outdoor outdoors is based on a study where the overall loss (including leaching, degradation and particulate loss due to wear/weathering) of phthalate plasticiser from roofing material was determined. In the study, it was not possible to distinguish between these types of loss and so it has been assumed that all the loss was due to leaching. The applicability of this approach to estimating the leaching loss of LCCPs from products outdoors is unknown.

## **F6 References**

ECPI, 1996 Assessment of the release, occurrence and possible effects of plasticisers in the environment. Phthalate esters used in plasticised PVC. European Council for Plasticisers and Intermediates, CEFIC, September 1996. (as quoted in the November 1999 draft of the ESR risk assessment report for DEHP).

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# Appendix G Assessment of C<sub>16-17</sub> impurities present in LCCPs

This appendix considers the risks to the environment from the presence of C<sub>16-17</sub> chlorinated paraffin impurities in some types of LCCPs. The levels of n-paraffin impurities present in the feedstocks used to manufacture LCCPs are shown in Table G1.

**Table G1** n-Paraffin impurities present in feedstocks used to manufacture LCCPs

Feedstock	Impurities present
C <sub>18-20</sub>	<1% C <sub>16</sub> (or lower n-paraffins) typically 17% C <sub>17</sub> (possible range 10-20%)
C <sub>&gt;20</sub>	0% C <sub>19</sub> (or lower n-paraffins) <0.2% C <sub>20</sub> paraffins

Since the C<sub>18-20</sub> feedstock contains a significant proportion of smaller chain length n-paraffins, the C<sub>18-20</sub> chlorinated paraffins produced from this feedstock would be expected to contain a similar amount of lower chain length chlorinated paraffins as impurities. Thus the C<sub>18-20</sub> LCCPs could act as a significant source of C<sub>16-17</sub> chlorinated paraffins, which are also components of medium-chain (C<sub>14-17</sub>) chlorinated paraffins.

The emission estimates for the C<sub>18-20</sub> chlorinated paraffins are shown in Table G2. These values are taken from the draft risk assessment report on LCCPs. The equivalent release estimates for the C<sub>16-17</sub> impurities (calculated by assuming the C<sub>16-17</sub> impurity typically accounts for 17 per cent of the product) are also shown in Table G2.

In order to assess the risk to the environment from these impurities, EUSES 2.0.3 has been used to estimate the resulting concentrations of the C<sub>16-17</sub> impurity. The physico-chemical, toxicological and other data used in the model are derived in the risk assessment report for medium-chain chlorinated paraffins (of which C<sub>16-17</sub> chlorinated paraffins are also a component). The values for these parameters are summarised in Table G3. The resulting PECs and PEC/PNEC ratios for surface water, sediment, soil and secondary poisoning are shown in Table G4 to Table G7.

This approach used here is considered a worst case approach as it assumes that all the toxicity seen with the medium-chain chlorinated paraffins is due mainly to the C<sub>17</sub> component. This is not likely to be the case as there appears to be a general trend that chlorinated paraffins become less toxic and bioavailable as their carbon chain length increases.

**Table G2 Summary of environmental release estimates for C<sub>18-20</sub> chlorinated paraffins and C<sub>16-17</sub> impurities**

Use	Comment	Type of LCCP	Estimated local release			Estimated regional release (kg/year)			Estimated continental release <sup>d</sup> (kg/year)		
			air (kg/day)	waste water (kg/day)	no of days <sup>j</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>
Production	Generic calculation	C <sub>18-20</sub> C <sub>16-17</sub> impurity		0.063 0.011	300 300	con	con	con	con	con	con
Use in PVC <sup>e</sup> – plastisol coating <sup>h</sup>	Compounding site (formulation)	C <sub>18-20</sub>		0.025 <sup>a</sup>	33						
		C <sub>16-17</sub> impurity		0.0043 <sup>a</sup>	33						
	Conversion site (processing)	C <sub>18-20</sub>	0.025 <sup>a</sup>	0.025 <sup>a</sup>	33						
		C <sub>16-17</sub> impurity	0.0043 <sup>a</sup>	0.0043 <sup>a</sup>	33						
Use in PVC <sup>e</sup> – extrusion/other	Combined compounding and conversion site	C <sub>18-20</sub>	0.025 <sup>a</sup>	0.050 <sup>a</sup>	33						
		C <sub>16-17</sub> impurity	0.0043 <sup>a</sup>	0.0085 <sup>a</sup>	33						
		C <sub>18-20</sub>	0.0075 <sup>a</sup> 0.040 <sup>b</sup> 0.0034 <sup>c</sup>	0.0445 <sup>a</sup> 0.24 <sup>b</sup> 0.0204 <sup>c</sup>	33						
	Conversion site (processing)	C <sub>16-17</sub> impurity	0.0013 <sup>a</sup> 0.0068 <sup>b</sup> 0.00029 <sup>c</sup>	0.0076 <sup>a</sup> 0.041 <sup>b</sup> 0.0035 <sup>c</sup>	33						
		C <sub>18-20</sub>	0.037 <sup>a</sup> 0.040 <sup>b</sup> 0.034 <sup>c</sup>	0.037 <sup>a</sup> 0.040 <sup>b</sup> 0.034 <sup>c</sup>	33						
		C <sub>16-17</sub> impurity	0.0063 <sup>a</sup> 0.0068 <sup>b</sup> 0.0058 <sup>c</sup>	0.0063 <sup>a</sup> 0.0068 <sup>b</sup> 0.0058 <sup>c</sup>	33						

