Institute for Health and Consumer Protection

European Chemicals Bureau

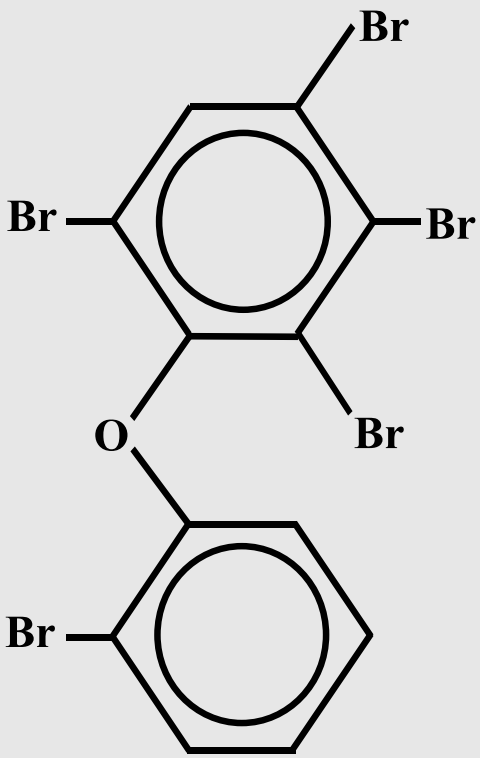
Existing Substances

European Union Risk Assessment Report

CAS No.: 32534-81-9

EINECS No.: 251-084-2

diphenyl ether, pentabromo deriv.



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DIPHENYL ETHER, PENTABROMO DERIVATIVE (PENTABROMODIPHENYL ETHER)

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RISK ASSESSMENT

Cataloguing data can be found at the end of this publication

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RISK ASSESSMENT

Final report, August 2000

United Kingdom

Rapporteur: United Kingdom

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Foreword

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

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

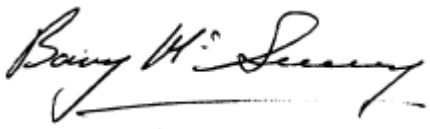
There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each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

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

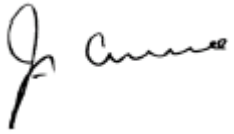
If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the "Rapporteur" to develop a proposal for a strategy to limit those risks.

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

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



Barry Mc Sweeney
Director-General
Joint Research Centre



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

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

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

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

0 OVERALL RESULTS OF THE RISK ASSESSMENT

CAS No 32534-81-9
EINECS No 251-084-2
IUPAC name Diphenyl ether, pentabromo derivative

Overall results of the Risk Assessment

The following conclusions relate to use of the substance as a flame retardant additive in polyurethane foams.

Environment

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

There is a data gap for toxicity to sewage microorganisms. However, a risk reduction strategy has been developed which proposes a restriction on the marketing and use of pentabromodiphenyl ether under Directive 76/769/EEC. If this strategy is adopted, then this testing requirement should be adjourned unless expert advice is provided which indicates that a test may be relevant to the controls which emerge from negotiations under Directive 76/769/EEC. A test on sewage treatment plant microorganisms would be required if this data gap were to be filled.

It is possible that in the long term levels in all compartments may increase as a result of releases from waste sites. No agreed methods for assessing this release currently exist in the Technical Guidance Document, but preliminary estimates have been incorporated into the assessment. These estimates are highly uncertain. This, and life-time exposure, may need to be considered further in any revision of this risk assessment report.

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

This conclusion applies to the assessment of risks to the aquatic compartment (surface water and sediment) and terrestrial compartment from regional sources, the assessment of risks to the aquatic compartment (surface water) from local sources, and the assessment of risks to the atmospheric compartment.

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

This conclusion applies to the assessment of secondary poisoning arising from use in polyurethane foams. High levels of pentabromodiphenyl ether have been both predicted and measured in fish and earthworms near to sources of release, and lead to a risk of secondary poisoning that is linked to local releases from foam production sites. A possible risk of secondary poisoning has also been identified at the regional level (linked to diffuse releases arising from use of the foam) for the earthworm-based food chain. The widespread environmental occurrence and bioaccumulative nature of the substance also lend support to the overall concern for this end-point. This conclusion also applies to the assessment of risks to the sediment and terrestrial compartment from local sources.

Human health effects

Occupational exposure

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

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

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

Conclusion (i) is reached because:

There are a considerable number of uncertainties regarding exposure data, the human health significance of the rodent liver effects and the bioaccumulative potential of this substance in humans. In addition, considerable uncertainties relate to the methods used to calculate the MOS. Further information, including the development of a suitable methodology for the risk assessment of bioaccumulative substances is required.

The information required is:

- Information is needed on the extent of dermal exposure in workers.

- The extent of dermal absorption (quantitative data) should be clarified by the conduct of an appropriate dermal absorption study using the substance (e.g. an *in vitro* study using human or pig skin); depending upon the outcome of this study (i.e. an indication of significant skin absorption) then it may be necessary to undertake an oral toxicokinetic study in order to provide adequate comparative information for interpretation of the oral dosing toxicity studies available.

- Health surveillance data are required to investigate signs of chloracne in workers.

- Further information should be obtained on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. A methodology should be developed to address this situation. This may involve the conduct of a lifetime study in rodents.

Consumer exposure

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

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

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

Conclusion (ii) is reached because risks to consumers from exposure to the substance are negligible since in the EU it is only used in polyurethane foam which is enclosed in products.

Indirect exposure via the environment

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

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

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

Conclusion (**i**) is reached because there are considerable uncertainties associated both with the toxicity data available and the approach to calculating the MOS for indirect exposure via the environment, and also with respect to the modelled exposure data used for local sources of exposure. Thus the uncertainties outlined for the worker risk assessment also apply to the exposure scenarios of regional and local sources of exposure. Consequently further information is required.

The information required is:

- Further information should be obtained on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. A methodology should be developed to address this situation. This may involve the conduct of a lifetime study in rodents.

- Information is required relating to actual measured exposure data from local sources.

Conclusion (ii) is reached for the potential development of a 'chloracne-like' response. Although a NOAEL cannot be identified from the available data, levels of exposure via local and regional sources are very low. It is, therefore, predicted that any risk to human health is likely to be minimal.

Combined exposure

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

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

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

The MOS values from the risk characterisation for both liver effects and behavioural effects are unacceptably low. The combined exposure is dominated by the occupational exposure. The estimates of both occupational exposure and exposure via the environment are derived from models. The estimates require revising either by refinement of the models or the provision of measured data in order to determine whether risk reduction measures should be considered. In addition, as described for workers, there is a need to obtain information on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. Hence **conclusion** (**i**) is reached.

Exposure to infants via milk

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

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

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

Conclusion (**i**) is reached for exposure via human breast milk because the MOS values calculated using the ADU_{infant}, NOAEL for liver effects and "LOEL" for differences in behaviour are clearly large being ~22 850-12 850 for polyBDPE and 84 000 – 47 360 for pentaBDPE. Normally such large MOS values would lead to little cause for concern and thus a **conclusion** (**ii**) under the Regulation. However, it is important to consider the interpretation of the MOS values in light of the state of scientific knowledge and uncertainties in the analysis. The estimates of ADU_{infant} are based on measurements of polyBDPE in human breast milk and numerous assumptions regarding the pentaBDPE content, the feeding infant and regarding the significance of toxicological endpoints of concern to the neonate (detailed in section 4.1.3.5.1).

It is clear that a considerable amount of uncertainty remains with respect to this risk assessment. Thus although large MOS values were calculated the uncertainties are such that it is currently not possible to say whether or not these MOSs provide reassurance of little or no risk to the breast feeding infant either at the present time or in the future. However, much of the uncertainty could be reduced by the gathering of further information and thus for exposure of infants via breast milk **conclusion** (**i**) is reached on a technical basis.

The following information is required:

- information on the toxicokinetics of pentaBDPE with respect to breast milk including uptake from breast milk into the infant, the time course of the excretion via breast milk during lactation in humans and the future trends in levels in human breast milk;

- information on the relative toxicity to the liver of pentaBDPE in young (neonatal) and adult animals;

- further studies on potential effects on behaviour following neonatal dosing in order to determine the reproducibility of effects, the effects of repeated dosing and the significance of the effects to human development;

- a multi-generation reproduction study in order to investigate whether or not other effects might be observed through exposure to breast milk. Designed correctly, such a study could address the issue of whether or not the young animal is more sensitive to liver effects and whether or not differences in behaviour are produced.

It is noted, however, that much of the information required above (and for other areas of the risk assessment such as the need for a long term toxicity study) would take some considerable time to be generated or gathered. There is evidence that pentaBDPE is highly persistent, bioaccumulative and of particular note has been detected, albeit at relatively low levels, in human breast milk, the levels increasing with time. These properties and data are of concern in themselves, although with the available information it is not possible to say whether or not

on a scientific basis there is a current or future risk to human health. However, given these properties, it would be of concern if once the further information had been gathered the analysis indicated a risk to breast feeding infants.

Thus, although it is concluded that further information should be gathered in order to refine the risk assessment, in light of the properties of pentaBDPE and the time it would take to gather the information, consideration should be given at a policy level of the need to take risk reduction measures now in the absence of adequate scientific knowledge and thus the need for consideration of risk reduction options at this time.

For infants fed cows' milk: the concern for risks to infants from exposure via cows' milk is likely to be similar to or greater than that from exposure to human breast milk. The risk characterisation is subject to the same uncertainties as those described for human breast milk, but in addition the exposures used are modelled estimates rather than measured values. In addition to some of the information required for the risk characterisation of infants exposed to human breast milk, the exposure estimates for cows' milk from local and regional sources should be investigated further in order for the risk characterisation to be refined.

Risks to human health from physico-chemical properties

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

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

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

Conclusion (ii) is reached because there are no risks from physico-chemical properties ising from the use of the substance.

Results of discussion at policy level

Following the agreement of the risk assessment conclusions reached on a technical basis as presented in this report, Member States noted the uncertainties expressed regarding the risk characterisation for infants exposed to pentabromodiphenyl ether from human breast milk (section 4.1.3.5.1). They also noted the conclusion that further information would be required to remove these uncertainties and refine the risk assessment. Member States were concerned that it would take a significant time to gather the information and that the resulting refined risk assessment could then indicate a risk to breast-feeding infants. Furthermore, the bioaccumulative properties of the substance could cause concentrations in breast milk to rise while the data was being gathered. Consequently Member States agreed that risk reduction measures should be considered without delay for the sources of this exposure. In the light of this agreement and as a consequence of the environmental risk assessment, a risk reduction strategy for this substance has been developed. This strategy proposes a restriction on the marketing and use of pentabromodiphenyl ether under Directive 76/769/EEC. If this strategy is adopted, then the proposed testing requirements listed under the **conclusion** (**i**) in section 3.3.1.3 and 4.1.3.5.1 should be adjourned in the interests of animal welfare and cost vs.benefit unless expert advice is provided which indicates that tests may be relevant to the controls which emerge from negotiations under Directive 76/769/EEC.

CONTENTS

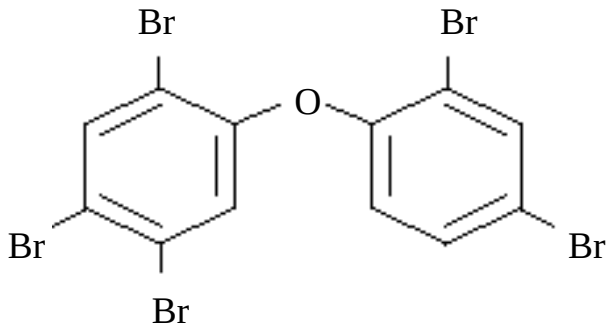
TABLES

1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

This assessment considers the following commercial substance:

CAS N.:	32534-81-9
EINECS N.:	251-084-2
IUPAC name:	Pentabromodiphenyl ether (diphenyl ether, pentabromo derivative)
Molecular formula:	$C_{12}H_5Br_5O$
Molecular weight:	564.7
Structural formula:	2,2',4,4',5-pentabromodiphenyl ether (example component)



Three polybrominated diphenyl ether flame retardants are available commercially. They are referred to as penta-, octa- and decabromodiphenyl ether, but each product is a mixture of diphenyl ethers with varying degrees of bromination. This assessment is specifically about pentabromodiphenyl ether. Information on other brominated diphenyl ethers is included where it is relevant to the assessment of this substance. Risk assessment reports for the other two commercially produced substances have been prepared separately under the Regulation.

Various synonyms and abbreviations for polybrominated diphenyl ethers exist and these are shown below:

polybrominated biphenyl ethers ≡	polybromobiphenyl ethers	-	PBBEs
polybrominated biphenyl oxides ≡	polybromobiphenyl oxides	-	PBBOs
polybrominated diphenyl ethers ≡	polybromodiphenyl ethers	-	PBDPEs
polybrominated diphenyl oxides ≡	polybromodiphenyl oxides	-	PBDPOs

Often a further letter is added to the beginning of the abbreviation to indicate the degree of bromination, for example:

pentabromodiphenyl ether ≡	PeBBE ≡	PeBBO ≡	PeBDPE ≡	PeBDPO ≡	PentaBDPE
octabromodiphenyl ether ≡	OBBE ≡	OBBO ≡	OBDPE ≡	OBDPO ≡	OctaBDPE
decabromodiphenyl ether ≡	DBBE ≡	DBBO ≡	DBDPE ≡	DBDPO ≡	DecaBDPE

Other synonyms include pentabromophenoxybenzene and benzene, 1,1'-oxybis-, pentabromo derivative. Unless otherwise stated, the term pentabromodiphenyl ether or the abbreviation pentaBDPE will be used in this report to refer to the commercially available product. Individual components will be identified more specifically where appropriate.

Commercially available pentaBDPE is not a pure substance but is instead a mixture of congeners (see section 1.2.1). The name pentabromodiphenyl ether denotes the main component of the mixture. Although the actual composition of commercially available pentaBDPE varies between manufacturers, it is felt that information available in most instances for one mix are comparable for all, and together enable a representative profile of pentaBDPE exposure and response to be drawn. DE-71, Bromkal 70 and Satyex 115 are representative commercial mixes of pentaBDPE although details of the percentage content of the different isomers are not available. The commercial products Bromkal 70 and Saytex 115 are no longer in production or supplied to the EU.

1.2 PURITY/IMPURITIES, ADDITIVES

1.2.1 Purity

The specification may vary, but is generally:

Pentabromodiphenyl ether	(CAS No 32534-81-9)	50-62% w/w
Tetrabromodiphenyl ether	(CAS No 40088-47-9)	24-38% w/w

Additionally, each congener will exhibit a number of isomeric forms, although it is not clear which, or in what proportion, and whether this will alter depending on the supplier/manufacturing process.

The significant impurities (where stated) comprise some or all of the following:

Tribromodiphenyl ether	(CAS No: 49690-94-0)	0-1% w/w
Hexabromodiphenyl ether	(CAS No: 36483-60-0)	4-12% w/w
Heptabromodiphenyl ether	(CAS No: 68928-80-3)	trace

The identity of some of the components of commercial pentabromodiphenyl ethers have been established by various techniques. Sondack et al (1993) analysed a commercial pentaBDPE and identified 2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether as the two major components by NMR. The same two isomers, along with a third pentabromodiphenyl ether, were identified in a sample of the commercial pentaBDPE Bromkal 70-5-DE. The approximate composition of this product was 41% 2,2',4,4'-tetrabromodiphenyl ether, 45% 2,2',4,4',5-pentabromodiphenyl ether and 7% of an unknown pentabromodiphenyl ether (Sundström and Hutzinger, 1976). Later, de Boer and Dao (1993) determined the concentration of 2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether in a similar commercial pentabromodiphenyl ether product (Bromkal 70 DE) as 36.1% and 35.5% respectively by reference to pure samples of the two isomers. The unknown pentabromodiphenyl ether isomer present in these products has recently been identified as 2,2’,4,4’,6-pentabromodiphenyl ether (Sellström et al, 1998).

Another commercial pentaBDPE product (Tardex 50) was reported to consist of 25-35% tetrabromodiphenyl ethers, 55-70% pentabromodiphenyl ethers, 0-5% hexabromodiphenyl ethers and 0-1% heptabromodiphenyl ethers. It was reported that the tetra-, hexa- and heptabrominated components were all solids and the commercial product could be thought of as a solution of these solids in the liquid pentabromodiphenyl ether.
It was also reported that an upper limit was set on the amount of tetrabromodiphenyl ethers in the product in order to prevent crystallisation of the product (Prescott, 1978).

1.2.2 Additives

The commercially available form of this substance has no stated additives.