Table G2 continued overleaf

**Table G2 continued**

Use	Comment	Type of LCCP	Estimated local release			Estimated regional release (kg/year)			Estimated continental release (kg/year) <sup>d</sup>		
			air (kg/day)	waste water (kg/day)	no of days <sup>j</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>
Use in PVC <sup>e</sup> – extrusion/other	Combined compounding and conversion site	C <sub>18-20</sub>	0.0445 <sup>a</sup>	0.0815 <sup>a</sup>	33						
		C <sub>16-17</sub> impurities	0.080 <sup>b</sup> 0.0374 <sup>c</sup> 0.0076 <sup>a</sup> 0.014 <sup>b</sup> 0.0064 <sup>c</sup>	0.28 <sup>b</sup> 0.0544 <sup>c</sup> 0.014 <sup>a</sup> 0.048 <sup>b</sup> 0.0092 <sup>c</sup>	33						
Use in PVC – regional and continental releases	Raw materials handling (formulation)	C <sub>18-20</sub>					5.2			47	
		C <sub>16-17</sub> impurities					0.88			8.0	
	Compounding (formulation)	C <sub>18-20</sub>				0.7	0.7		6.6	6.6	
		C <sub>16-17</sub> impurities				0.12	0.12		1.1	1.1	
Conversion <sup>f</sup> (processing)	C <sub>18-20</sub>				12	12		106	106		
	C <sub>16-17</sub> impurities				2.0	2.0		18	18		
Paints and varnishes	Formulation	C <sub>18-20</sub>	negligible	negligible	300	negligible	negligible		negligible	negligible	
		C <sub>16-17</sub> impurities	negligible	negligible	300	negligible	negligible		negligible	negligible	
	Industrial application of paints (Processing)	C <sub>18-20</sub>		0.06	300		180			1,620	
		C <sub>16-17</sub> impurities		0.010	300		31			275	

Table G2 continued overleaf

Table G2 continued

Use	Comment	Type of LCCP	Estimated local release			Estimated regional release (kg/year)			Estimated continental release (kg/year) <sup>d</sup>		
			air (kg/day)	waste water (kg/day)	no of days <sup>j</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>
Paints and varnishes	Application by general public (private use)	C <sub>18-20</sub> C <sub>16-17</sub> impurity	negligible	negligible							
Metal cutting/ working fluids	Formulation	C <sub>18-20</sub>	4×10 <sup>-4</sup>	5×10 <sup>-4</sup>	<10						
		C <sub>16-17</sub> impurity	7×10 <sup>-5</sup>	9×10 <sup>-5</sup>	<10						
	Use in oil-based fluids (processing; small site)	C <sub>18-20</sub>			0.30	300					
		C <sub>16-17</sub> impurity			0.60 0.051 0.10						
Use in emulsifiable fluids (processing)	C <sub>18-20</sub>			0.025 (plus an intermittent discharge of 25 kg/event)	300						
	C <sub>16-17</sub> impurity			4.3×10 <sup>-3</sup> (plus 4.3 kg/event)							
Leather fat liquors	Formulation	C <sub>18-20</sub>	0.055 <sup>i</sup>	0.15 <sup>i</sup>	300	17	49		149	444	
		C <sub>16-17</sub> impurity	9.4×10 <sup>-3</sup> <sup>i</sup>	0.026 <sup>i</sup>	300	2.9	8.3		25	75	
	Use – complete processing of raw hides	C <sub>18-20</sub>			0.9	100		332			2,988
		C <sub>16-17</sub> impurity			0.15	100		56			508

Table G2 continued overleaf

Table G2 continued

Use	Comment	Type of LCCP	Estimated local release			Estimated regional release (kg/year)			Estimated continental release (kg/year) <sup>d</sup>		
			air (kg/day)	waste water (kg/day)	no of days <sup>j</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>	air	waste water <sup>g</sup>	soil <sup>m</sup>
Textiles		C <sub>18-20</sub>	8.3	4.3	300						
		C <sub>16-17</sub>	1.4	0.73	300						
Articles – volatile and leaching loss	Service life	C <sub>18-20</sub>				18,060– 25,270	10+ 881– 1,550 <sup>k</sup>	881– 1,550	162,540– 227,430	95+ 7,929– 13,950 <sup>k</sup>	7,929– 13,950
		C <sub>16-17</sub>				3,070– 5,296	1.7+ 150– 264 <sup>k</sup>	150– 264	27,632– 38,663	16+ 1,348– 2,372 <sup>k</sup>	1,348– 2,372
“Waste remaining in the environment”	Service life and disposal	C <sub>18-20</sub>				8	1,986– 2,072 <sup>k</sup> +87– 157	5,981– 6,241	73–75	17,871– 18,647 <sup>k</sup> + 779–1,413	53,832– 56,169
		C <sub>16-17</sub>				1.4	338–352 <sup>k</sup> + 15–27	1,017– 1,061	12–13	3,038– 3,170 <sup>k</sup> +132–240	9,151– 9,549
Total emissions		C <sub>18-20</sub>				18,098– 25,308	541–597 via WWTP 3,002– 3,771 direct to surface water	6,862– 7,791	162,875– 227,767	4,868– 5,376 via wwtp 27,017– 33,941 direct to surface water	61,761– 70,119
		C <sub>16-17</sub>				3,077– 4,302	92–101 via WWTP 510–641 direct to surface water	1,167– 1,324	27,689– 38,720	828–914 via wwtp 4,593– 5,770 direct to surface water	10,499– 11,920



- Notes: <sup>a</sup> Open systems (as defined in OECD, 2004b).  
<sup>b</sup> Partially open systems (as defined in OECD, 2004b).  
<sup>c</sup> Closed systems (as defined in OECD, 2004b).  
<sup>d</sup> Continental release = total EU release - regional release.  
<sup>e</sup> Releases estimated from OECD (2004b) assuming that 50 per cent of the initial release to air will condense and eventually reach waste water.  
<sup>f</sup> Regional and continental releases from conversion assume 50 per cent of sites have air emission control. The actual overall proportion of the industry with such controls is unknown, but is likely to be higher than this figure.  
<sup>g</sup> An 80 per cent connection rate to waste water treatment plants will be assumed.  
<sup>h</sup> Releases from car underbody coating and sealing, and rotational moulding are thought to be negligible during the processing step.  
<sup>i</sup> Industry-specific release information is also available and has been used to estimate the  $PEC_{local}$  in preference to these default values.  
<sup>j</sup> Number of days/year over which the local emission occurs.  
<sup>k</sup> Emissions occur directly to surface water.  
<sup>m</sup> Direct emissions to urban/industrial soil.  
con = confidential information – the regional and continental releases from this source are small compared with the total releases from other sources.

**Table G3** Data used for EUSES modelling of C<sub>16-17</sub> impurities

Property	Value
Molecular weight	488 g/mole
Melting point	0°C
Boiling point	>200°C
Vapour pressure	2.7×10 <sup>-4</sup> Pa at 25°C
Log octanol-water partition coefficient (log K <sub>ow</sub> )	7
Water solubility	0.027 mg/l
Organic carbon-water partition coefficient	5.89×10 <sup>5</sup> l/kg
Fish bioconcentration factor	1,087 l/kg
BMF	1 (TGD method) 1–3 (alternate method)
Earthworm bioconcentration factor	5.6 kg/kg
Biodegradability	Not degradable
Rate constant for reaction with atmospheric hydroxyl radicals (k <sub>OH</sub> )	8×10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
Regional concentration in surface water <sup>a</sup>	0.1 µg/l
Regional concentration in sediment	0.7 mg/kg wet wt.
Regional concentration in agricultural and natural soil <sup>a</sup>	0.088 mg/kg wet wt.
PNEC for surface water	1 µg/l
PNEC for sediment	5 mg/kg wet wt.
PNEC for soil	10.6 mg/kg wet wt.
PNEC for secondary poisoning	10 mg/kg food <sup>b</sup>

Notes: <sup>a</sup> In the medium-chain chlorinated paraffins assessment, the regional concentrations in surface water, sediment and agricultural soil were derived based on the available monitoring data, which would include the contribution from all sources of C<sub>14-17</sub> chlorinated paraffins, including the impurities present in LCCPs.

<sup>b</sup> The PNEC<sub>oral</sub> for medium-chain chlorinated paraffins in the published risk assessment is currently 0.17 mg/kg. However, since the assessment was published further information has become available that shows that the actual NOAEL from mammalian studies for medium-chain chlorinated paraffins is around 300 mg/kg food for repeated dose exposure (90-day studies) and 100–1,000 mg/kg food for reproduction. Applying an assessment factor of 30 to these data would give a revised PNEC<sub>oral</sub> of 10 mg/kg food based on the repeated dose studies and 3.3–33 mg/kg food based on the reproduction endpoints. The PNEC<sub>oral</sub> of 10 mg/kg food is considered to be most reliable for medium-chain chlorinated paraffins as the effects seen at 1,000 mg/kg food in the reproduction study were not statistically significant from controls and this dose level was thought to be very close to the true NOAEL from this study.