1.3 PHYSICO-CHEMICAL PROPERTIES

The physico-chemical properties of pentaBDPE are shown in **Table 1.1**.

Table 1.1 Physico-chemical properties of commercial pentabromodiphenyl ethers

Property	Value
Chemical formula	$C_{12}H_5Br_5O$
Molecular weight	564.7 (70.8% bromine by weight)
Melting point	-7 to -3°C (commercial product)
Boiling point	Decomposes at >200°C (commercial product)
Relative density	2.25-2.28 (commercial product)
Vapour pressure	$4.69 \cdot 10^{-5}$ Pa (commercial product)
Water solubility	13.3 µg/l (commercial product) pentabromodiphenyl ether component = 2.4 µg/l tetrabromodiphenyl ether component = 10.9 µg/l
Log octanol/water partition coefficient (K_{ow})	6.57 (measured; commercial product) 7.88 (calculated)
Flammability	Not applicable - flame retardant
Autoflammability	Decomposes above 200°C (commercial product)
Explosive properties	None
Oxidising properties	None
Viscosity	Highly viscous at room temperature (circa $2 \cdot 10^6$ cps at 25°C). Varies between manufacturers
Conversion factor	1 ppm = 23.48 mg/m³ at 20°C

Commercial pentaBDPEs are mixtures. Some of the physico-chemical properties have been derived for the mixture as a whole and some have been derived for the pentabromodiphenyl ether components of the mixture. Wherever possible, this distinction is made in **Table 1.1.** Appendix E considers further the possible variability of some of these data and how they might influence the environmental modelling and resulting predicted environmental concentrations of this substance.

1.3.1 Physical state (at n.t.p)

Technical pentaBDPE is an amber viscous liquid or semi-solid at 20°C and 101.325 kPa. Pure pentaBDPE is reported to be a white crystalline solid.

1.3.2 Melting point

The melting point of pentaBDPE has been reported as -7 to -3°C (WHO, 1994). Original test reports have not been submitted and so it is not possible to comment on the validity of the data.

1.3.3 Boiling point

No boiling point is available. It decomposes in the temperature range 200-300°C. Also, since the commercial substance is a mixture, it would be expected to exhibit a wide temperature range for decomposition. This particular physico-chemical parameter is not really applicable to this type of substance (WHO, 1994).

1.3.4 Density

The relative density (D_4^{25}) of commercial pentaBDPE is quoted as 2.25 (Dead Sea Bromine Group), 2.27 (Albemarle, 1994) and 2.28 (WHO, 1994). A value of 2.25-2.28 is taken to be representative in the absence of any further information.

1.3.5 Vapour pressure

The vapour pressure of the substance has been measured as $4.69 \cdot 10^{-5}$ Pa at 21°C using a spinning rotor gauge in a GLP study (Stenzel and Nixon, 1997). The technical specification for the instrument used indicates that the low end of the recommended measurement range is $1 \cdot 10^{-5}$ and so the measured value is within the designed range of the instrument.

The material tested was a composite sample from three manufacturers and had the following composition: 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether. The method used is not able to separate the contributions of the individual components to the total vapour pressure and so is likely to represent the vapour pressures of the more volatile components present. Thus the value can be considered the upper limit to the vapour pressure of pure pentabromodiphenyl ether.

Watanabe and Tatsukawa (1990) determined the vapour pressures for a range of brominated diphenyl ethers at 25°C using a GC technique. No information was given as to the actual composition of the substances tested, however, the method is based on the determination of GC retention times under specific chromatographic conditions and so if the substances are mixtures of isomers, as is very likely to be the case, a range of retention times and hence vapour pressures will be obtained from the method. For pentaBDPE, a vapour pressure of $2.9\text{-}7.3 \cdot 10^{-5}$ Pa was determined. This value is in good agreement with the value obtained above. The vapour pressure was found to increase as the degree of bromination decreased (see Section 3.1.0.5.1).

The vapour pressure of commercial pentaBDPE has also been reported, without supporting evidence, as $<1.33 \cdot 10^{-7}$ kPa (temperature not stated; USEPA, 1986). A value of 9.3 mmHg at 20°C is quoted in WHO (1994), but this value is almost certainly incorrect when compared to the more recent data on substances of known composition.

A value of $4.69 \cdot 10^{-5}$ Pa will be used for the vapour pressure in the environmental assessment.

1.3.6 Solubility

The water solubility of pentaBDPE has recently been determined using a generator column method carried out according to the principles of Good Laboratory Practice (GLP) (Stenzel and Markley, 1997).

In this study a composite sample of pentabromodiphenyl ether from three producers was used (composition was 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether). In the test, the commercial pentabromodiphenyl ether (302.2 mg) was dissolved in ethyl acetate and added to a round-bottom flask containing 72.2 g of glass beads. The solvent was removed on a rotary evaporator at 49^{o}C in order to coat the glass beads with the test substance. Water (20 ml) was then added to the beads and the slurry was used to fill the generator column. Water was then pumped through the column at 0.5 ml/minute and the effluent was collected (50 ml samples). After 121 consecutive 50 ml samples had been obtained, the flow rate was reduced to 0.25 ml/minute and 50 ml effluent samples were again collected. Analysis of the column effluent samples was carried out by gas chromatography with electron capture detection (GC-ECD). Under the chromatographic conditions used, the pentabromodiphenyl ether and tetrabromodiphenyl ether components of the commercial mixture both gave two peaks. Quantification was carried out for both the pentabromodiphenyl ether and tetrabromodiphenyl ether components separately using standard solutions of the commercial pentaBDPE prepared in diphenyl ether solvent (in this approach the above composition of the commercial product was assumed in order to construct a calibration curve for the two components).

Such a calibration method requires the composition of the substance in test water to be the same as it is in the calibration standards in order for the method to accurately reflect the concentration of the commercial substance. Example chromatographs are given in the report and these show that there is a small change in the relative magnitude of the two tetrabromodiphenyl ether peaks in the example trace from some, but not all, of the test solutions compared to the standard solutions. This indicates that one of the tetrabromodiphenyl ether components may have slightly higher water solubility than the other. However, in terms of determining the total water solubility of the tetrabromodiphenyl ether components the method used will give accurate results provided the two tetrabromodiphenyl ether components give a similar detector response, which is likely to be the case with the ECD.

The mean total water solubility was found to be 13.3 µg/l, based on the sum of the solubilities of the two main components, pentabromodiphenyl ether (2.4 µg/l) and tetrabromodiphenyl ether (10.9 µg/l).

The water solubility of pentaBDPE has also been quoted as <0.6 µg/l at 25^{o}C (USEPA, 1986) and $9 \cdot 10^{-7}$ mg/l at 20^{o}C (original reference not indicated). The purity of the substance used was not stated.

A water solubility of 2.4 µg/l will be used for environmental modelling purposes.

Solubility in other solvents:	Methanol	1g/100g
	Methylene chloride	completely miscible
	Toluene	completely miscible
	Dioctylphthalate	>100g/100g
	Freon 11	completely miscible
	Polyol	completely miscible
	Styrene	completely miscible
	Methyl ethyl ketone	completely miscible

1.3.7 Octanol-water partition coefficient (log K_{ow})

A log K_{ow} of 7.88 (calculated; USEPA, 1986) is quoted, although the theoretical basis for the calculated value or the original evidence have not been evaluated. Watanabe and Tatsukawa (1990) gave a value of 6.46-6.97 using a HPLC technique.

A similar value of 6.57 has recently been measured at 25^{o}C using a generator column method (GLP study; MacGregor and Nixon, 1997). In this study, a composite sample from two current suppliers was used as the test substance and had the following composition: tetrabromodiphenyl ether 33.7%; pentabromodiphenyl ether 54.6%; and hexabromodiphenyl ether 11.7%. A stock solution of the test substance was prepared by dissolving 100 mg in 25 g of octanol followed by centrifuging and filtering to remove any undissolved test material (the actual concentration of the test substance in the octanol was determined by analysis). The octanol solution (15 ml) of the test substance was added to a generator column containing an inert support material. Water that had previously been saturated with octanol was then pumped through the column at a rate of 1 ml/minute and sample collection commenced after 1 hour to allow equilibration of the system. Three separated ~250 ml samples of effluent water were collected from the column and analysed for the presence of the test substance.

The analytical method used was gas chromatography with electron capture detection (GC-ECD). Calibration of the method was by standard solutions of the commercial pentaBDPE mixture made up in diphenyl ether solvent. The sum of the areas of the peaks corresponding to the penta- and tetrabromodiphenyl ether components was used for quantification. Such a calibration/quantification method requires the composition of the substance in test water to be the same as it is in the calibration standards in order for the method to accurately reflect the concentration of the commercial substance. Example chromatographs are given in the report and these allow the following ratios for the peak heights (the peak areas are not reported, so the estimated peak heights have to be used for this comparison) for the main tetra- and pentabromodiphenyl ether components to be compared: low-level calibration standard penta:tetra 1.53:1; high-level calibration standard penta:tetra 1.55:1; 0.2 µg/l matrix fortification standard penta:tetra 1.71:1; 5 µg/l matrix fortification standard 1.79:1; test aqueous solution penta:tetra 1.06:1. From these ratios it can be seen that the relative concentrations of the two main components of the commercial pentaBDPE used for quantification differs in the aqueous test solution (column effluent) compared with the standards. This example effluent sample has an enhanced tetrabromodiphenyl ether component compared with the pentabromodiphenyl ether component. This indicates that the octanol-water partition coefficients for the tetrabromodiphenyl ether components are lower than for the pentabromodiphenyl ether components, as would be expected. It is not possible from the data reported to estimate separate octanol-water partition coefficient values for the penta and tetrabromodiphenyl ether components. However, given that the enhancement seen

in the chromatographic peak height for the tetrabromodiphenyl ether component of the aqueous effluent samples compared to the standard solutions is relatively small, the actual difference in the log K_{ow} value between the two main components is also expected to be small. This is born out in the results obtained by Watanabe and Tatsukawa (1990) using the HPLC method where log K_{ow} values of 5.87-6.16 for the tetrabromodiphenyl ethers were determined.

A log K_{ow} value of 6.57 will be used in the assessment.

1.3.8 Flash point

The substance is used as a flame retardant, and so this parameter is not relevant. The substance does not have a flash point.

1.3.9 Autoignition

This material does not undergo autoignition but decomposes at elevated temperatures (200->300^{o}C). The decomposition properties are consistent with the use of this material as a flame retardant.

1.3.10 Explosivity

Explosive properties are not expected on the basis of chemical structure and physical properties. PentaBDPE is not known to exhibit explosive properties with other materials.

1.3.11 Oxidising properties

Testing for this property is not applicable due to the physical nature of this substance (semi-solid or viscous liquid). Commercial pentaBDPE does not contain any substance with structural alerts for oxidising effects. PentaBDPE is therefore not considered to be an oxidiser.

1.3.12 Granulometry

Not applicable - the technical substance is a liquid.

1.3.13 Surface tension

No value could be found for surface tension of an aqueous solution. As the solubility is less than 1 mg/l, this is not part of the base set requirement.

1.3.14 Other physico-chemical properties

The viscosity is quoted as >2,000,000 cps at 25^{o}C and 220 cps at 70^{o}C (Albemarle, 1997). The viscosity will depend on the origin and composition of any commercial material. WHO quote a value of 150,000 cps at 25^{o}C although no further details of the origin of this value are known.

The Albemarle (1997) value will be used as it is from an industry data sheet. However, the uncertainty in the WHO value may be a reflection of transcription errors or relate to a specific product from the manufacturer. Viscosity may reflect the presence of impurities in products that vary between manufacturers.

1.3.15 Hazardous chemical reactions

When pyrolysed at up to 900^{o}C, pentaBDPE releases brominated dibenzofurans and dibenzo-*p*-dioxins, in common with other brominated diphenyl ethers.

1.4 CLASSIFICATION

1.4.1 Current classification

Pentabromodiphenyl ether was not previously listed in Annex I to Directive 67/548/EEC. However, the proposed classification indicated below (section 1.4.2) has now been adopted by EU Member States and pentaBDPE will be listed in Annex I to Directive 67/548/EEC with this classification.

1.4.2 Proposed classification

The proposed classification and labelling for human health is:

Xn; R48/21/22 R64

The text of R48/21/22 is: *"Harmful: danger of serious damage to health by prolonged exposure in contact with the skin or if swallowed"*.

The text for R64 is: *"May cause harm to breast fed babies"*.

The proposal is based on evidence for effects in the liver of rats exposed in the diet to a commercial preparation of pentaBDPE. At 2 mg/kg/day in a 90-day study, the effects observed were marginal in nature. However, at 10 mg/kg/day there was evidence for functional disturbance, with two-fold increases in liver porphyrin levels, accompanied by increases in liver weight and histopathological changes of uncertain character in enlarged parenchymal liver cells of both sexes. At 100 mg/kg/day (the next highest dose used) the liver disturbance was more pronounced, including a 400-fold increase in liver porphyrin levels. Overall, it is predicted that the effect on rat liver at the cut-off for application of R48/22 would constitute serious damage to health. In the absence of data on human responsiveness to pentaBDPE, and the uncertainty surrounding the underlying mechanisms of the liver effects seen in the rodents, there is no reason to discount the relevance of the rodent observations in relation to human health.

The proposal from R48/21 is based on evidence of a 'chloracne-like' response following repeated dermal exposure, in the rabbit ear model. Although there is no information regarding the dose-response for this effect, the nature of the dermal reaction induced is considered to present a potentially serious human health concern.

R64 was assigned by Member States in view of concerns about the biopersistent nature of pentaBDPE, its systemic toxicity following repeated oral and dermal exposures, and observations of pentaBDPE in human breast milk.

The proposed classification for the environment is:

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

This proposal is based on the toxic effects seen in a 48-hour *Daphnia* study (EC_{50}= 14 µg/l), the lack of biodegradation seen in standard tests and the high bioconcentration factors measured for components of the commercial formulation.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

2.1.1 Production volumes

Production of pentaBDPE ceased in the EU in 1997.

Information on the production of polybrominated diphenyl ethers in general is given in the Environmental Health Criteria document on brominated diphenyl ethers (WHO, 1994). In this report it was stated that there were eight producers of polybrominated diphenyl ethers (penta-, octa- and/or deca-) in the world, although industry indicate that there are nine producers world-wide.

The annual world-wide production of all polybrominated diphenyl ethers has been estimated as 40,000 tonnes/year, which was broken down as 30,000 tonnes (i.e. 75%) of decabromodiphenyl ether, 6,000 tonnes (i.e. 15%) of octabromodiphenyl ether and 4,000 tonnes (i.e. 10%) of pentabromodiphenyl ether (KEMI, 1994).

WHO (1994) gave production figures for the EU and these are reproduced in **Table 2.1**. The figures refer to total polybrominated diphenyl ethers.

Table 2.1 Production of total polybrominated diphenyl ethers in the EU (WHO, 1994)

Year	Production (tonnes)
1986	4,276
1987	3,624
1988	4,066
1989	3,843

2.1.2 Production methods

Pentabromodiphenyl ether was produced in the EU by the direct bromination of diphenyl ether using a Friedel-Crafts catalyst. PentaBDPE is a viscous liquid or semi-solid at ambient temperature and is supplied drummed as either the pure product or blended with a synergist.

2.2 USE

2.2.1 Quantities used

WHO (1994) gave import figures for the EU and these are reproduced in **Table 2.2**. The figures refer to total polybrominated diphenyl ethers. It is thought that the major compound imported at the time was decabromodiphenyl ether (see ESR assessment of that substance).

Table 2.2 Import figures for total polybrominated diphenyl ethers in the EU

Year	Imports (tonnes)
1986	4,310
1987	3,492
1988	4,955
1989	7,103

The combined import and production figure for the EU (i.e. the total EU consumption) of all polybrominated diphenyl ethers was 10,946 tonnes/year in 1989 (WHO, 1994). An industry source gave a very similar figure for current EU usage of total polybrominated diphenyl ethers as 10,000-11,000 tonnes/year.

Assuming that pentaBDPE accounts for 10% of the total EU usage of polybrominated diphenyl ethers (see Section 2.1.1), it can be estimated that around 1,100 tonnes of pentaBDPE are used each year in the EU.

WHO (1994) gave figures for the use of polybrominated diphenyl ethers in several European countries. These figures are reproduced in **Table 2.3** and refer to total polybrominated diphenyl ethers. It is not known to what year these figures relate.