**Table G4 Estimated PEC/PNEC ratios for surface water**

Scenario	Step	Estimated PEC for C <sub>16-17</sub> impurity (µg/l)	PEC/PNEC
Production	Generic	0.12	0.12
Use in PVC – plastisol applications	Compounding (O)	0.11	0.11
	Conversion (O)	0.11	0.11
	Compounding/conversion (O)	0.12	0.12
Use in PVC – extrusion/other	Compounding (O)	0.11	0.11
	Compounding (PO)	0.18	0.18
	Compounding (C)	0.11	0.11
	Conversion (O)	0.11	0.11
	Conversion (PO)	0.11	0.11
	Conversion (C)	0.11	0.11
	Compounding/conversion (O)	0.13	0.13
	Compounding/conversion (PO)	0.19	0.19
Use in paints	Formulation	negligible	<1
	Industrial application	0.12	0.12
	Domestic application	negligible	<1
Metal cutting/working fluids	Formulation	0.10	0.10
	Use in oil based fluids (small site)	0.20–0.29	0.20–0.29
	Use in emulsifiable fluids	0.11	0.11
	Use in emulsifiable fluids – intermittent release	8.1	<b>8.1</b>
Use in leather fat liquors	Formulation	0.13	0.13
	Use – complete processing of raw hides	0.38	0.38
Textiles		1.5	<b>1.5</b>

**Table G5 Estimated PEC/PNEC ratios for sediment**

<b>Scenario</b>	<b>Step</b>	<b>Estimated PEC for C<sub>16-17</sub> impurity (mg/kg wet wt.)</b>	<b>PEC/PNEC</b>
Production	Generic	1.5	0.30
Use in PVC – plastisol applications	Compounding (O)	1.4	0.28
	Conversion (O)	1.4	0.28
	Compounding/conversion (O)	1.5	0.30
Use in PVC – extrusion/other	Compounding (O)	1.5	0.30
	Compounding (PO)	2.3	0.46
	Compounding (C)	1.4	0.28
	Conversion (O)	1.4	0.28
	Conversion (PO)	1.4	0.28
	Conversion (C)	1.4	0.28
	Compounding/conversion (O)	1.6	0.32
	Compounding/conversion (PO)	2.4	0.48
Use in paints	Formulation	negligible	<1
	Industrial application	1.5	0.30
	Domestic application	negligible	<1
Metal cutting/working fluids	Formulation	1.3	0.26
	Use in oil based fluids (small site)	2.5–3.7	0.50–0.74
	Use in emulsifiable fluids	1.4	0.28
	Use in emulsifiable fluids – intermittent release	104 or 2.0–3.1	<b>21</b> or 0.40–0.62
Use in leather fat liquors	Formulation	1.7	0.34
	Use – complete processing of raw hides	4.9	0.98
Textiles		19	<b>3.8</b>

**Table G6 Estimated PEC/PNEC ratios for agricultural soil**

<b>Scenario</b>	<b>Step</b>	<b>Estimated PEC for C<sub>16-17</sub> impurity (mg/kg wet wt.)</b>	<b>PEC/PNEC</b>
Production	Generic	negligible	<1
Use in PVC – plastisol applications	Compounding (O)	0.16	0.015
	Conversion (O)	0.16	0.015
	Compounding/conversion (O)	0.24	0.023
Use in PVC – extrusion/other	Compounding (O)	0.22	0.021
	Compounding (PO)	0.80	0.075
	Compounding (C)	0.15	0.014
	Conversion (O)	0.20	0.019
	Conversion (PO)	0.21	0.020
	Conversion (C)	0.19	0.018
	Compounding/conversion (O)	0.33	0.031
	Compounding/conversion (PO)	0.92	0.086
Use in paints	Compounding/conversion (C)	0.25	0.024
	Formulation	negligible	<1
	Industrial application	0.26	0.025
Metal cutting/ working fluids	Domestic application	negligible	<1
	Formulation	0.090	8.5×10 <sup>-3</sup>
	Use in oil based fluids (small site)	0.97–1.8	0.092–0.17
	Use in emulsifiable fluids	0.16	0.015
Use in leather fat liquors	Use in emulsifiable fluids – intermittent release	47	<b>4.4</b>
	Formulation	0.54	0.051
	Use – complete processing of raw hides	2.7	0.25
Textiles		13	<b>1.2</b>

**Table G7 Estimated PEC/PNEC ratios for secondary poisoning**

Scenario	Step	Estimated PEC for C <sub>16-17</sub> impurity (mg/kg)		PEC/PNEC	
		Fish	Earthworm	Fish	Earthworm
Production	Generic	0.12–0.48	negligible	0.012–0.048	<1
Use in PVC – plastisol applications	Compounding (O)	0.11–0.44	0.69	0.011–0.044	0.069
	Conversion (O)	0.11–0.44	0.69	0.011–0.044	0.069
	Compounding/conversion (O)	0.11–0.44	0.92	0.011–0.044	0.092
Use in PVC – extrusion/ other	Compounding (O)	0.11–0.44	0.86	0.011–0.044	0.086
	Compounding (PO)	0.11–0.44	2.5	0.011–0.044	0.25
	Compounding (C)	0.11–0.44	0.67	0.011–0.044	0.067
	Conversion (O)	0.11–0.44	0.81	0.011–0.044	0.081
	Conversion (PO)	0.11–0.44	0.83	0.011–0.044	0.083
	Conversion (C)	0.11–0.44	0.78	0.011–0.044	0.078
	Compounding/conversion (O)	0.11–0.44	1.2	0.011–0.044	0.12
	Compounding/conversion (PO)	0.11–0.44	2.8	0.011–0.044	0.28
	Compounding/conversion (C)	0.11–0.44	0.95	0.011–0.044	0.095
	Use in paints	Formulation	negligible	negligible	<1
Industrial application		0.12–0.48	0.97	0.012–0.048	0.097
Domestic application		negligible	negligible	<1	<1
Metal cutting/ working fluids	Formulation	0.11–0.44	0.50	0.011–0.044	0.050
	Use in oil based fluids (small site)	0.15–0.76	3.0–5.3	0.015–0.076	0.30–0.53
	Use in emulsifiable fluids	0.11–0.44	0.69	0.011–0.044	0.069
	Use in emulsifiable fluids – intermittent release	0.13–0.52	132	0.013–0.052	13.2
Use in leather fat liquors	Formulation	0.11–0.44	1.8	0.011–0.044	0.18
	Use – complete processing of raw hides	0.15–0.60	7.8	0.015–0.060	0.78
Textiles		0.72–2.9	37	0.072–0.29	3.7

The resulting analysis indicates that PEC/PNEC ratios >1 could occur for surface water, sediment, soil and secondary poisoning from the intermittent release of LCCP product used in emulsion metalworking/cutting fluids, and from their use in textiles. For the intermittent release scenario for metalworking/cutting fluids, it is not clear if C<sub>18-20</sub> liquid chlorinated paraffins are actually used in this application. In addition, it is likely that at most sites in the EU the spent emulsion fluid is treated prior to discharge to the environment (the emulsion is likely to be split and the oil-phase separated for suitable disposal), so an actual risk from this use is unlikely to occur in reality. For the textile use, very little information is currently available on the process used, or the amounts of C<sub>18-20</sub> liquid chlorinated paraffins that could be released from the process. The current scenario is based entirely on worst case default assumptions. Further information on the actual emissions from this process could therefore refine the PECs for this scenario.

It should be noted that in this assessment, the background regional concentration has been assumed to be that from C<sub>14-17</sub> chlorinated paraffins, not just the C<sub>16-17</sub> chlorinated paraffins. This assumption is likely to overestimate the actual contribution from the C<sub>16-17</sub> fraction.

# Appendix H Chloroalkenes (chlorinated olefins)

## 1 Introduction

During the evaluation of long-chain chlorinated paraffins, some information has been identified for a related chemical group, the chloroalkenes or chlorinated olefins. The following two CAS numbers appear to be relevant (these are used on the US TSCA Inventory list and the Canadian Domestic Substance List (DSL)).

Alkenes, polymerized, chlorinated	CAS No 68410-99-1 (not on EINECS)
Alkenes, C <sub>12-24</sub> , chloro 1)	CAS No 68527-02-6 (EINECS no. 271-247-1)

## 2 Production and Use

Euro Chlor has confirmed that chlorinated olefins are not manufactured in the EU but the Chlorinated Paraffins Industries Association (CPIA) have indicated that they are produced in North America. It should also be noted that other manufacturers of chlorinated paraffins are known to exist in Asia. There is no information about whether or not they might produce such compounds. Company specific details have been retrieved from Industry product literature, including Internet websites (where available). Further details are provided in a confidential annex. This can be made available to regulatory authorities on request. Non-confidential information on the substances manufactured under CAS No 68410-99-1 and CAS No 68527-02-6 is available in the USEPA Inventory Update Reporting IUR database for 2006<sup>1</sup>. This indicates that in 2005 there were two companies producing substances under both of these CAS numbers. The uses given for both CAS Numbers are lubricants and flame retardants.

A search of the internet has identified information on some of these products (either formerly supplied or currently supplied). The products appeared under the trade name CHLOROWAX with the CAS number 68527-02-6, which referred to "Alkenes, C<sub>12</sub>-C<sub>24</sub> Chloro". The CAS number 68927-02-6 also appeared on some of the literature for these products but this was probably an error.

The product description did not distinguish between the chlorinated paraffins and chlorinated alpha-olefins in terms of the possible applications, and no details of the actual uses of the chlorinated alpha-olefins were given.

The Material Safety Data Sheet (MSDS) gave chemical formulas for these substances that indicated they may have been of a single carbon chain length, although this was by no means clear. A range of chlorine contents was given. This probably reflected the variation between batches in the chlorination reaction.

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<sup>1</sup> Available at <http://www.epa.gov/opptintr/iur/tools/data/index.htm> (accessed on 6th March 2009).



The products identified have similarities with chlorinated paraffins are shown in **Table H1**. As can be seen at least one of these substances has some similarity to long-chain chlorinated paraffins. Example formulae were given in the MSDS. These indicate that the products were actually effectively chlorinated alkanes rather than alkenes (formulae for alkenes would require two less hydrogen atoms/molecule) – however, there were several inconsistencies in the MSDS and so this information should be treated with caution. This company appeared to make no clear distinction between its chlorinated alpha-olefin products and its chlorinated paraffin products (they are all sold under the trade name CHLOROWAX, although the alpha-olefin products have AO at the end of the name). This means that there is the possibility that they could be used interchangeably in some or all applications, although reliable information on the actual uses is not available.