Table 2.3 Quantities of polybrominated diphenyl ethers used in some European countries (WHO, 1994)

Country	Quantity used
Germany	3,000-5,000
Sweden	1,400-2,000[a]
The Netherlands	2,500-3,700
United Kingdom	up to 2,000

[a]Figures refer to total brominated flame retardants

As can be seen from **Table 2.3**, up to 5,000 tonnes of polybrominated diphenyl ethers are used in any one EU country. Assuming that this use is made up of 10% pentaBDPE, then the usage figure for an EU country can be estimated at up to 500 tonnes/year pentaBDPE. This figure is reasonably consistent with the data reported for the Netherlands, where around 350 tonnes/year of pentaBDPE were thought to be used as a flame retardant (Klingenberg, 1989).

Information provided by industry indicates that there has been a decline in the import and hence usage of pentaBDPE in the EU in recent years. Imports were <500 tonnes/year in circa 1997 and <300 tonnes/year in 1998. This latter figure will be used in the assessment when considering the processing of pentaBDPE. However, there is also the possibility of pentaBDPE entering the EU in finished articles, and so the actual amount of pentaBDPE present at any one time in the EU could be higher than this figure, although the actual figure is unknown and very difficult to estimate.

Further information on the amounts of pentaBDPE used in the EU has recently become available. Industry has indicated that the EU consumption has fallen further to <150 tonnes/year in 1999. As part of the work on the risk reduction strategy for this substance,

the current level of use in the EU has been determined to be around 100-125 tonnes/year, with a similar amount being estimated to be imported into the EU in finished goods (DETR, 2000). However, since higher amounts appear to have been used in the recent past, and the usage could in theory increase again in the future, the assessment is based on a total amount of 1,100 tonnes/year of the substance being present in articles in the EU. It is important to take this into account in the assessment as articles containing pentaBDPE may be used over relatively long periods of time and so could act as sources of release over several years. Thus yearly fluctuations in the amounts used or imported in articles are less important to the assessment than a realistic estimate for the current potential overall market. However, since data are scarce, particularly on the amounts of pentaBDPE imported into the EU in finished articles, this necessarily introduces some uncertainty into the assessment.

2.2.2 Uses

2.2.2.1 General

Pentabromodiphenyl ether is a flame retardant of the additive type, i.e. it is physically combined with the material being treated rather than chemically combined (as in reactive flame retardants). This means that there is the possibility that the flame retardant may diffuse out of the treated material to some extent. Phosphorus derivatives are generally used with pentaBDPE in polyurethane foams.

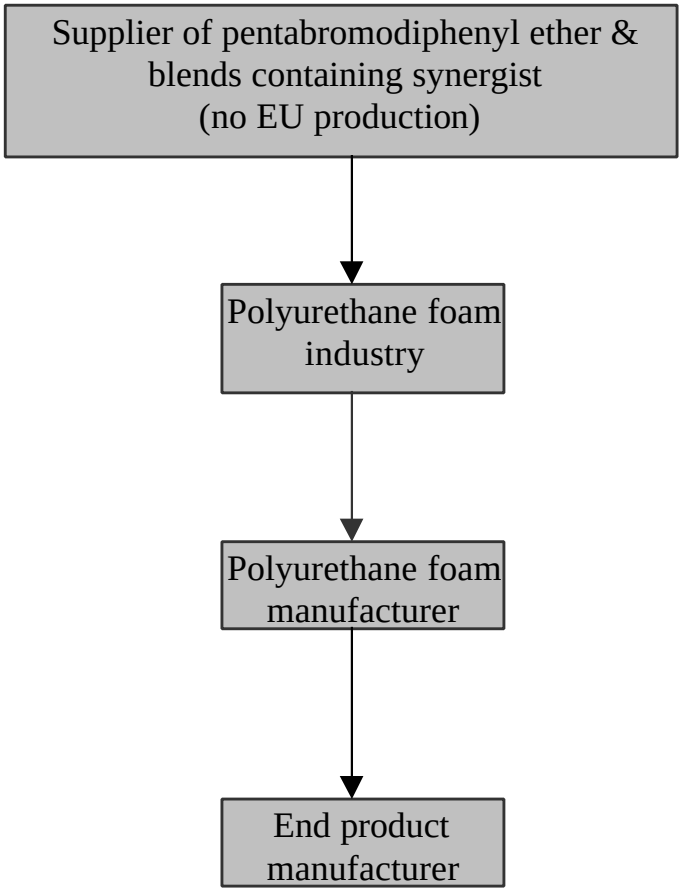
The amount of flame retardant used in any given application depends on a number of factors such as the flame retardancy required for a given product, the effectiveness of the flame retardant and synergist within a given polymer system, the physical characteristics of the end product (e.g. colour, density, stability, etc.) and the use to which the end product will be put. Typically, the flame retardants are added at concentrations between 5 and 30% by weight (i.e. 1 kg of polymer would contain 50-300 g of flame retardant) (WHO, 1994).

Information on the exact uses of pentaBDPE is difficult to find. It appears that the major use is as a flame retardant additive in flexible polyurethane foam for furniture and upholstery (DoE, 1992). Other reported uses include as a flame retardant additive in epoxy resins, phenolic resins, unsaturated polyesters and textiles (WHO, 1994).

Four main uses of polyurethane containing pentaBDPE have been identified in the EU (DETR, 2000). Around 95% is used in the manufacture of flexible polyurethane foams. These are used: a) in foam-based laminated automotive applications such as headrests; b) for domestic furniture, some of which includes cot mattresses; and c) in foam-based packaging. A small amount is used in the production of various small run components such as rigid polyurethane elastomer instrument casings.

For the purpose of this assessment, it will be assumed that all of the pentaBDPE used in the EU is for polyurethane foam. This is in line with the current use pattern provided by Industry. It was not possible to obtain information on the use of the total volume of substance imported into the EU from all sources, and so some uses may exist which are not covered by this risk assessment. It *is* known that use of pentaBDPE for textile applications no longer occurs in the EU. This and other (possibly historic) uses are considered further in Section 2.2.2.3.
Figure 2.1 shows the life-cycle of pentaBDPE in the EU. There is a lack of information regarding the actual amounts of pentaBDPE used in the various applications in the EU.

Figure 2.1 The life-cycle for pentabromodiphenyl ether in the EU (personal communication)



2.2.2.2 Polyurethane foams

Polyurethanes are step addition polymers made by reacting isocyanate compounds with compounds containing active hydrogen groups, usually hydroxyl groups, on the ends of long polyether or polyester chains. The isocyanate groups can also react with water to form carbon dioxide and this reaction is used as the principle source of gas for blowing the foam, as well as a source of heat for the expansion and curing of the foam. Other blowing agents may also be added to the foam. The density of the foam can be progressively reduced by increasing the water content of the formulation and adding sufficient isocyanate to react with it. This also leads to a stiffening of the polymer and so the density of the foam can be reduced without greatly reducing the load-bearing properties of the foam. However, the exothermic heat of reaction effectively limits the amount of water in the formulation to about 4.6-5.5 parts of water to 100 parts of the polyether polyol, depending on the scale of manufacture, rate of heat dissipation, amount of excess isocyanate present and many other factors.

Since the foam product is a good insulator, overheating of the foam can sometimes occur due to the heat release from reactions during its production and/or curing (for instance excess isocyanate in the foam could react with atmospheric moisture during curing, releasing heat). In some situations, the temperature of the interior of the foam can rise until the polyether chains begin to oxidise and produce more heat.

In extreme cases, the foam may spontaneously ignite. The first sign of overheating is the formation of a yellow-brown discolouration in the centre of the foam. Typically, antioxidants are added to the polyether polyols used in flexible foam production to minimise these "scorch" effects (Woods, 1982). The most common type of halogenated flame retardants used in polyurethane foams appear to be halogenated phosphorus based chemicals. However, these types of flame retardant can contribute to scorch problems, particularly in some low density flexible foams. PentaBDPE does not appear to suffer from some of these problems and so is sometimes used in flexible polyurethane foams. PentaBDPE is normally used in some flexible polyurethane foams as an admixture with aromatic phosphate esters (Larsen and Ecker, 1988; Rose and Hughes, 1982).

Flexible polyurethane foams can be manufactured in continuous or batch processes, with cross-sections of up to about 2.2 m wide by 1.25 m high. In a typical process the initial ingredients (mainly water, isocyanate, polyether polyols and any other additive such as a flame retardant) are mixed together at around 20^{o}C and placed into a mould. There then follows an induction period ("cream time") before bubbles appear and the foam begins to rise. The maximum temperature in the system occurs 30 minutes to 1 hour after the end of the foam rise, with the internal temperature remaining near this maximum temperature for 1-8 hours, depending on the block size. In a typical low density foam, the temperature of the interior could be around 160^{o}C. The foam is then left to cure for around 48 hours (Woods, 1982).

Slabstock foam is usually made by continuously metering all the foam reactants to a mixing head, where they are mechanically mixed and immediately applied to the bottom lining of a continuously moving trough formed by a horizontal bottom paper or foil and two vertical side papers or foils. If the top of the foam is unrestrained, a continuous "domed" block is formed. As the final users usually require foam in sheets of uniform thickness, a domed top is often undesirable as it increases the amount of scrap foam during trimming. Several processes are used in order to reduce this effect such as: a) constraining the rise of the foam by using a paper or foil on the top of the mould; b) distributing the foam mixture onto a shaped base plate that allows foam to expand downwards; c) using a vertical process (Woods, 1982). Continuous foaming machines can produce polyurethane foam at rates up to 500 kg/minute. The density of the foam produced is generally in the range 10-60 kg/m^3, with most being in the range 15-27 kg/m^3 (Woods, 1982).

It has been estimated that 120,000 tonnes of polyurethanes are used in the United Kingdom each year. Of this, 30% (36,000 tonnes) is thought to be used in furniture and 18% (21,600 tonnes) is used in automotive applications (UCD, 1994). These are likely to be the major uses of flexible polyurethane foams in the United Kingdom and the EU in general. Some of this flexible foam is likely to contain flame retardants, but many different types of flame retardant could be used. It is not known what fraction of this foam will contain pentaBDPE.

There are two sectors of industry to be considered for the polyurethane industry:

a) ***Polyurethane foam producers.*** Companies producing polyurethane foam incorporate pentaBDPE during the manufacture of the foam.

b) ***End product manufacturers.*** The polyurethane foam is supplied to end product manufacturers, where it is used in, for example, domestic and automotive furniture. End product manufacturers may carry out hot wire cutting of polyurethane foam.

Due to the extensive use of flame retardants in polyurethane foam there are potentially tens of thousands of workers exposed during manufacture. However, there are many different flame retardants used and suppliers did not report pentaBDPE's share of the market.

2.2.2.3 Other possible uses

Although use in polyurethane foams is the current major use of pentaBDPE within the EU, several other uses, some of which may be historic, have been reported in the literature. It should be noted that there is sometimes confusion in the literature between uses of polybrominated diphenyl ethers in general and use of pentaBDPE in particular which may have led in the past to misunderstandings over the actual uses of pentaBDPE. Some of these reported uses are considered further below.

2.2.2.3.1 Textiles

Pentabromodiphenyl ether may have been used in the past as a flame retardant in some textile applications (e.g. speciality fire-resistant clothing using polyurethane treatment, and in polyurethane coatngs in carpets). The main brominated diphenyl ether used in textile applications is decabromodiphenyl ether, but pentaBDPE may have had a small share of the market, particularly where softness and clarity of the product was important. The amount of pentaBDPE used in the past in this application is unknown, but is thought to be small. This use was thought to be discontinued in the early 1990's at the latest. It has been confirmed by various industry sources that pentaBDPE is not currently used in this application in the EU.

2.2.2.3.2 Electronic equipment

With the exception of a small use in rigid polyurethane elastomers for instrument casings (DETR, 2000), pentaBDPE does not appear to be used in electronic equipment in the EU. However, it is possible that electronic equipment containing pentaBDPE produced in other countries (principally Asian) could be imported into the EU. Although there are no data available on the amounts of pentaBDPE involved to confirm or refute this hypothesis, there is some evidence that this may be the case, and a belief by industry that use in this application is decreasing.

WHO (1994) gave the use of pentaBDPE as an additive for epoxy resins, phenolic resins and unsaturated polyesters, as well as flexible polyurethane foams and textiles. Prescott (1978) indicated potential uses for pentaBDPE in copper clad phenolic laminate circuit boards. It is not known if pentaBDPE is still used in these types of resins and polymers in countries outside the EU. A study of the presence of flame retardants present in electrical and electronic equipment has been carried out in Germany (Doedens and Cuhls, 1997). Nearly every fraction prepared for recycling contained tetra- and pentabromodiphenyl ether congeners in a range of 10 to 80 mg/kg. Few other details of this study are currently available.

This provides some evidence that pentaBDPE could be present in electrical and electronic equipment within the EU. There is also some evidence of elevated levels of the main components of commercial pentaBDPE in air in computer rooms and at electronics equipment dismantling/recycling sites (see Section 3.1.3.3), which is indicative of the presence of the substance in electronic equipment. However, these results should be treated with caution as the overall data set of air levels is not extensive and is generally lacking in control data to determine the background levels.

2.2.2.3.3 Hydraulic fluids

There is a suggestion that pentaBDPE could have been used at one time in hydraulic fluids in underground mines as a polychlorinated diphenyl replacement [for example see de Boer (1990)]. Industry has indicated that it is not currently used for this application in the EU. If this use did occur it might account for some of the reported occurrences of the substance in remote areas (for instance, there are many mining areas situated in Sweden; see Sections 3.1.1.2.2 and 3.1.4.3). However, after intensive investigation (KEMI, 1999b), this use has not been confirmed in the areas sampled.

Similarly, industry indicates that there is a possible use in completion fluids used in oil wells/drilling in the North Sea (e.g. on the basis of patents). Again, such a use could explain some of the reported occurrences of the substance in marine environments. However, a survey by KEMI (1999b) indicated that one company looked into the possible use in this area 15-20 years ago, but no product was marketed in Sweden. The survey did provide some circumstantial evidence that pentaBDPE may have been used in an early HFD fluid designed to be used as a heat exchange medium rather than a hydraulic oil. There are no indications that pentaBDPE is still used in these applications today within the EU.

2.2.2.3.4 Rubbers

Initial consultation revealed one UK company that had been using small quantities of pentaBDPE in the manufacture of flame retarded speciality rubber conveyor belts for the mining industry. This was likely to have been in products based upon polyurethane elastomers. The company involved has since ceased using pentaBDPE for this purpose and it is believed that use of pentaBDPE no longer occurs in this sector.

2.3 SUMMARY OF PRODUCTION AND USAGE FIGURES

Given the above findings, only the use of pentaBDPE in polyurethane is considered in the remainder of this report. The following figures are derived for pentaBDPE from the information in Sections 2.1 and 2.2 and will be used later in this assessment as the basis of the PEC calculations.

Usage within EU	=	300 tonnes/year (processing)
Main use	=	polyurethane foam
Total amount present in EU in finished articles	=	1.100 tonnes/year

2.4 BREAKDOWN/TRANSFORMATION PRODUCTS

There is a large body of literature that shows that under certain conditions pentabromodiphenyl ether (and indeed polybrominated diphenyl ethers in general) can form brominated dibenzofurans and brominated dibenzo-*p*-dioxins on combustion. This is discussed in detail for all the commercial polybrominated diphenyl ethers in Appendix A and has also been reviewed by WHO (1998). Factors that appear to affect the formation include the temperature, residence time at the temperature, the presence of oxygen, the type of polymer matrix and the presence of other additives (e.g. antimony trioxide). The possible risks from this transformation reaction are discussed qualitatively in section 3.3.5. Other disposal/recycling practices for articles containing polybrominated diphenyl ethers may have the potential to release polybrominated dibenzofurans and dibenzo-*p*-dioxins to the environment, and these are considered further in Appendix A.

3 ENVIRONMENT

The environmental risk assessment has been carried out using the methods described in the Technical Guidance Document (TGD) for risk assessment of new and existing substances (see Foreword) and the associated EUSES program. The EUSES output is attached as Appendix B.

3.1 EXPOSURE ASSESSMENT

3.1.0 General discussion

It should be born in mind in the following sections that the releases estimated refer to the commercial pentaBDPE product. As was discussed in Section 1, the commercial products are mixtures of congeners, of which pentabromodiphenyl ether isomers make up approximately 50-62%. Appendix E considers the environmental release of the individual components of the commercial pentaBDPE in more detail, and also considers the possible contribution to environmental levels from impurities present in other polybrominated diphenyl ethers (see also Appendix D).

3.1.0.1 Emissions from production

Production of pentaBDPE no longer occurs in the EU. The following discussion is therefore for information only.