### H1 Former commercial chlorinated alkenes of relevance to chain chlorinated paraffins

Trade Name	Carbon chain length	Example formula	Chlorine content
Chlorowax 500AO	C <sub>12</sub>	C <sub>12</sub> H <sub>20</sub> Cl <sub>6</sub>	57-60%
Chlorowax 45AO	C <sub>12</sub>	C <sub>12</sub> H <sub>23</sub> Cl <sub>3</sub>	40-43%
Chlorowax 52AO	C <sub>12</sub>	C <sub>12</sub> H <sub>21</sub> Cl <sub>5</sub>	51.0-53.5%
Chlorowax 54-120AO	C <sub>16</sub>	C <sub>16</sub> H <sub>28</sub> Cl <sub>6</sub>	53-55%
Chlorowax 100AO	C <sub>21</sub> ?	C <sub>21</sub> H <sub>39</sub> Cl <sub>5</sub>	38-40.5%

### 3 Possible environmental effects of chlorinated alkenes

Few details are available on how the chlorinated alkenes were made. It is most likely that they were produced in a similar way as the chlorinated paraffins, which is by free radical chlorination.

As olefins contain carbon-carbon double bonds, it is possible that addition of chlorine to this double bond could occur during the chlorination reaction, as well as substitution of chlorine for hydrogen along the alkyl chain. If chlorine addition to the double bond does occur, then the product of the reaction would essentially be a chlorinated paraffin rather than a chlorinated olefin. The available information is a little unclear as to exactly how these chlorination reactions would proceed and hence what the exact products would be. However, mechanistic organic chemistry books indicate that the hydrogen substitution reactions would generally become more favoured over the chlorine addition reaction to the double bond as the temperature is raised. Thus the actual products may be dependent on the reaction conditions used, and so may be a mixture of chlorinated paraffins and chlorinated olefins.

In this respect, several studies included in the respective risk assessment reports for short-, medium and long-chain chlorinated paraffins have used various alkene feedstocks in order to synthesise chlorinated paraffins of known structure by gas-phase free-radical chlorination. The products from these reactions were chlorinated paraffins derived by chlorine addition across the double bond. The properties (water solubility, vapour pressures, accumulation behaviour and toxicity to fish) of these products were in line with those obtained for chlorinated paraffins produced by the chlorination of an alkane feedstock. Again, the properties of these products were

found to depend on the carbon chain length and degree of chlorination. This indicates that chlorinated alkenes, if produced in this manner, would be expected to be effectively indistinguishable from chlorinated alkanes in terms of the environmental behaviour and effects.

#### **4 Summary**

Euro Chlor has confirmed that there is no European manufacture of chlorinated alkenes. However, the CPIA have confirmed that they are produced in the United States (two manufacturers existed in 2005) The situation in Asia is unknown. The products formed from the chlorination of alkenes are expected to have a similar environmental hazard profile as the equivalent chlorinated paraffin. Their uses are unknown, but would be expected to be similar to the equivalent chlorinated paraffin as well.

# Appendix I Comparison of the mammalian toxicity of short-, medium- and long-chain chlorinated paraffins

## I1 Comparison of short-, medium and long-chain products

A detailed comparison of the known physico-chemical and toxicological properties of the three chlorinated paraffin categories is presented in Table I1. Concerning physico-chemical properties, all the categories of chlorinated paraffins are liquids at normal temperature and pressure, except for the LCCP C<sub>>20</sub> 70% Cl products which are solid. All have relatively low vapour pressure. All have relatively high log Kow values, which tend to increase with increasing carbon chain length. Water solubility tends to decrease with increasing chain length. These differences in log Kow and water solubility would suggest that the extent of systemic absorption of the longer chain chlorinated paraffins might be less (and therefore toxicity would be lower), but this prediction is not supported by the available toxicity information. The influence of the degree of chlorination on log Kow and water solubility cannot be determined from the information available.

Concerning toxicity, all short-, medium- and long-chain chlorinated paraffins that have been tested are of low acute toxicity and many can cause slight skin and eye irritation. Two tested short-chain products were not skin sensitisers, but one of two tested LCCP products had skin sensitising properties; no skin sensitisation data are available for the medium-chain substances.

Although N(L)OAELs for repeated dose toxicity for tested members of the three categories of chlorinated paraffins are generally similar, there are qualitative differences in the repeated exposure toxicity. The liver is the main target organ for the LCCPs whereas the kidney is the main target organ of relevance to humans for the short- and medium-chain products. Testing of all the categories of chlorinated paraffins for genotoxicity is limited; all the available tests are negative.