No information was provided in IUCLID on the releases of pentaBDPE from production. Emission factors from production are given in Appendix 1 of the Technical Guidance Document. For substances in Industry Category 11 (polymers) or Industry Category 13 (textiles) and Main Category 1c (substances produced in dedicated equipment) the following emission fractions are obtained: release fraction to air = 0 (vapour pressure <1 Pa); release fraction to waste water = 0.003 (i.e. 3 kg/tonne).

Information on the release of polybrominated diphenyl ethers in general is discussed in EEC (1993). The information appears to have been derived from discussions with industry representatives, as well as data on chemicals produced by similar methods, for example polybrominated biphenyls. The estimated release of pentaBDPE to air (mainly in the byproduct hydrogen bromide stream) from the reactor was thought to be very low, around 0.5 mg/tonne of product. This waste stream is likely to pass through an absorber/scrubber system before discharge. It was also pointed out that emissions of pentaBDPE could also occur by a similar route during the early stages of production of octa- and decabromodiphenyl ethers, since the reaction occurs by step-wise addition of bromine to the aromatic rings. In addition, it was thought that the most likely possible route of release to waste water would be from washing out the reactor with water. It was thought that this release would be unlikely to exceed 0.5 kg/tonne.

Some information on possible releases from production has been obtained from discussions with a manufacturer of pentaBDPE. They estimated that the major source of release was due to filter waste and reject material. This waste was disposed of to landfill. The only regular release to waste water from the process was thought to be spent scrubber solutions, but it was not possible to quantify this.

Using the emission estimates given in EEC (1993) and the Technical Guidance default values, the following releases can be estimated for a site producing 500 tonnes/year of pentaBDPE. The releases are estimated to occur over 50 days (Table B1.1 of Appendix 1 of the Technical Guidance Documents). Since production of pentaBDPE does not occur in the EU, the estimates are for information only and although predicted environmental concentrations are given in section 3.1.1.1.1, the significance of the values is not considered further in the assessment.

Amount of pentaBDPE produced	=	500 tonnes/year
Estimated emission to air	=	0 or 250 mg/year
Estimated emission to waste water	=	1,500 or 250 kg/year

3.1.0.2 Emissions from use in polymer applications

3.1.0.2.1 Polyurethane foam production

The major use of commercial pentaBDPE flame retardants appears to be in flexible polyurethane foam production, mainly for furniture and automobile use.

It is estimated that around 120,000 tonnes of polyurethane foam is produced each year in the United Kingdom. Around 30% of this is thought to be used in furniture and 18% in automobiles (UCD, 1994). A typical concentration of flame retardant in the foam is 10%. It should be noted that flame retardants other than pentaBDPE are used in polyurethane foams.

The major sources of environmental release during the manufacture of polyurethane foam are likely to be associated with:

- the handling of the flame retardant prior to mixing with other ingredients (pentaBDPE is reported to be a viscous liquid or semi-solid);
- volatilisation from the foam while at elevated temperatures; and
- washing out of equipment.

Mixing of the components required for the foam is usually carried out by a mixing head immediately prior to feeding into the moulding system. The flame retardant additives can either be metered directly to the mixing head or may be premixed with the polyol component of the foam before feeding to the mixing head. Two main types of mixing head are commonly used: low pressure and high pressure. Low pressure mixing heads need to be cleaned out between cycles by flushing with a suitable solvent (e.g. methylene chloride) or may be flushed with further polyol which can then be reused if the formulation allows. High pressure (impingement) mixing heads do not require solvent flushing between batches (HMIP, 1995).

In Section 2 it was estimated that around 300 tonnes/year of pentaBDPE represents a realistic worst case for the amount used in the EU for the production of polyurethane foams. The regional usage of pentaBDPE is taken as 10% of this figure (30 tonnes/year).

No information was provided in IUCLID on the release of pentaBDPE from the production of polyurethane foams. Default emission factors are given in Appendix 1 of the Technical Guidance Document for processing of polymers. Using Table A3.11 for flame retardants in

hermosetting resins the default emission fractions are: release to air = 0; release to waste water = 0.0005 (i.e. 0.5 kg/tonne).

Using Table B3.9 for polymer processing and a total regional usage figure of 30 tonnes of pentaBDPE (i.e. 300 tonnes of polyurethane foam containing 10% pentaBDPE), the default fraction of polyurethane foam processed on one site is 0.25 (i.e. 75 tonnes/year of foam) and the number of days of use at any one site is estimated at 30.

Using these default figures, the release of pentaBDPE to water can be estimated at 3.75 kg/year (0.125 kg/day) at a site, 15 kg/year in a region and 150 kg/year in the EU as a whole. The releases are estimated to occur over 30 days.

Information on the release of flame retardants during the processing of plastics and foams is also given in a Use Category Document on plastics additives (UCD, 1994). The main source of release for liquid (flame retardant) additives is associated with the handling of the raw material (e.g. splashes, spills etc.) prior to the foaming process, where releases to waste water are estimated to be around the order of 0.01% (i.e. 0.1 kg/tonne). Although the default emission factors suggest a zero release to air of pentaBDPE during processing of polyurethanes, there is a potential release during the curing phase, since the foam is at elevated temperatures, e.g. up to 160^{o}C for several hours (depending on the size of the block). UCD (1998) gives estimated releases of 0.1% (i.e. 1 kg/tonne) to air for pentaBDPE (vapour pressure $4.69 \cdot 10^{-5}$ Pa) during the conversion of foams in open systems. This release is initially to the atmosphere, but it is possible that condensation of the flame retardant may occur as it cools and so some of this release may end up in waste water as a result of general cleaning etc. Thus the release of pentaBDPE to waste water could be of the order of a maximum of 0.11% (1.1 kg/tonne), although some of this loss would also be to air as vapour. For the risk assessment, it will be assumed that half of the loss during conversion is to air and half eventually ends up in waste water. Thus the release figures obtained are 0.6 kg/tonne to waste water and 0.5 kg/tonne to air.

The Use Category Document also allows estimates for the amount of polyurethane foam containing pentaBDPE produced on a worst case site. In the UK, 120,000 tonnes of polyurethane foam are produced and it is estimated that the amount containing a given additive would be 0.62% of this, based on the known size distribution of plastics producers in the United Kingdom. Thus the worst case amount of foam produced on one site is estimated as 744 tonnes/year, which is equivalent to 74.4 tonnes/year of pentaBDPE (if all the foam contains the flame retardant at 10% by weight).

Using the information given in the Use Category Document, the releases of pentaBDPE to waste waster at a site are estimated to be 44.6 kg/year, or 0.15 kg/day over 300 days. The release to air from a site would be 37.2 kg/year. These values will be used in the PEC calculations. The values obtained for waste water are similar to those obtained using the default calculations in the Technical Guidance Document.

For the regional assessment, it is usually assumed that 10% of the flame retardant (i.e. 30 tonnes) is used in the region. However, in this case, as a larger amount is used on a worst case site, the releases in the region will be taken as the same as at a worst case site, i.e. 44.6 kg/year to waste water and 37.2 kg/year to air. Based on the total EU usage of pentaBDPE of 300 tonnes/year the total release is estimated to be 180 kg/year to waste water and 150 kg/year to air.

3.1.0.2.2 Polyurethane foam cutting and fabrication

Blocks of polyurethane foam generally have to be cut into the required size/shape of the final product. This operation usually occurs after the blocks have cured and cooled. For some applications, polyurethane foam can be produced in a mould of the desired shape and so cutting is not required.

When fabricating a block, the first stage is usually to trim the sides and top of each block to give a block with uniform faces. This is carried out using vertical and horizontal band knifes. The amount of scrap foam removed from the block depends on the size of the block and the type of machine used to produce it. For instance, it has been estimated for a block of foam of density 22 kg/m^3 and having dimensions 2 m ·1.5 m · 1 m, the scrap foam generated from trimming will vary from around 15% to <5%, depending on the machine used. The highest wastage figures are from "domed-topped" blocks made in machines with unrestrained tops, with lower figures being obtained from machines/processes designed to minimise the formation of a domed top (see Section 2.2.2.2) (Woods, 1982).

Finally, the trimmed block of foam is cut into the required shapes/pieces by hand-knives or high speed cutting wires. The waste generated at this stage depends on the geometry of the parts being fabricated.

The flame retardant lost during these processes will be entirely contained within the scrap foam. Foam scrap is often recycled into carpet underlay (rebond), particularly in the United States [the EU is an exporter of scrap foam (around 40,000 tonnes/year) to the United States for this use (ENDS, 1998)]. In the process, the scrap foam from various sources is shredded into small pieces and mixed with an adhesive under pressure to form a large cylinder or block. The foam product is then “peeled” from the block at the desired thickness and a suitable backing is then applied. Other uses for scrap foam such as regrinding and subsequent use as a filler in a variety of applications (e.g. car seats, addition to virgin polyol in the manufacture of slabstock foam) have been reported (Ulrich, 1997). It is also possible that scrap foam will be disposed of to landfill (or possibly incinerated). Thus it can be considered to be disposed of in a similar way to the fabricated articles containing the flame retardant. For the purpose of the risk assessment, losses from re-use or disposal of scrap foam will not be separated from losses during use and disposal of finished articles (Sections 3.1.0.2.3 and 3.1.0.2.4).

3.1.0.2.3 Losses during use of articles containing polyurethane foam

Since pentaBDPE is an additive flame retardant it may be subject to volatilisation or leaching from the polymer matrix during the lifetime of the use of an article. Losses of foam particles containing the substance (e.g. due to abrasion) may also occur.

<u>Volatilisation</u>

Pentabromodiphenyl ether has a very low vapour pressure and so losses from polyurethane foam due to volatilisation would be expected to be low.

An equation for estimating this possible loss for an additive in plastics has been given as (UCD, 1994):

Percentage loss due to volatilisation = $1.1 \cdot 10^6 \cdot P \cdot N$ %

where P = vapour pressure of flame retardant (mmHg at 20^oC)
N = service life of product (estimated to be 10 years for furniture foam)

This equation was derived for the loss of plasticiser additives in various plastics, and is derived from data from thin films rather than bulk material. In the absence of any other information it will be used here to estimate possible releases of pentaBDPE from polyurethane foams as a worst case.

Using a vapour pressure for pentaBDPE of $3.5 \cdot 10^{-7}$ mmHg ($4.69 \cdot 10^{-5}$ Pa), the loss during the service life of a product would be around 3.9%, or 0.39%/year over 10 years. Given that commercial pentaBDPE is a mixture of components with differing vapour pressures (see Section 3.1.0.5.1), some components might be expected to be more or less volatile than this. However, the figure obtained probably represents a reasonable figure for the commercial product.

Assuming that around 110 tonnes/year of pentaBDPE are present in new foam products in a region, and 1,100 tonnes/year are present in the EU as a whole[4], then the yearly release of pentaBDPE due to volatilisation from finished articles could be around 0.43 tonnes/year in a region and 4.3 tonnes/year in the EU as a whole. However, given that the lifetime of the finished articles containing the flame retardant may be around 10 years, and that each year new products containing pentaBDPE are likely to enter into use, the actual amount of pentaBDPE present in foam products, and hence potentially released, could be around 10 times higher than this estimated amount. Thus, for the purposes of the assessment the estimated releases of pentaBDPE from volatilisation from foam products will be taken as around 4.3 tonnes/year in a region and 43 tonnes/year in the EU as a whole. These losses will be initially to the atmosphere. It should also be noted that the amounts of pentaBDPE used in foam have fallen recently and so the amount of pentaBDPE present in finished articles would also be expected to fall in the future if this trend continues.

Leaching

Given that the major use of pentaBDPE appears to be in foam for furniture/seating/automobile use, the actual potential for leaching from the foam during use would appear to be minimal. This is because, although it is likely that the covers may be washed during the lifetime of the furniture, it is very unlikely that the actual foam cushioning will be washed.

Waste remaining in the environment

Waste remaining in the environment can be considered to be particles of polymer (foam) products which contain pentaBDPE. These particles are primarily released to the urban/industrial soil compartment, but may also end up in sediment or air. End-products with

[4] These figures are higher than the current EU usage figure for pentabromodiphenyl ether and so make some allowance for the fact that: a) higher amounts may have been used in the past; and b) unknown amounts of polyurethane foam (both new and recycled) or other products (see Section 3.1.0.2.5) containing pentabromodiphenyl ether may be imported into (or possibly exported from) the EU.

outdoor uses are most likely to be sources of this waste. The release can occur over both the lifetime of the product (due to weathering, wear, etc.) and at disposal (particularly where articles are dismantled or subject to other mechanical processes).

At present there is no agreed methodology given in the Technical Guidance Document for assessing the risks from this type of waste. However, a methodology was outlined in the draft risk assessment report for di(2-ethylhexyl)phthalate (DEHP) and a similar approach is taken here. The estimates obtained are open to a high degree of uncertainty, particularly since the availability of the substance in the particles is unknown.

In the draft DEHP risk assessment, waste remaining in the environment was identified to be produced from the following outdoor applications of PVC:

- car undercoating;
- roofing material;
- coil coating;
- fabric coating;
- cables and wires;
- hoses and profiles;
- shoe soles.

The emission factors used for these types of losses in the draft DEHP risk assessment were around 2-10% over the lifetime of the product, with the higher factor being applied to articles subject to high wear rates (such as car underbodies and shoe soles), and 2% during disposal operations. The assumptions behind the derivation of these factors were not given in the report. These releases were thought to occur mainly to urban/industrial soil. A similar approach is taken here as a worst case, using the same factors as used for DEHP. Only outdoor applications and ultimate disposal are considered to contribute significantly to the waste over the lifetime of the articles.

This approach assumes the following:

- the quantity of articles/products containing pentaBDPE disposed of each year is equal to the quantity of new articles/products containing pentaBDPE produced each year; and

- the emissions are likely to be mainly to soil. In the draft DEHP assessment it was assumed that 75% of the emission would be to industrial/urban soil and 0.1% to air, with the remainder occurring to surface water (sediment). The same split of the emissions will be used here in the absence of any further information.

Since pentaBDPE is used mainly in polyurethane foams, the potential for release of particulate waste from weathering, wear, etc., during the service life of the product/article is low, because the foam will be used mainly in interior applications (e.g. car interiors, furniture, etc.) and will have a protective covering. Release to the environment could occur at the end of the articles' service life during disposal operations, where particles of foam containing pentaBDPE could be generated. A loss rate of 2% will be assumed for this disposal step.

In the calculations, the amount of pentaBDPE lost by volatilisation and/or leaching and during processing is also taken into account to avoid double counting.

The amount of waste remaining in the environment can therefore be estimated as follows:

Total amount of pentaBDPE present in articles	= 1,100 tonnes/year
Amount lost through volatilisation over service life	= 43 tonnes/year
Total amount remaining in articles at end of service life	= 1,057 tonnes/year
Amount lost as waste remaining in the environment at disposal	= 2%
Emission at disposal	= 21.14 tonnes/year
Amount of pentaBDPE remaining in articles at disposal	= 1,036 tonnes/year

The estimated amount of waste remaining in the environment is 21.14 tonnes/year for the EU as a whole. The regional amount will be taken as 10% of this figure. It will be assumed that this is released to industrial/urban soil, air and surface water as follows:

		Total EU	Region
75% to industrial soil	=	15.86 tonnes/year	1.59 tonnes/year
0.1% to air	=	0.021 tonnes/year	0.002 tonnes/year
24.9% to surface water	=	5.26 tonnes/year	0.53 tonnes/year

3.1.0.2.4 Losses from landfill and incineration

Since the major use of pentaBDPE is in polyurethane foam for furniture use it is probable that much of this will eventually end up being disposed of to landfill or possibly incinerated at the end of the articles' useful life.

No information is available on the leachability of pentaBDPE from foams. However, given the physico-chemical properties of the substance (low water solubility, high octanol-water partition coefficient) it is considered very unlikely that significant amounts of pentaBDPE will leach from landfills as the substance would be expected to adsorb strongly onto soils.

Movement of polymer (foam) particles containing pentaBDPE within the landfill could provide a transport mechanism leading to entry into leachate water or groundwater. However, it is not currently possible to assess the significance of this type of process. Well-designed landfills already include measures to minimise leaching in general, and these measures would also be effective to minimise the leaching of any pentaBDPE present.

The actual volume of foam containing pentaBDPE that eventually ends up in landfill or is incinerated is unknown, although it is likely that all pentaBDPE (including that present in recycled products) will eventually be disposed of by these routes. Assuming that the use of pentaBDPE has been approximately constant over the last 10 years and that the lifetime of finished articles containing pentaBDPE is around 10 years, then the amount of pentaBDPE disposed of each year is estimated to be approximately 1,036 tonnes/year in the EU as a whole and 103.6 tonnes/year in a region (see Section 3.1.0.2.3).

Potentially toxic products may be released during incineration of articles containing pentaBDPE. This is considered further in Appendix A and Section 3.3.5.

3.1.0.2.5 Release from other possible uses

There is some evidence that pentaBDPE may be present in some polymeric materials other than polyurethane, some of which may be imported (see Section 2.2.2.3.) The actual amounts involved are unknown, but appear to be small compared with the amounts used in foam. The emissions from these types of product, particularly those occurring over the products' lifetime are relevant to this assessment as they can contribute to the regional release. The general lack of information on these uses makes it difficult to carry out an assessment of them in a quantitative manner. However, as general emission factors for polymeric materials have been used to estimate the emissions from polyurethane foam, the same factors could equally well apply to other polymeric uses.

As the overall amounts of pentaBDPE present in these applications is unknown, this adds further uncertainty in the assessment.

3.1.0.3 Summary of environmental releases

The estimated releases of pentaBDPE into the environment are summarised in **Table 3.1**. These values will be used later as the basis for calculation of PECs.

There are many uncertainties inherent in these emission estimates, as described in the preceding sections. Furthermore, since the "waste remaining in the environment" essentially consists of polymeric particles containing pentaBDPE, it is not known if this is "available" in the environment and so would lead to actual exposure of organisms to pentaBDPE. In order to model this release from the data available it has to be assumed that the pentaBDPE present in this "waste" is available immediately (and/or behaves identically to "free" pentaBDPE), which may not be the case. For this reason, the PEC calculations in the following Sections have been carried out without this contribution. However, the effect of adding in this "waste" on the regional PECs is also considered where appropriate.

Table 3.1 Estimated release of pentabromodiphenyl ether from various sources

Source	Estimated release at a site	Estimated release in a region[a]	Estimated total lease in the EU	Estimated continental release[b]
Polyurethane foam manufacture	0.15 kg/day to waste water and 0.124 kg/day to air	44.6 kg/year to waste water and 37.2 kg/year to air	180 kg/year to waste water and 150 kg/year to air	135.4 kg/year to waste water and 112.8 kg/year to air
Polyurethane foam use		4.3 tonnes/year to air	43 tonnes/year to air	38.7 tonnes/year to air
Polyurethane foam "waste remaining in the environment"[c]		0.53 tonnes/year to surface water 0.002 tonnes/year to air 1.59 tonnes/year to industrial soil	5.26 tonnes/year to surface water 0.021 tonnes/year to air 15.86 tonnes/year to industrial soil	4.73 tonnes/year to surface water 0.019 tonnes/year to air 14.27 tonnes/year to industrial soil
Polyurethane foam disposal		103.6 tonnes/year to landfill (or incineration)	1,036 tonnes/year to landfill (or incineration)	932.4 tonnes/year to landfill (or incineration)
Total		44.6 kg/year to waste water[d], 0.53 tonnes/year to surface water[c] 4.3 tonnes/year to air, 1.59 tonnes/year to industrial soil[c] and 103.6 tonnes/year to landfill (or incineration)	180 kg/year to waste water, 5.26 tonnes/year to surface water[c], 43.2 tonnes/year to air, 15.86 tonnes/year to industrial soil[c] and 1,036 tonnes/year to landfill (or incineration)	135.4 kg/year to waste water[d], 4.73 tonnes/year to surface water[c], 38.7 tonnes/year to air, 14.27 tonnes/year to industrial soil[c] and 932.4 tonnes/year to landfill (or incineration)

[a]The regional model is based on 10% of the total EU activity. However, for polyurethane foam manufacture the release at a single site accounts for more than 10% to the total release and so the region is assumed to contain this site as a worst case approach
[b]Continental release = total EU release minus regional release
[c]Release estimates for particulate matter containing pentaBDPE
[d]In the EUSES modelling, a 70% connection rate to the waste water treatment plant is assumed

3.1.0.4 Degradation

3.1.0.4.1 Abiotic degradation

No information is currently available on the abiotic degradation of pentaBDPE in aqueous solution. It is thought that pentaBDPE will be hydrolytically stable under conditions found in the environment. By comparison with decabromodiphenyl ether, it is likely that pentaBDPE may photodegrade in water, although it is not currently possible to comment on the likely extent and rate of this reaction (see Appendix F).

A rate constant for the reaction of 2,2',4,4',5-pentabromodiphenyl ether with atmospheric hydroxyl radicals has been estimated as $1.27 \cdot 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} using the Syracuse Research Corporation AOP estimation program. Assuming an atmospheric concentration of hydroxyl radicals of $5 \cdot 10^5$ molecules/cm^3, an atmospheric half-life of around 12.6 days can be estimated for this reaction. This value will be used in the EUSES modelling.

3.1.0.4.2 Biodegradation

No degradation (as CO_2 evolution) was seen in 29 days in an OECD 301B ready biodegradation test carried out to GLP (Schaefer and Haberlein, 1997).

The substance tested was a composite sample from two producers and had the following composition: 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether. The substance was tested at a concentration of 10 mg C/l and was added to the test medium by direct weight addition. An activate sludge inoculum was used. The theoretical carbon content of the test material was estimated to be 26.2%. The test was extended to 93 days to allow sufficient opportunity for adaptation to occur and at the end of 93 days, 2.4% of the theoretical amount of CO_2 had been evolved. A positive control (sodium benzoate) showed 97.8% CO_2 evolution degradation (with >60% evolution within 5 days), indicating the viability of the test organisms used. It can be concluded that pentaBDPE is not readily biodegradable.

No information is available on the anaerobic biodegradability of pentaBDPE. From the data generated for other halogenated aromatic substances (see Appendix F), there is a possibility for reductive dehalogenation of polybrominated diphenyl ethers to occur under some conditions. If this occurs for pentaBDPE then this could provide a removal mechanism from the environment. Studies are being carried out on the higher brominated diphenyl ethers in order to assess the environmental significance of such reactions (August 2000).

3.1.0.5 Distribution

Since commercial pentaBDPEs are mixtures of compounds of differing degrees of bromination (ranging from tetra- to hexabrominated diphenyl ethers), the environmental distribution of the mixture will be governed, to some extent, by the physico-chemical properties of the individual components. For this reason, data on the diphenyl ethers of all degrees of bromination have been considered in order to identify trends, and extrapolations have been made from one chemical to the other in the absence of data. Appendix E considers this further, and looks at the effects of possible uncertainties in the available physico-chemical properties on the environmental modelling/behaviour. Overall, it was found that varying the physico-chemical properties (e.g. log K_{ow}, water solubility, vapour pressure) over quite a wide range had very little effect on the predicted local concentrations in water, sediment and soil, but showed a much larger effect on the predicted local air concentrations.

3.1.0.5.1 Volatilisation

Brominated diphenyl ethers all have low vapour pressures, the vapour pressure tending to decrease with increasing bromination. Watanabe and Tatsukawa (1990) determined the vapour pressures for a range of brominated diphenyl ethers at 25^{o}C using a GC technique. The results are shown in **Table 3.2**. No information was given as to the actual composition of the substances tested. However, the method was based on the determination of GC retention times under specific chromatographic conditions and so if the substances are mixtures of isomers, as is very likely to be the case, a range of retention times and hence vapour pressures will be obtained from the method. The results can thus be taken to represent the vapour pressures of the most and least volatile components in the products tested. These results agree well with the direct measurement given in **Table 3.2**.

Table 3.2 Vapour pressures of polybrominated diphenyl ethers (Watanabe and Tatsukawa, 1990)

Polybrominated diphenyl ether	Vapour pressure at 25°C (Pa)
Dibromodiphenyl ether	0.013-0.019
Tribromodiphenyl ether	$1.6 \cdot 10^{-3}$ - $2.7 \cdot 10^{-3}$
Tetrabromodiphenyl ether	$2.5 \cdot 10^{-4}$ - $3.3 \cdot 10^{-4}$
Pentabromodiphenyl ether	$2.9 \cdot 10^{-5}$ - $7.3 \cdot 10^{-5}$
Hexabromodiphenyl ether	$4.3 \cdot 10^{-6}$ - $9.5 \cdot 10^{-6}$
Octabromodiphenyl ether	$1.2 \cdot 10^{-7}$ - $2.3 \cdot 10^{-7}$

A vapour pressure of $4.69 \cdot 10^{-5}$ Pa at 21°C has been determined for a commercial pentaBDPE mixture (33.7% tetra-, 54.6% penta- and 11.7% hexabromodiphenyl ether) using a spinning rotor gauge (Stenzel and Nixon, 1997). This value has been used in the EUSES modelling for pentaBDPE.

Low vapour pressures have been determined for all the components of pentaBDPE and so they are unlikely to volatilise from spillage to land. However, given the low water solubility of these substances, volatilisation from solution may still be significant, particularly for the moderately brominated components. For example, based on the water solubility of 2.4 µg/l for pentabromodiphenyl ether and a vapour pressure of $4.69 \cdot 10^{-5}$ Pa, a Henry's Law constant of 11 Pa m^3 $mole^{-1}$ can be estimated. Once in the atmosphere, they are likely to adsorb strongly onto atmospheric particles and subsequently be removed by wet or dry deposition. This could provide a transport mechanism for these compounds in the environment. The available monitoring data, particularly in biota samples (see Section 3.1.4.3) indicates that the main components of the commercial pentaBDPE are widely distributed in the environment, and occur in organisms from areas remote from possible sources of release. This, along with the physico-chemical properties of the substance indicates that long-range transport via the atmosphere may be occurring for these substances.

3.1.0.5.2. Adsorption

Sediment - water partition coefficients ($Kp_{(sed)}$) have been measured for several components of commercial pentaBDPE (Watanabe, 1988). The values obtained are shown in **Table 3.3**.

Table 3.3 Measured sediment - water partition coefficients for pentabromodiphenyl ether

Component	Concentration in sediment (mg/kg)	Concentration in water (mg/l)	$Kp_{(sed)}$ (l/kg)
Tetrabromodiphenyl ether	116	0.0041	28,293
Pentabromodiphenyl ether	118	0.0024	49,167
Hexabromodiphenyl ether	138	0.0022	62,727

High octanol-water partition coefficients (K_{ow}) have been determined for polybrominated diphenyl ethers using a HPLC technique (Watanabe and Tatsukawa, 1990). The results are shown in **Table 3.4**. No information was given as to the actual composition of the substances tested. However, the method is based on determining the HPLC retention time under specific

chromatographic conditions and so, if the substances are mixtures of isomers, as is very likely to be the case, a range of retention times and hence partition coefficients will be obtained from the method. The results can thus be taken to represent the range of octanol-water partition coefficients for the components of the products tested.

Table 3.4 Octanol-water partition coefficients for polybrominated diphenyl ethers (Watanabe and Tatsukawa, 1990)

Polybrominated diphenyl ether	log K_{ow}
Dibromodiphenyl ether	5.03
Tribromodiphenyl ether	5.47-5.58
Tetrabromodiphenyl ether	5.87-6.16
Pentabromodiphenyl ether	6.46-6.97
Hexabromodiphenyl ether	6.86-7.92
Octabromodiphenyl ether	8.35-8.90
Decabromodiphenyl ether	9.97

Recently, the log K_{ow} value for pentaBDPE has been determined as 6.57 using a generator column method (MacGregor and Nixon, 1997), which agrees well with the values reported in **Table 3.4**. This value is used in the EUSES modelling for this substance.

According to Chapter 4 of the Technical Guidance Document, soil organic carbon - water partition coefficients can be estimated for hydrophobic chemicals from:

$$\log K_{oc} = 0.8 \cdot \log K_{ow} + 0.10 \text{ (equation derived for a log } K_{ow} \text{ range of 1-7.5).}$$

Thus K_{oc} values of 215,080-556,801 l/kg can be estimated for pentaBDPE using this relationship (a similar K_{oc} value of 264,058 l/kg is estimated if the latest log K_{ow} value of 6.57 is used). The standard fractional organic carbon content of soil, sediment and suspended sediment are taken to be 0.02, 0.05 and 0.1 respectively, thus the following Kp values can be estimated for pentaBDPE based on the estimated K_{oc} value:

Soil	-	$Kp_{(soil)}$= 4,302-11,136 l/kg
Sediment	-	$Kp_{(sed)}$= 10,754-27,840 l/kg
Suspended sediment	-	$Kp_{(susp)}$= 21,508-55,680 l/kg

The upper end of predicted values for sediment agree reasonably well with the measured values for sediment in **Table 3.3** (the organic carbon content of the sediment used for the actual determinations is not known). The K_{oc} value of 556,801 l/kg will be used in the assessment for environmental modelling. Based on this value, the following total compartment-water partition coefficient can be estimated:

$$K_{soil\text{-}water} = 16{,}704 \text{ m}^3/\text{m}^3, K_{sed\_water} = 13{,}921 \text{ m}^3/\text{m}^3 \text{ and } K_{susp\text{-}water} = 13{,}921 \text{ m}^3/\text{m}^3.$$

Since commercial pentaBDPE is a mixture of several congeners, the behaviour of some of the other components should also be considered. From the information given in **Table 3.3** and **3.4**, it is clear that tetrabromodiphenyl ethers will have slightly lower Kp values and hexabromodiphenyl ethers slightly higher Kp values than pentabromodiphenyl ether. Thus it

can be concluded that all three major components are likely to adsorb strongly onto soils and sediments, but the lower brominated components are likely to be slightly more mobile in soil/sediment than the more highly brominated components. Appendix E considers the environmental modelling of the individual components of pentaBDPE in more detail.

From the above information, the main components of commercial pentaBDPE can be considered to be immobile in soil and are unlikely to leach into groundwater. Results obtained using the SAMS model for both the tetrabromodiphenyl ether and pentabromodiphenyl ether components support this conclusion. The model was run for a 2 year period, assuming an initial nominal soil concentration of 1 kg/m^3 at a depth of 1 cm in the soil. No degradation was assumed and K_{oc} value of 555,680 l/kg was assumed for pentaBDPE. A lower K_{oc} value of around half this value (i.e. 280,000 l/kg) was assumed for tetrabromodiphenyl ether for this exercise based on the data reported in **Table 3.3**. Slightly higher K_{oc} values were estimated in Appendix E for these two components, but in terms of leaching behaviour, the use of these lower values can be considered as worst case approach. Water solubilities of 2.4 µg/l and 10.9 µg/l were used for the penta- and tetrabromodiphenyl ether respectively (measured values – see Section 1). The results indicated that the majority of tetra- and pentabromodiphenyl ether would occur in the top few centimetres of the soil, with an insignificant amount (zero) leaching into groundwater. The full output of the model can be found in Appendix C.

3.1.0.5.3 Accumulation

The bioaccumulation of a commercial pentaBDPE product has been studied in carp (*Cyprinus carpio*) (CITI, 1982). The material used contained tetra- to hexabrominated congeners, with the major components being a pentabromodiphenyl ether (47.4%) and a tetrabromodiphenyl ether (37.6%). The composition of the product used is shown in **Table 3.5**. No other details on the identity of the commercial product or the components of the product were given in the report. However, it is clear from the distribution of the penta- and tetra- bromodiphenyl ether components present that this substance is similar in composition to those used within the EU.

The bioaccumulation study was carried out under continuous flow conditions. The fish used had an average body weight of 23.7 g, average length of 9.8 cm and a lipid content of 4.8%. Two concentrations of the commercial pentaBDPE product were tested, 10 and 100 µg/l. Stock solutions of pentaBDPE (1 g/l) in water were made by using DMSO (10 g/l) and a dispersing agent (polyoxyethylene hydrogenated castor oil; 20 g/l). Thus the 100 µg/l test solution would also have contained around 1 mg/l of DMSO and 2 mg/l of the dispersing agent. Since no actual pure analytical standards were available for each component of the pentaBDPE, the calibration curves for each component (chromatographic peak) were determined on the basis of the total nominal concentration of pentaBDPE added. Thus although the exposure concentrations are given as 10 or 100 µg/l, the actual concentration of the individual components will be lower than these values (dependant on their percentage composition in the commercial product; see below). However, since final BCF value depends only on the relative concentration of the substance in fish compared to water, this approach is appropriate to the determination of BCFs for the individual components. The BCFs determined are shown in **Table 3.6**.