A short-chain product was carcinogenic in a rodent model (causing kidney tumours), although there are uncertainties regarding the relevance of this finding for humans. An LCCP product caused carcinogenicity in a rodent model (malignant lymphomas), but only at extremely high exposure levels. No medium-chain products have been tested for carcinogenicity.

Fertility studies have been conducted only on the medium-chain chlorinated paraffins, in which no evidence of effects was seen. No effects on the reproductive organs have been seen in the repeated dose toxicity studies conducted on members of all three categories of the chlorinated paraffins. No specific effects on development have been seen in conventional developmental toxicity studies conducted on short-, medium- or long-chain products. A medium-chain product caused maternal deaths at the time of parturition and deaths of neonatal offspring due to haemorrhaging resulting from low vitamin K levels; the potential to cause such effects has not been investigated for short- or long-chain chlorinated paraffins.

Overall, the data relating to investigated human/mammalian health endpoints for the three categories of product are generally similar, indicating that carbon chain length has little identifiable influence on toxicity. Thus, a read-across between the three classes has some justification.

However, any read-across needs to be conducted cautiously because some differences in the toxicity profiles have been identified, notably qualitative differences with respect to repeated dose toxicity and carcinogenicity and in skin sensitising potential. There is also no information on the influence of a product's chlorination state on its toxicity. Finally, as a category, the LCCPs have been defined with a wide range of carbon chain lengths (C<sub>18-30</sub>), but the toxicity of only those with lengths in the middle of the range has been investigated.

To account for these uncertainties any read-across predictions between the chlorinated paraffins have been conducted using conservative assumptions and additional assessment factors have been used in the risk assessment where appropriate.

## **I2 References**

ECB, 2000 *European Union Risk Assessment Report: Alkanes, C<sub>10-13</sub>, chloro*. Series: 1<sup>st</sup> Priority List, Volume 4. European Commission, Joint Research Centre, Institute for Health and Consumer Protection, European Chemicals Bureau.

ECB, 2007 *European Union Risk Assessment Report: Alkanes, C<sub>14-17</sub>, chloro*. Final draft human health assessment report of September 2007 for submission to SCHER. R331\_0907\_hh, European Commission, Joint Research Centre, Institute for Health and Consumer Protection, European Chemicals Bureau.

**Table I1 Summary of the available physico-chemical and toxicity data for the three categories of chlorinated paraffins**

<b>Property</b>	<b>SCCPs (C<sub>10-13</sub>)</b>	<b>MCCPs (C<sub>14-17</sub>)</b>	<b>LCCPs (C<sub>18-30</sub>)</b>
Physical state at normal temp/pressure	Liquid (49–70% CI)	Liquid (40–60% CI)	Liquid (C <sub>18-20</sub> ) Liquid (C <sub>&gt;20</sub> , 40–54% CI) Solid (C <sub>&gt;20</sub> , 70–72% CI)
Boiling point	> 200°C	> 200°C	> 200°C
Density	1.2–1.6 g/cm <sup>3</sup> (49–70% CI, 25°C)	1.1–1.3 g/cm <sup>3</sup> (40–50% CI, at 25°C)	1.1–1.6 g/cm <sup>3</sup> (at 20°C)
Vapour pressure	2.1x10 <sup>-2</sup> Pa (50% CI, 40°C)	2.7x10 <sup>-4</sup> Pa (52% CI, 20°C)	2.7x10 <sup>-4</sup> Pa (C <sub>23</sub> , 42% CI, 20°C)
Log Kow	4.4–6.9 (49% CI) 5.4–8.0 (71% CI)	5.5–8.0 (45% CI) 5.5–8.0 (52% CI)	7.63–>12.83 (42–49% CI)
Water solubility (at 20°C)	0.15–0.47mg/l (59% CI, 20°C)	0.005–0.027 mg/l (?% CI, 20°C)	0.003 mg/l (C <sub>25</sub> 42% CI, 16–20°C) 0.0059 mg/l (C <sub>25</sub> , 70% CI, 25°C)
Classification	Carc Cat 3 R40	No Annex 1 entry. R64, R66 proposed	No Annex 1 entry.
Toxicokinetics	Limited information. For oral route ~60% absorption, possibly greater for shorter chains and lower chlorination states. No inhalation or dermal data.	~50% absorption by oral and inhalation routes, 1% by dermal route. Preferential distribution to fatty tissues. Found in breast milk	Few data
Acute	Inhalation: 48 g/m <sup>3</sup> for 1 h, C <sub>7</sub> 50% CI: slight eye nose irritation Oral: very low toxicity; some signs of toxicity at 2 g/kg Dermal: no systemic toxicity at ~2.5 g/kg	Oral data only: very low toxicity; clinical signs at 15 g/kg	Oral data only. Number of studies conducted on C <sub>&gt;20</sub> , mainly 40–50% CI, available. Generally no evidence of toxicity reported. LD <sub>50</sub> >10 ml/kg
Irritation	C <sub>10-13</sub> , 59 & 63% CI: very slight skin and eye irritation	Slight skin and eye irritation (40–51% CI). Assumed to cause skin dryness or cracking on repeated exposure.	C <sub>19-30</sub> , various CI levels tested. Very slight skin and eye irritation
Sensitisation	C <sub>10-13</sub> , 50 & 56% CI negative	No data	C <sub>22-26</sub> , 42% CI: negative in GPMT. C <sub>18-27</sub> 40% CI: positive GPMT. C <sub>22-26</sub> : negative in Buehler