Table 3.5 Composition of the commercial pentabromodiphenyl ether used in the bioaccumulation study

Number of bromine atoms	Component (identification letter)	Approximate % composition
Unknown	F	0.13
Unknown	G	0.62
4	A	37.67
5	B	7.89
5	C	47.40
5	H	1.14
6	D	2.51
6	E	2.64

Using the data presented in **Table 3.5** and **3.6**, it is possible to estimate a BCF for the commercial product by weighting the BCF for the individual components to their percentage composition in the formulation. Thus, an overall BCF of 14,350 l/kg can be estimated assuming the following percentage compositions and BCFs: component A, 37.67%, BCF=35,100 l/kg; component B, 7.89%, BCF=11,700 l/kg; component C, 47.40%, BCF=73 l/kg; component D, 2.51%, BCF=5,620 l/kg and component E, 2.64%, BCF=1,080 l/kg.

When interpreting the results of the CITI (1982) bioconcentration study, the concentration of the commercial substance used needs to be considered further. The actual water solubility of the currently supplied pentaBDPE is around 13.3 µg/l (being the sum of 10.9 µg/l for tetrabromodiphenyl ether and 2.4 µg/l for pentaBDPE; see Section 1.3.6). Thus, the highest concentration used in the CITI (1982) study is well above the water solubility of the substance. The effect of the cosolvent and emulsifiers on the water solubility of the commercial substance in the test media is unknown, but an upper limit for the BCFs from the study can be estimated if it is assumed that the concentration of each component is limited to its water solubility in the test media.

Table 3.6 Bioconcentration factors for the components of a pentabromodiphenyl ether

Component	Identification	Nominal exposure concentration (mg/l)	Whole body bioconcentration factor			
			2 weeks	4 weeks	6 weeks	8 weeks
A	Tetrabromo-diphenyl ether	10	14,200-16,100	26,400-27,100	33,800-34,700	28,800-35,100
		100	6,190-6,930	10,400-11,300	15,400-18,400	17,000-19,300
B	Pentabromo-diphenyl ether	10	4,480-4,600	7,580-8,610	9,120-10,100	10,200-11,700
		100	1,650-2,020	2,880-2,980	4,310-4,830	5,260-5,380
C	Pentabromo-diphenyl ether	10	<3.4	<3.4	5	<3.4
		100	24-73	<0.3	24-35	14-39
D	Hexabromo-diphenyl ether	10	2,240-2,480	4,090-4,140	4,330-4,630	5,480-5,620
		100	769-996	1,240-1,300	1,580-1,590	2,030-2,090
E	Hexabromo-diphenyl ether	10	385-468	664-1,130	572-909	1,030-1,080
		100	466-558	384-545	566-660	732-979

In the experiment, the exposure solutions were made up using the following methodology:

- Firstly, 1 g of test material was dissolved in 10 g of dimethylsulphoxide (DMSO). Then, 20 g of a dispersing agent (polyoxyethylene hydrogenated castor oil) was added and finally water was added to prepare a 1 g/l stock solution of the test substance (also containing 10 g/l DMSO and 20 g/l of the dispersing agent).

- This stock solution was diluted to give two further solutions of 10 mg/l and 1 mg/l of the test substance. These were then fed into the reactor at a rate of 4 ml/minute, along with water at 400 ml/minute to give the nominal test exposure concentrations of 10 and 100 µg/l. The concentration of DMSO present in these test solutions was 0.1 and 1 mg/l respectively, and that of the dispersing agent was 0.2 and 2 mg/l.

- The exposure concentrations for the commercial product were verified in both the 10 and 100 µg/l experiments by analysis of the two pentabromodiphenyl ether components over the 8 week period. Both components gave similar results close to the nominal value.

From the way that the stock solutions were made up, there is a possibility that not all of the commercial product was dissolved. If it is assumed that a saturated solution was present, then the concentration of the tetra- and pentabromodiphenyl ethers would be expected to be around 10.9 µg/l and 2.4 µg/l, based on their known water solubility. The water solubility of the hexabromodiphenyl ether component is not known, but is likely to be around 1-4 µg/l, based on the solubility values measured for tetra-, penta- and octabromodiphenyl ether (see **Table E3** of Appendix E).

In order to carry out a re-analysis of the data, the concentrations found in the fish for the various components of the commercial substance have to be back-calculated from the BCF values reported in the paper. This arises from the way the calibration of the analytical method was carried out in the original study. When the calibration standards were analysed, instead of correcting the concentration of the commercial product for the relative fraction of each isomer present, the actual calibration curve was constructed for each component assuming that it was present at the total concentration (e.g. if 10 µg/l of the commercial product was used as one of the calibration standards, the calibration curve for each component was constructed assuming that its concentration was 10 µg/l). This method gives a reliable quantitation of the concentration in terms of the commercial formulation, and is acceptable even though it does not directly determine the actual concentrations of each component present in the water or fish phases. This is because the actual BCF value for each component depends only on the relative concentration in fish compared to that in water.

Therefore in order to calculate the actual concentration of each component present, the given concentrations have to be multiplied by the known fractional composition of the commercial product. In **Table 3.7** below, the actual (corrected) concentration that must have been present in the fish has been calculated using the BCF and the known composition of the commercial product.

From **Table 3.7**, the highest values for the BCFs for the various components are recalculated as:

Component A (TetraBDPE)	~	66,700 l/kg
Component B (PentaBDPE)	~	17,700 l/kg
Component C (PentaBDPE)	~	1,440 l/kg
Component D (HexaBDPE)	~	5,640 l/kg
Component E (HexaBDPE)	~	2,580 l/kg

These values are generally around a factor of 2 larger than were determined in the original paper. The only exception to this is the major pentabromodiphenyl ether component C (probably 2,2',4,4',5-pentabromodiphenyl ether), which in the original paper has a small BCF, but in this recalculation has a value around 10 times lower than the other pentabromodiphenyl ether component B (probably 2,2'4,4',6-pentabromodiphenyl ether). This recalculated value for component C is more in keeping with its widespread occurrence in biota (see below).

From the data reported in **Table 3.7**, it is clear that all the components of commercial pentaBDPE bioconcentrate and so are potentially bioaccumulative. It is interesting to note that the major pentabromodiphenyl ether component (C) of the formulation tested appears to bioconcentrate to a lesser extent (by a factor of around 10 in the recalculation) than the minor pentabromodiphenyl ether component (B). This is born out in the measured levels in fish of the two pentabromodiphenyl ether components reported in Section 3.1.4.2, where the major component of the commercial product is frequently present at a similar concentration to the minor component. This indicates that although both components are bioconcentrated in fish, the BCF for the minor component is the higher of the two (e.g. since component C is present at around 45-47% and component B is present at around 7-8% in the commercial formulation, in order for them to be present at the same concentration in fish, the BCF for component B would need to be around 6-7 times higher than that for component C, which is consistent with the recalculation of the experimental BCF above).

The overall BCF for the commercial product is now calculated as ~27,400 l/kg ($0.3767 \cdot 6{,}700 + 0.0789 \cdot 17{,}700 + 0.474 \cdot 1{,}440 + 0.0251 \cdot 5{,}640 + 0.0264 \cdot 2{,}580$). This is slightly higher (by a factor of 2) than the value originally obtained of 14,350 l/kg.

The other possible area of uncertainty with the CITI (1982) bioconcentration study is that while it is clear from the data that equilibrium appears to have been reached for the tetra- and pentabromodiphenyl ether components, it is not clear that this is the case for hexabromodiphenyl ether component D (and also possibly E). However, the overall BCF estimated for the commercial product is dominated by the tetrabromodiphenyl ether, and so the fact that the hexabromodiphenyl ether data may not have reached equilibrium has little effect on the overall BCF (unless much higher levels of accumulation are reached over extended periods).

Table 3.7 Re-analysis of the CITI (1982) bioconcentration data

Isomer	No of Br	Nominal water concentration (µg/l)	Percentage of commercial product	Exposure period (weeks)	BCF from original paper (l/kg)	Apparent concentration in fish (mg/kg)	Corrected (actual) concentration in fish (mg/kg)[c]	Water concentration based on solubility (µg/l)	Recalculated log BCF[d] (l/kg)
A	4	100	37.67%	2	6,190-6,930	619-693	233-261	10.9[a]	4.33-4.38
			37.67%	4	10,400-11,300	1,040-1,130	392-426	10.9[a]	4.56-4.59
			37.67%	6	15,400-18,400	1,540-1,840	580-693	10.9[a]	4.73-4.80
			37.67%	8	17,000-19,300	1,700-1,930	640-727	10.9[a]	4.77-4.82
		10	37.67%	2	14,200-16,100	142-161	53.5-60.6	3.8[b]	4.14-4.20
			37.67%	4	26,400-27,100	264-271	99.4-102	3.8[b]	4.42-4.43
			37.67%	6	33,800-34,700	338-347	127-131	3.8[b]	4.52-4.54
			37.67%	8	28,800-35,100	288-351	108-132	3.8[b]	4.45-4.54
B	5	100	7.89%	2	1,650-2,020	165-202	13.0-15.9	2.4[a]	3.73-3.82
			7.89%	4	2,880-2,980	288-298	22.7-23.5	2.4[a]	3.98-4.00
			7.89%	6	4,310-4,830	431-483	34.0-38.1	2.4[a]	4.15-4.20
			7.89%	8	5,260-5,380	526-538	41.5-42.4	2.4[a]	4.24-4.25
		10	7.89%	2	4,480-4,600	44.8-46.0	3.53-3.62	0.79[b]	3.65-3.66
			7.89%	4	7,580-8,610	75.8-86.1	5.98-6.79	0.79[b]	3.88-3.93
			7.89%	6	9,120-10,100	91.2-101	7.20-7.97	0.79[b]	3.96-4.00
			7.89%	8	10,200-11,700	102-117	8.05-9.23	0.79[b]	4.01-4.07
C	5	100	47.40%	2	24-73	2.4-7.3	1.14-3.46	2.4[a]	2.67-3.16
			47.40%	4	<0.3	<0.03	<0.014	2.4[a]	<0.77
			47.40%	6	24-35	2.4-3.5	1.14-1.66	2.4[a]	2.68-2.84
			47.40%	8	14-39	1.4-3.9	0.66-1.85	2.4[a]	2.44-2.89
		10	47.40%	2	<3.4	<0.034	<0.016	2.4[a]	<0.82
			47.40%	4	<3.4	<0.034	<0.016	2.4[a]	<0.82
			47.40%	6	5	0.05	0.024	2.4[a]	1.0
			47.40%	8	<3.4	<0.034	<0.016	2.4[a]	<0.82

Table 3.7 continued overleaf

Table 3.7 continued

Isomer	No of Br	Nominal water concentration (µg/l)	Percentage of commercial product	Exposure period (weeks)	BCF from original paper (l/kg)	Apparent concentration in fish (mg/kg)	Corrected (actual) concentration in fish (mg/kg)[c]	Water concentration based on solubility (µg/l)	Recalculated log BCF[d] (l/kg)
D	6	100	2.51%	2	769-996	76.9-99.6	1.93-2.50	1[a]	3.28-3.40
			2.51%	4	1,240-1,300	124-130	3.11-3.26	1[a]	3.49-3.51
			2.51%	6	1,580-1,590	158-159	3.97-3.99	1[a]	3.60
			2.51%	8	2,030-2,090	203-209	5.10-5.25	1[a]	3.71-3.72
		10	2.51%	2	2,240-2,480	22.4-24.8	0.56-0.62	0.25[b]	3.35-3.39
			2.51%	4	4,090-4,140	40.9-41.4	1.03-1.04	0.25[b]	3.61-3.62
			2.51%	6	4,330-4,630	43.3-46.3	1.09-1.16	0.25[b]	3.64-3.67
			2.51%	8	5,480-5,620	54.8-56.2	1.38-1.41	0.25[b]	3.74-3.75
E	6	100	2.64%	2	466-558	46.6-55.8	1.23-1.47	1[a]	3.09-3.17
			2.64%	4	384-545	38.4-54.5	1.01-1.44	1[a]	3.00-3.16
			2.64%	6	566-660	56.6-66.0	1.49-1.74	1[a]	3.17-3.24
			2.64%	8	732-979	73.2-97.9	1.93-2.58	1[a]	3.29-3.41
		10	2.64%	2	385-468	3.85-4.68	0.10-0.124	0.26[b]	2.58-2.68
			2.64%	4	664-1,130	6.64-11.3	0.175-0.30	0.26[b]	2.83-3.06
			2.64%	6	572-909	5.7-9.1	0.15-0.24	0.26[b]	2.76-2.97
			2.64%	8	1,030-1,080	10.3-10.8	0.27-0.29	0.26[b]	3.02-3.05

[a]Concentration in test media based on water solubility
[b]Based on the composition of the test substance since this is less than the solubility of the component
[c]Corrected using the known percentage composition of the substance
[d]log BCF recalculated based on the actual concentration in the fish and the concentration in water (based on solubility) for each component

Although the original CITI (1982) bioconcentration study appears to have been carried out in an acceptable manner, the above re-analysis indicates that the method used could potentially have lead to an underestimate of the actual bioconcentration, particularly for the main pentabromodiphenyl ether isomer (component C). It should be stressed that this is only a theoretical point, and it cannot be proven that this occurred. As a result, the EUSES modelling in Appendix B has been carried out using the original BCF value of 14,350 l/kg, but the effect of the re-calculated value of 27,400 l/kg will also be taken into account in the assessment. The environmental modelling for the individual components of the commercial product, using both the original and recalculated values, is considered in Appendix E.

A recent study has looked at the uptake and accumulation of several components of commercial pentaBDPE in blue mussel (*Mytilus edulis*). Solutions of a mixture of five polychlorinated biphenyls and three polybrominated diphenyl ethers (2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and 2,2',4,4',5,5'hexabromodiphenyl ether) were prepared using a generator column. Exposures were carried out using mussels (initial tissue dry weight 27±1.1 mg) in a flow-through system for 44 days, followed by a 26-day depuration period. The mussels were fed on algae (*Scenedesmus obtusiusculus*) throughout the experiment and the test water had a temperature of 7.6-9.6^{o}C and a salinity of 6.8‰. Mussel samples were collected and analysed for the presence of the brominated flame retardants on days 0, 3, 7, 15 and 44 of the uptake phase and days 5, 12 and 26 of the depuration phase. Water samples were collected from the outlets of the mixing chambers at the same time. The mean water concentrations found during the exposure part of the experiment were 0.31 ng/l, 0.070 ng/l and 0.086 ng/l for the tetrabromo, pentabromo- and hexabromodiphenyl ether compounds respectively. The uptake and depuration rate constants were determined for each compound and the bioconcentration factors derived from these values were $13 \cdot 10^5$ l/kg dry weight for 2,2',4,4'-tetrabromodiphenyl ether, $14 \cdot 10^5$ l/kg dry weight for 2,2',4,4',5-pentabromodiphenyl ether and $2.2 \cdot 10^5$ l/kg dry weight for 2,2'4,4',5,5'-hexabromodiphenyl ether. The depuration half-life for all three substances was found to be similar at 5.6-8.1 days (Gustafsson et al, 1999).

The uptake of pentaBDPE by fish from food has been studied as part of a reproduction study (Holm et al, 1993). In the experiment, female three-spined stickleback (*Gasterosteus aculeatus*) (20 per group; initial weight 0.9±0.1g; salinity of water 6‰) were fed freeze-dried chironomids (at around 2% of body weight/day) contaminated with pentaBDPE (Bromkal 70-5DE) for three months. Two exposure concentrations were used, 6.29 and 10.39 mg of the substance in food [this was total amount of pentaBDPE fed to the exposed fish over approximately 100 days (3.5 months)]. These concentrations are equivalent to initial exposure concentrations (doses) in food of 3.5 mg/kg food/day and 5.77 mg/kg food/day. After 3.5 months exposure, levels of pentaBDPE in the exposed fish were 72 mg/kg wet weight in the low dose group and 94 mg/kg wet weight in the high dose group. Thus bioaccumulation factors (BAFs - defined as concentration on fish (mg/kg wet weight)/concentration in food (mg/kg wet weight)) of around 20 and 16 for the low and high dose groups respectively can be derived, based on the initial concentration in food. Pentabromodiphenyl ether was not detected in non-exposed control fish.

Burreau et al (1997) investigated the uptake of pentaBDPE in predatory fish [Pike (*Esox lucius*)] fed live rainbow trout containing a mixture 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and 2,2',4,4',5,5'-hexabromodiphenyl ether, along with 5 polychlorinated diphenyls and 3 polychlorinated naphthalenes. The chemicals used were dissolved in lipids extracted from trout muscle and then injected into the dorsal muscle of live

rainbow trout immediately before the trout was fed to the pike. Around 9 days after feeding (to allow enough time for complete digestion to occur) the amounts of the brominated diphenyl ethers present in the pike were determined (after removal of the gastrointestinal tract). The uptake efficiency (amount of substance present in pike/amount of substance fed) was estimated as 90% for the tetrabromodiphenyl ether isomer, 60% for the pentabromodiphenyl ether isomer and 40% for the hexabromodiphenyl ether isomer.

Further evidence of the bioaccumulative nature of certain components of commercial pentaBDPE comes from studies in laboratory mammals. The half-life of a commercial pentaBDPE product (Bromkal 70) has been studied in rats (von Meyerinck et al, 1990). The product tested consisted mainly of tetrabromodiphenyl ether (36%) and pentabromodiphenyl ethers (64%). Male and female rats were given a single oral dose of 300 mg/kg body weight of the product in peanut oil. At various times during the 10 week experiment, adipose tissues were analysed for brominated diphenyl ethers using a HPLC method with dibromodiphenyl ether as internal standard. This method of analysis gave 5 major peaks from the commercial pentaBDPE product corresponding to a tetrabromodiphenyl ether (peak 1), two pentabromodiphenyl ethers (peaks 2 and 3), a mixture of a penta- and hexabromodiphenyl ether (peak 4) and a mixture of 3 hexabromodiphenyl ethers (peak 5). The half-lives of each component was determined in adipose tissue of both male and female rats and the results are shown in **Table 3.8**.

Table 3.8 Half-lives of the components of a commercial pentabromodiphenyl ether in rat adipose tissue (von Meyerinck et al, 1990)

Component	Peak	Half-life in female rats (days)	Half-life in male rats (days)
Tetrabromodiphenyl ether	Peak 1	29.9*	19.1*
Pentabromodiphenyl ether	Peak 2	47.4	36.8
Pentabromodiphenyl ether	Peak 3	25.4	24.9
Penta/hexabromodiphenyl ether	Peak 4	44.6	55.1
Hexabromodiphenyl ethers (3 isomers)	Peak 5	90.9	119.1

* Significant difference between male and female rats at p=0.01 level

There was no significant difference (p=0.01) between the half-lives in male and female rats except for the tetrabromodiphenyl ether (peak 1). The results show that all components, especially some penta- and hexabromodiphenyl ethers, are removed only slowly from adipose tissue and indicate that bioaccumulation may be of concern for some if not all of the components of the commercial pentaBDPE product.

In a recent study, Örn and Klasson-Wehler (1998) investigated the uptake and metabolism of ^{14}C-labelled 2,2',4,4'-tetrabromodiphenyl ether (a major component of commercial pentaBDPE) in rats and mice. In the experiment, the animals were given a single oral dose of 15 mg/kg body weight of the isomer dissolved in corn oil, and then feces and urine were collected for 5 days. The substance was found to be well adsorbed in both rat (95% of the dose adsorbed) and mouse (~93% of the dose adsorbed). In the rat, around 86% of the dose remained in tissues, mainly as the parent compound, 5 days after exposure. Around 14% of the dose was found to be excreted in feces, with <0.5% excreted in urine after 5 days. The substance was found to be poorly metabolised in the rat, with around 3% of the dose being excreted as metabolites after 5 days. In the mouse, around 47% of the dose remained in

tissues after 5 days, with around 20% of the dose was excreted via feces and 33% excreted via urine. In this case, at least 39% of the dose excreted was as metabolites.

Hakk et al (1999) and Larsen et al (1999) have investigated the uptake and metabolism of ^{14}C-labelled 2,2',4,4',5-pentabromodiphenyl ether in male rats. A single dose of 2.2 mg/rat was administered orally in peanut oil and the tissue disposition, excretion and metabolite formation was studied over 72 hours using both conventional and bile-duct cannulated rats. Metabolism to water-soluble metabolites or conjugates was low as cumulative urinary excretion was <1% of the total dose in conventional rats and ~0.3% in bile-duct cannulated rats. Biliary elimination was also found to be low (~3.7% of total dose) over 72 hours. Faecal excretion was found to be the main route of elimination with 43% of the total dose being excreted in conventional rat faeces and 86% excreted in bile-duct cannulated rat faeces. Analysis of the conventional faecal extracts indicated that only minor amounts (<10% of the ^{14}C present) of metabolites were present, with >90% of the ^{14}C present being parent compound. Following methylation, two monomethoxy pentabromodiphenyl ether metabolites and two monomethoxy tetrabromodiphenyl ether metabolites were tentatively identified. Bile was also analysed for metabolites in a similar way. Two monohydroxy pentabromodiphenyl ether metabolites and two dihydroxy pentabromodiphenyl ether metabolites were identified, along with some evidence for the formation of two thiosubstituted pentabromodiphenyl ethers. The disposition data indicated that the substance was preferentially deposited in adipose tissue, blood, carcass and G.I. tract, with no other tissue contained more than 1% of the ^{14}C-label at 72 hours.

Further information on the uptake and metabolism in mammalian systems can be found in Section 4 (Human health).

Resistance of pentaBDPE to metabolism has also been shown in certain marine mammals. Hepatic microsomes of a white beaked dolphin, sperm whale and a harbour seal were used in *in vitro* assays with 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and an unknown pentabromodiphenyl ether isomer. Incubations took place for 90 minutes at 37^{o}C and the total concentration of pentabromodiphenyl ether congeners used was 1.7 µg/ml. No indication of biotransformation of the polybrominated diphenyl ethers was seen in the test (de Boer et al, 1998b). Relatively high levels of the three congeners had been found by de Boer et al (1998b) in samples of white beaked dolphin (total 6,700 µg/kg wet weight), sperm whale (79-136 µg/kg wet weight) and harbour seal (438-1,470 µg/kg wet weight taken from the North Sea (See Section 3.1.4.3).

The results of an unpublished study on the uptake of a commercial pentaBDPE by root crops from soil have been provided (CSTEE, 2000). In the study, the concentrations of the main components of the commercial product in sugar beet were compared with the concentrations in the surrounding soil. The accumulation factors [defined as concentration in beet (mg/kg wet weight)/concentration in soil (mg/kg wet weight)] were found to be 0.13 for 2,2'4,4'-tetrabromodiphenyl ether, 0.06 for 2,2',4,4',5-pentabromodiphenyl ether and 0.07 for 2,2',4,4',6-pentabromodiphenyl ether. No other details of this study are currently available.

Methods for predicting uptake from soil by root crops are given in the Technical Guidance Document. Using a log K_{ow} of 6.57, the $K_{plant\text{-}water}$ (the partition coefficient between plant tissue and soil pore water) can be estimated as $1.74 \cdot 10^4$ m^3/m^3 using the following equation:

$$K_{plant-water} = Fwater_{plant} + Flipid_{plant} \cdot K_{ow}^{\ b}$$

where $Fwater_{plant}$ = volume fraction of water in plant tissue = 0.65 m^3/m^3
$Flipid_{plant}$ = volume fraction of lipids in plant tissue = 0.01 m^3/m^3
B = correction factor for differences between plant lipids and octanol = 0.95
K_{ow} = octanol-water partition coefficient = $3.715 \cdot 10^6$ m^3/m^3 for pentabromodiphenyl ether (i.e. log K_{ow} = 6.57)
$K_{plant-water}$ = partition coefficient between plant tissue and water [mg/m^3(plant)/mg/m^3(water)] = $1.74 \cdot 10^4$ m^3/m^3 for pentabromodiphenyl ether

In order to compare this estimated partition coefficient with the measured data for uptake in beet, the $K_{plant-water}$ has to be converted to represent concentrations on a mass rather than volume basis. This can be done using the following equations from the Technical Guidance Document.

$$Croot_{plant} = \frac{K_{plant-water} \cdot C_{porewater} \cdot 1000}{RHO_{plant}} \cdot \qquad (1)$$

where $C_{porewater}$ = concentration in soil porewater (mg/l)
RHO_{plant} = bulk density of plant tissue = 700 kg/m^3
$Croot_{plant}$ = concentration in root tissue of plant (mg/kg wet weight)

$$\text{and } C_{porewater} = \frac{C_{soil} \cdot RHO_{soil}}{K_{soil-water} \cdot 1000} \qquad (2)$$

where C_{soil} = concentration in soil (mg/kg wet weight)
RHO_{soil} = bulk density of wet soil = 1,700 kg/m^3
$K_{soil-water}$ = soil-water partitioning coefficient = 16,704 for pentabromodiphenyl ether

Rearranging equations 1 and 2 above gives

$$\frac{Croot_{plant}}{C_{soil}} = \frac{K_{plant-water} \cdot RHO_{soil}}{RHO_{plant} \cdot K_{soil-water}}$$

Therefore the estimated accumulation factor [expressed as concentration in root (mg/kg wet weight)/concentration in soil (mg/kg wet weight)] for pentaBDPE is 2.5. This value is around 20-40 times larger than that measured above for the main components of commercial pentaBDPE. However, this comparison assumes that the composition of the sugar beet and the soil used in the experiment (in terms of properties such as bulk density, water content, lipid content, organic carbon content, etc.) is the same as described by the default values in the Technical Guidance Document. These details are currently not available for the tests carried out with sugar beet and so the comparison should be treated with caution.

3.1.0.5.4 Structure-activity Relationship (SAR) data

Since few data are available on the environmental fate of polybrominated diphenyl ethers the EPI estimation program (Syracuse Research Corporation) was run for some representative compounds. This program estimates various properties from the chemical structure. The values obtained should be treated with caution, although it is possible to deduce likely trends in the environmental behaviour of the substances. The results are shown in **Table 3.9**.

As can be seen from **Table 3.9**, the estimated octanol-water partition coefficient (K_{ow}) and soil organic carbon-water partition coefficient (K_{oc}) increase with increasing bromination. This implies that adsorption onto soil and sediment should increase with increasing bromination but adsorption will still be high for the lower brominated compounds.

The model results also predict that volatility, as measured by Henry's law constant, decreases with increasing bromination across the group and that atmospheric degradation by reaction with hydroxyl radicals also decreases with increasing bromination.

The model estimates that none of the compounds are degraded to any significant extent in sewage treatment works, however, significant removal would be expected by adsorption to sewage sludge and this removal would be expected to increase with increasing bromination.

The predicted environmental behaviour of the individual components of the commercial pentaBDPE is considered further in Appendix E.

Table 3.9 Results of EPI estimation program for some representative polybrominated diphenyl ethers

Property	Bromo diphenyl ether	Dibromo diphenyl ether	Tribromo diphenyl ether	Tetrabromo diphenyl ether	Pentabromo diphenyl ether	Hexabromo diphenyl ether	Heptabromo diphenyl ether	Octabromo diphenyl ether	Nonabromo diphenyl ether	Decabromo diphenyl ether
log K_{ow}	4.94	5.83	5.88	6.77	7.66	8.55	9.44	10.33	11.22	12.11
log K_{oc}	3.62	3.83	4.05	4.27	4.48	4.72	4.93	5.16	5.38	5.61
Henry's law constant (atm m^3/mole)	[a] $4.69 \cdot 10^{-5}$ [b] $1.17 \cdot 10^{-4}$	[a] $1.87 \cdot 10^{-5}$ [b] $4.88 \cdot 10^{-5}$	[a] $7.45 \cdot 10^{-6}$ [b] $2.03 \cdot 10^{-5}$	[a] $2.97 \cdot 10^{-6}$ [b] $8.48 \cdot 10^{-6}$	[a] $1.18 \cdot 10^{-6}$ [b] $3.54 \cdot 10^{-6}$	[a] $4.71 \cdot 10^{-7}$ [b] $1.47 \cdot 10^{-6}$	[a] $1.88 \cdot 10^{-7}$ [b] $6.14 \cdot 10^{-7}$	[a] $7.48 \cdot 10^{-8}$ [b] $2.56 \cdot 10^{-7}$	[a] $2.98 \cdot 10^{-8}$ [b] $1.07 \cdot 10^{-7}$	[a] $1.19 \cdot 10^{-8}$ [b] $4.45 \cdot 10^{-8}$
Volatilisation half-life from river	9.5 hours	23.6 hours	60.1 hours (2.5 days)	154.4 hours (6.4 days)	396 hours (16.5 days)	1010 hours (42.1 days)	2564 hours (106.8 days)	270 days	678 days	1698 days
Volatilisation half-life from lake	236 hours (9.8 days)	409 hours (17 days)	825 hours (34.4 days)	1869 hours (77.9 days)	4518 hours (188 days)	468 days	1175 days	2953 days	7405 days	18530 days
Half-life for reaction with hydroxyl radicals[c]	0.86 days	1.95 days	3.0 days	6.9 days	8.4 days	11.0 days	18.0 days	51.0 days	55.7 days	61.5 days
Total removal in waste water treatment plant:	76.21%	91.29%	91.57%	93.7%	93.99%	94.03%	94.04%	94.04%	94.04%	94.04%
Biodegraded:	0.65%	0.76%	0.76%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%
Adsorbed onto sludge:	74.41%	90.45%	90.78%	92.93%	93.22%	93.25%	93.26%	93.26%	93.26%	93.26%
To air:	1.15%	0.08%	0.03%	0%	0%	0%	0%	0%	0%	0%

[a]Estimated by bond method
[b]Estimated by group method
[c]Calculated from OH reaction rate constant estimated by the method of Atkinson and assuming a OH radical concentration of $1.5 \cdot 10^6$ molecules/cm^3 and 12 hours sunlight/day

Models such as the EPI program are not usually sensitive to the individual isomer structures within a group with the same number of bromine atoms (e.g. the penta isomers). Isomers have been identified in this table to show that the calculations can be repeated exactly for each, and to avoid confusion when calculated and measured data are used together.

3.1.0.6 Natural sources

A number of brominated compounds that are structurally similar to the brominated diphenyl ethers have been found to be present in some marine species, especially marine sponges (Faulkner, 1988; Gribble, 2000). No brominated diphenyl ethers themselves have been found so far. The compounds identified all have the diphenyl ether ring structure but contain a further group/groups on one or both of the aromatic rings. Typical substituents include hydroxyl and methoxy groups. Many of the compounds have been shown to posses antimicrobial properties (Sharma et al, 1969).

Carté and Faulkner (1981) isolated substituted brominated diphenyl ether compounds from marine sponges (*Dysidea herbacea*, *Dysidea chlorea* and *Phyllospongia foliascens*).

The compounds identified were:

2-(2',4'-dibromophenoxy)-3,4,5-tribromophenol,
2-(2',4'-dibromophenoxy)-4,5,6-tribromophenol and
2-(2',4'-dibromophenoxy)-3,5-dibromophenol from *D. heracea*,
2-(2',4'-dibromophenoxy)-4,6-dibromophenol from *D. chlorea* and
2-(3',5'-dibromo-2'-methoxy-phenoxy)-3,5-dibromoanisole,
2-(3',5'-dibromo-2'-hydroxyphenoxy)-3,5,6-tribromophenol and
2-(3',5'-dibromo-2'-hydroxyphenoxy)-3,4,5,6-tetrabromophenol from *P. foliascens.*

Similar compounds have been isolated from *Dysidea* species by Salva and Faulkner (1990), Norton and Wells (1980), Norton et al (1981), Fu et al (1995), Llîn et al (1996) and Anjaneyulu et al (1996). Generally compounds with between 4 and 6 bromine atoms/molecule have been detected. Salva and Faulkner (1990) found that the brominated compounds appeared to found only in the tropical species of *Dysidea* that also contained large populations of cyanophytes in their tissues. Unson et al (1994) demonstrated that the presence of 2-(2',4'-dibromophenyl)-4,6-dibromophenol in *Dysidea herbacea* was associated with the symbiotic filamentous cyanobacterium (similar to *Oscillatoria spongeliae*) present within the organism, rather than the sponge cells, and concluded that the brominated compounds are biosynthesised by the cyanobacterium.

Similar compounds as above have also been found to be produced by acorn worm *Ptychodera flava laysanica* from Hawaii (Higa and Scheuer, 1977) and the green alga *Cladophora fascicularis* (Kuniyoshi et al, 1985) taken from marine waters around Japan. Species of the green algal genus *Cladophora* are known to occur in a variety of marine and freshwaters, including the Baltic Sea (Dodds and Gudder, 1992).