Table I1 continued overleaf

**Table I1** continued

Property	SCCPs (C <sub>10-13</sub> )	MCCPs (C <sub>14-17</sub> )	LCCPs (C <sub>18-30</sub> )
Repeated dose toxicity	Oral only, for C <sub>10-13</sub> , C <sub>12</sub> , C <sub>10-12</sub> 52–60% CI. Liver, thyroid identified as target organs in rodents, but these changes were considered unlikely to be relevant to humans. Reduction in bodyweight gain and increase in kidney weight considered relevant to human health: NOAEL 100 mg/kg in rats.	Oral only, for C <sub>14-17</sub> , 52% CI. Liver, thyroid, kidney target organs. Liver changes considered adaptive. Thyroid changes seen in rats considered to be not relevant to humans. NOAEL 23 mg/kg/day, based on kidney toxicity.	Oral only, standard studies are available for two LCCPs with 43% CI (either C <sub>22-26</sub> or C <sub>23av</sub> ) and for a 70% CI LCCP with C <sub>20-26</sub> . Liver identified as main target organ. Kidney, lymphatic system and eye also identified as possible targets. LOAEL of 100 mg/kg/day for the 43% CI product and a NOAEL of 900 mg/kg/day for the 70% CI product identified.
Genotoxicity	Data for 50–60% CI: Ames negative (C <sub>10-13</sub> , C <sub>12</sub> ); in vitro mammalian gene cell mutation negative (C <sub>10-13</sub> ); in vivo chromosome aberration negative (C <sub>10-12</sub> ), dominant lethal negative (C <sub>10-12</sub> )	Data for C <sub>14-17</sub> , 40 & 52% CI: Ames negative, in vivo bone marrow chromosomal aberration and micronucleus negative	Ames negative: C <sub>23av</sub> , 43% CI & C <sub>22-26</sub> , 42% CI. <i>In vitro</i> cytogenetics and SCE positive: C <sub>23</sub> , 43% CI. <i>In vivo</i> cytogenetics negative: C <sub>22-26</sub> , 43% CI & C <sub>20-26</sub> , 70% CI.
Carcinogenicity	Data for C <sub>12</sub> 60% CI: in rodents, increased incidence of tumours in liver, thyroid, kidney. The 1 <sup>st</sup> two considered to be not relevant to humans. Uncertainly regarding the relevance of the kidney tumours, hence Carc Cat 3 classification. Risk assessment assumed no risk of tumour development below the NOAEL for kidney toxicity	No data	Data for C <sub>23av</sub> , 43% CI Rat: marginal increase in adrenal medullary phaeochromocytomas in female rats from 100 mg/kg/day, not considered to be convincing evidence of carcinogenicity. Mice: increased incidence of malignant lymphoma in males at 5000 mg/kg/day, providing clear evidence of carcinogenicity; marginal increase in hepatocellular carcinomas in females at 5000 mg/kg/day, not considered to be convincing evidence of carcinogenicity.

Table I1 continued overleaf

**Table I1** continued

<b>Property</b>	<b>SCCPs (C<sub>10-13</sub>)</b>	<b>MCCPs (C<sub>14-17</sub>)</b>	<b>LCCPs (C<sub>18-30</sub>)</b>
Reproductive toxicity	No fertility studies, but reproductive organs not affected in RDT studies. Negative in rat (C <sub>10-13</sub> , 58% CI) and rabbit (C <sub>10-12</sub> , 58% CI) developmental toxicity studies	Most data are for C <sub>14-17</sub> , 52% CI. No effects on fertility. Maternal deaths at time of parturition at 538 mg/kg/day, due to reduced vitamin K levels. No effects in conventional developmental toxicity studies. Pup deaths at maternal doses of ~74 & 463 mg/kg/day, due to reduced vitamin K levels – NOAEL of 47 mg/kg/day identified.	No fertility studies, but reproductive organs not affected in RDT studies. Developmental toxicity studies: C <sub>22-25</sub> , 43% CI, C <sub>22-26</sub> : 70% CI rat negative C <sub>22-26</sub> , 43% CI, C <sub>22-26</sub> : rabbit, slight increase in implantation loss at 5000 mg/kg/day C <sub>22-26</sub> , 70% CI rat & rabbit negative
Main literature reference	European Union Risk Assessment Report for Alkanes C <sub>10-13</sub> , Chloro (ECB, 2000).	European Union Risk Assessment Report for Alkanes, C <sub>14-17</sub> , Chloro, draft (ECB, 2007).	This report.

Notes: SCCPs = short-chain chlorinated paraffins; MCCPs = medium-chain chlorinated paraffins; LCCPs = long-chain chlorinated paraffins.

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