As can be seen above, there are a wide range of chemical substances formed naturally in some marine species that are similar to the polybrominated diphenyl ether flame retardants. It is possible that some of these naturally occurring compounds may cause interferences in analytical methods used to detect the polybrominated diphenyl ether flame retardants in the marine environment. At the extreme, such interference could result in the misidentification of a natural product as a commercial brominated diphenyl ether flame retardant. Since the natural products generally have between 4 and 6 bromine atoms/molecule, this interference is likely to be a consideration only in the determination of the levels of the commercial pentaBDPE flame retardant. Most of the analyses of the polybrominated diphenyl ether flame retardants carried out so far for the marine environment rely mainly on comparison of gas

chromatography (GC) retention times with those of reference materials to identify the various congeners. Interference could therefore occur in such analyses if the natural product a) behaved similarly to the commercial brominated diphenyl ether flame retardant through all clean-up steps of the extraction method and b) had the same GC retention time as that of the commercial product. Given that, in the case of commercial pentaBDPE, there are three main components (and hence GC retention times), the natural products would have to co-elute with all three components in order for all components to be misidentified. Further, in a recent paper by Haglund et al (1997) both polybrominated diphenyl ethers and methoxy-polybrominated diphenyl ethers were detected in biotic samples using GC-mass spectroscopy (MS). In this study, it was seen that the retention times of the methoxylated compounds were different from those of the commercial products under the chromatographic conditions used. This study confirmed the presence of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5- and 2,2',3,4,4'-pentabromodiphenyl ether and 2,2',3,4,4',5'-hexabromodiphenyl ether in samples of ringed and grey seals and herring from along the Swedish coast, and also salmon, fish oil and human adipose tissue by comparison of the mass spectra with that from reference material. The source of the methoxy-derivatives found in this study was not identified, but the possibility of a natural source of these compounds was not ruled out. Other analyses [e.g. Law et al (1996) and GFA (1998)] have also used methodology (e.g. two different analytical columns and/or identification by GC-MS), which provide more positive identification for the commercial substance being analysed.

There is other, indirect, evidence that indicates that at least some of the available analytical results for commercial pentaBDPE represent the commercial product rather than natural sources. For instance, time trends in the levels found in sediment and biota have been found, with increases and decreases following the known trends in usage. If the measured levels represented natural sources then such levels would be expected to be constant with time. Also, the pattern of congeners generally found in biota samples is consistent with the known behaviour of the components of the commercial substances.

Thus, although it is impossible to rule out that the measured levels of the commercial pentaBDPE components found in the environment may actually represent natural products, it is very unlikely that this is the case in all analyses.

3.1.1 Aquatic compartment

3.1.1.1 Calculation of PECs

It should be born in mind in the following sections that the PECs estimated refer to the commercial pentaBDPE products. As was discussed in Section 1, the commercial products are mixtures of congeners, of which pentabromodiphenyl ether isomers make up 50-62%. Some information is available on the individual isomers present in commercial pentaBDPE (particularly regarding levels in the environment) which could allow the estimation of PECs for individual components. However, this information is of limited use in the final risk assessment since the effects data are generated for the commercial product rather than the individual components of the product. Thus, PECs will be derived based on a commercial product basis. This is considered to be a reasonable approach since although preferential uptake of some components of the commercial product by aquatic organisms is observed, this will also occur in the aquatic toxicity tests.

3.1.1.1.1 Production

No production of pentaBDPE currently occurs in the EU and so this will not be considered further in the risk assessment. A PEC is calculated below for information only using the release estimates derived in Section 3.1.0.1. Recent monitoring data in sediments near to a former production site are also available (see Section 3.1.1.2.2), which give an indication of the environmental levels that might be expected.

Based on the physical properties of pentaBDPE, the removal in the sewage treatment plant is estimated to be 90.89%, mainly due to adsorption on sludge [90.7% to sludge; (EUSES; log K_{ow}=6.57, K_{oc} = 556,801 l/kg and H = 11 Pa m^3/mol].

The PEC_{local} for surface water from a production site can be estimated as follows:

Amount released	= 1,500 or 250 kg/year
No of days of operation	= 50
Amount released on each day	= 30 or 5 kg/day
Size of wwtp	= 2,000 m^3/day
Concentration in influent to wwtp	= 15 or 2.5 mg/l
Removal in wwtp	= 90.89%
Concentration in effluent	= 1.37 or 0.23 mg/l
Dilution in receiving water	= 10
Concentration in receiving water ($Clocal_{water}$)	= 137 or 23 µg/l

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

$$PEC_{local}(water) = C_{local\text{-}water}/(1+K_{susp} \cdot C_{susp}) + PEC_{regional}$$

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

Since no measured K_{susp} is available for pentaBDPE, the value of 55,680 l/kg, estimated in Section 3.1.0.5.2 is used, thus:

PEC_{local}(water) from production = 74.7 or 12.5 µg/l

The PEC_{local}(sediment) is estimated for freshly deposited sediment using the equation:

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

where $K_{susp\text{-}water}$ = suspended matter - water partition coefficient (m^3/m^3) = 13,921 m^3/m^3 (using Kp_{susp}= 55,680 l/kg).
RHO_{susp} = bulk density of suspended matter = 1,150 kg/m^3

Thus the PEC_{local}(sed) = 904 or 151 mg/kg (wet weight).

3.1.1.1.2 Polyurethane production

In Section 3.1.0.2.1 it was estimated that 0.15 kg/day of pentaBDPE could be released to waste water from a site producing polyurethane foams.

Using the Technical Guidance Document, this effluent is assumed to pass through a waste water treatment plant of 2,000 m^3/day size (default). Based on the physical properties of pentaBDPE, the removal in the sewage treatment plant is estimated to be 90.89%, mainly due to adsorption on sludge (90.7% to sludge; (EUSES; log K_{ow}= 6.57, K_{oc} = 556,801 l/kg and H = 11 Pa m^3/mol).

The PEC_{local} for surface water from use in polyurethane can be estimated as follows:

Amount released on each day	= 0.15 kg/day
Size of wwtp	= 2,000 m^3/day
Concentration in influent to wwtp	= 75 µg/l
Removal in wwtp	= 90.89%
Concentration in effluent	= 6.83 µg/l
Dilution in receiving water	= 10
Concentration in receiving water ($C_{local\text{-}water}$)	= 0.68 µg/l

$$PEC_{local}(water) = \frac{C_{local\text{-}water}}{(1 + K_{susp} \cdot C_{susp})} + PEC_{regional}$$

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

Since no measured K_{susp} is available for pentaBDPE, the value of 55,680 l/kg, estimated in Section 3.1.0.5.2 is used, thus:

PEC_{local}(water) from polyurethane production = 0.37 µg/l (+ $PEC_{regional}$)

According to the Technical Guidance Document, the $PEC_{regional}$ should be added to this figure to give the final PEC_{local}. The $PEC_{regional}$ has been calculated as 0.0015 µg/l (see Section 3.1.1.1.3) and so the PEC_{local} (water) from polyurethane production = 0.37 µg/l.

{For the indirect human exposure and secondary poisoning scenarios, the Technical Guidance Document suggests that an annual average concentration in surface water is used. Thus the annual average concentration is 0.304 µg/l + $PEC_{regional}$ = 0.305 µg/l}.

The PEC_{local} (sediment) is estimated for freshly deposited sediment using the equation:

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

where $K_{susp\text{-}water}$ = suspended matter - water partition coefficient (m^3/m^3) = 13,921m^3/m^3 (using Kp_{susp}= 55,680 l/kg).
RHO_{susp} = bulk density of suspended matter = 1,150 kg/m^3

Thus the PEC_{local}(sed) = 4.48 mg/kg (wet weight).

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

The estimation of the concentration of pentaBDPE at the regional and continental level can be made using EUSES. The results are reported in **Table 3.11**.

For all runs, release to the continental model was taken to be the release estimated for the total EU minus the release estimated for the region. No release from production was assumed in the model.

The EUSES modelling for the commercial pentaBDPE is complicated by the fact that the substance is a complex mixture and each component of the mixture is likely to behave differently in its partitioning in the environment. The modelling here has been done using the physico-chemical properties shown in **Table 3.10**. Appendix E looks in more detail at the EUSES modelling for this substance and shows that the values used here give results that should be reasonably representative of the commercial substance as a whole.

No biodegradation was assumed in the model, but an atmospheric half-life of 12.6 days (see Section 3.1.0.4.1) was assumed. Regional and continental releases are averaged over 365 days. A full summary of the modelling results is given in Appendix B. No direct release to soil was included in the model. Pentabromodiphenyl ether may be disposed of via landfill and this is a possible route into the soil compartment.

Table 3.10 Data used for estimation of $PEC_{regional}$ and $PEC_{continental}$

Input		Local model	Regional model[a]	Continental model[b]
Releases to air	Polyurethane foam manufacture	0.124 kg/day	37.2 kg/year	112.8 kg/year
	Polyurethane foam use		4,300 kg/year	38,700 kg/year
Release to waste water	Polyurethane foam manufacture	0.15 kg/day	44.6 kg/year	135.4 kg/year
Molecular weight		564.72 g/mol		
Vapour pressure		$4.69 \cdot 10^{-5}$ Pa		
log K_{ow}		6.57		
Fish bioconcentration factor		14,350 l/kg (and 27,400 l/kg)		
K_{oc}		556,801 l/kg		
Water solubility		~2.4 µg/l for pentabromodiphenyl ether		

[a]Releases in the regional model are taken as 10% of the total EU release except in the case of polyurethane foam manufacture, where, the estimated local source may account for >10% of the EU total, and so the figure for the local source is used
[b]Releases in Continental model are estimated from release in total EU - release estimated for Region

Table 3.11 Summary of EUSES modelling for the aquatic environment

Compartment	Local model		Regional model	Continental model
Surface water (dissolved)	Polyurethane foam manufacture	0.37 µg/l (emission episode) 0.305 µg/l (annual average)	1.5 ng/l	0.6 ng/l
Sediment	Polyurethane foam manufacture	4.49 mg/kg wet weight (emission episode)	0.032 mg/kg wet weight	0.013 mg/kg wet weight

The values calculated in **Table 3.11** do not include the regional release to air, surface water and industrial/urban soil estimated as "waste remaining in the environment" (see Section 3.1.0.3). When this particulate waste is included, the regional concentrations become 5.3 ng/l for surface water and 0.114 mg/kg wet weight for sediment. There are considerable uncertainties in these modelled results resulting from both the release estimates themselves and also the modelling of such release. In particular, the availability and distribution behaviour of the pentaBDPE contained within the particulates is unknown.

3.1.1.2 Measured levels in water and sediment

This Section reports the levels of pentaBDPE measured in water and sediments.

The analysis of pentaBDPE is complicated by the fact that the commercial product is a mixture and that there was a lack of analytical standards for individual isomers/congeners of the mixture, particularly for the older analyses. This situation has recently improved and most modern analysis use relatively pure samples of specific congeners present in the commercial products for identification and quantification (Örn, 1997; Örn et al, 1998).

Since the commercial product is a mixture, it is also important to obtain some indication of the levels and distribution of the components of the mixture in the environment. These are included in the following Sections, along with the measured levels of pentabromodiphenyl ether isomers.

3.1.1.2.1 Water

No levels of pentaBDPE have been reported in water. The only analyses relevant to pentaBDPE are for hexabromodiphenyl ether (a possible minor component of commercial pentabromodiphenyl ethers). This substance was analysed for in a large number of water samples from in and around Japan in 1987 and 1988, but was not detected in any sample (detection limit 0.04 μg/l). The samples are thought to be representative of industrial, urban and rural areas of Japan. It is not known if any of the sampling sites were in the vicinity of a polybrominated diphenyl ether production site or other sites of potential release. The results are reported in **Table 3.12**.

Table 3.12 Levels of Hexabromodiphenyl ether in water

Location	Comments	Level	Reference
Japan, 1987	Detection limit 0.04 μg/l	Not detected in 75 samples	Environment Agency Japan, 1991
Japan, 1988	Detection limit 0.04 μg/l	Not detected in 150 samples	Environment Agency Japan, 1991

3.1.1.2.2 Sediment

Several studies have measured levels of commercial pentaBDPE in sediments. In most cases the commercial compound Bromkal 70 was used as reference for identification and quantification.

This substance has been shown to consist mainly of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and an unknown pentabromodiphenyl ether and the levels are sometimes reported for the individual components and sometimes reported in terms of the commercial formulation. The unknown pentabromodiphenyl ether isomer has recently been

shown to be 2,2',4,4',6-pentabromodiphenyl ether (Sellström et al, 1998). In addition, some commercial pentaBDPE products contain small amounts of hexabrominated diphenyl ethers. Although the commercial compound Bromkal 70 is no longer supplied in the EU, the currently supplied pentaBDPE compounds appear to have very similar compositions to this compound (see Section 1.2) and so, although the results are expressed as Bromkal 70, they are likely to represent the total concentrations of all commercial pentaBDPEs in the environment. It is also likely that individual components of the commercial products will distribute in the environment in different ways (e.g. the more highly brominated components may be expected to adsorb more strongly onto sediment than the components with a lower degree of bromination). This further complicates the interpretation of the measured data, particularly if they are based on the commercial formulation. The levels measured of the various components of commercial pentaBDPE are shown in **Tables 3.13** to **3.17**. Wherever possible details of the actual component measured are given.

It is not possible to compare all the measured levels directly with each other as several different units have been used in the various studies. Thus, measured levels are obtained on both a wet weight and dry weight basis, as well as a dry weight ignition loss basis (weight loss obtained by heating a dried sample at around 550^{o}C for 2 hours). Some comparison can be made between the various levels if it is assumed that the sediments are all approximately 80% water by volume or 62% by weight (Technical Guidance Defaults) and have an organic carbon content of 10%. Thus dry weight values can be converted to approximate wet weight values by dividing by 2.6. For most of the results reported on a dry weight ignition loss basis (Nylund et al, 1992) actual ignition loss and water content values are given, allowing conversion of the data to wet or dry weight values. For the results of Sellström et al (1990), no information on ignition weight loss or water contents was given and so these results have tentatively been converted to wet weight values by assuming 80% water content and 20% dry weight ignition loss (based on the ignition loss being due to organic matter loss and the organic matter content being approximately twice the organic carbon content of 10%). These values are in line with the values reported by Nylund et al (1992) for surface sediment (water content 82%; dry weight ignition loss 18%).

A recent study in the United Kingdom has shown that elevated levels of pentaBDPE are found in sediments downstream from a production site (production since ceased), and also at sites where pentaBDPE may be used (Law et al, 1996; Allchin et al, 1999).

The highest level reported in this study was 1,271 µg/kg dry weight. A commercial product of similar composition to Bromkal 70-5DE and a standard solution of known amounts of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5- and 2,2',3,4,4'-pentabromodiphenyl ether were used for quantification. The levels found are reported in **Table 3.13**. A further study of levels in sediment near to possible sources of release has been carried out (Environment Agency, 1997). In this study, a number of watercourses near to brominated flame retardant use, storage and disposal sites were monitored. The samples were analysed by GC-MS. The authors indicated that the lack of certified reference materials means that the results can only be considered approximate to a factor of 2 or 3. The results are shown in **Table 3.14**.

Watanabe (1987a) reported the results of a survey of sediments in Japan from 1981 to 1983. Results were reported for both tetrabromodiphenyl ether and pentabromodiphenyl ether, but no indication as to the isomers detected was given. The detection limit for the analyses was 2 µg/kg dry weight. In river sediments, tetrabromodiphenyl ether was detected in 5/6 samples at levels of 12-31 µg/kg dry weight, and pentabromodiphenyl ether was detected in 5/6

samples at 9-28 µg/kg dry weight. In estuary sediments, neither tetra- or pentabromodiphenyl ether were detected in the 7 samples analysed. Similarly, in marine sediment samples, neither compound was detected in the 2 samples taken. Generally, brominated diphenyl ethers were found only in river sediments near to possible point sources and not in estuary or marine sediments (Watanabe and Tatsukawa, 1990).

Nylund et al (1992) carried out an investigation of the levels of polybrominated diphenyl ethers in a sediment core taken from the Baltic Sea. A commercial pentaBDPE, Bromkal 70-5DE was used as reference (this consists of 41% 2,2',4,4'-tetrabromodiphenyl ether, 45% 2,2',4,4',5-pentabromodiphenyl ether and 7% of an unidentified pentabromodiphenyl ether). Levels of the tetra- and pentabromodiphenyl ethers were found to be low in the lower depths of the sediment (samples were though to relate to 1939-1970) but were found to increase in the upper 40 mm of the core. The most rapid increase occurred in the top 20 mm, corresponding to the beginning of the 1980s. The levels measured are shown in **Table 3.16**.

The levels of 2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether have been determined in sediments taken both upstream and down stream of a factory (type not specified in the original paper but KEMI (1999a) indicated that it was a polymer processing site which produced, amongst other things, printed circuit boards. The measurements were performed in 1988, and it is not known if the factory also processed polyurethane foam at this time). The levels measured were 3.5 and 8.2 µg/kg IG (dry weight ignition loss basis) for the two substances respectively in sediments from upstream of the factory. Much higher levels, 840 and 1,200 µg/kg IG, were found for the two substances respectively in sediments downstream of the factory (Sellström et al, 1990). The results are shown in **Table 3.16**. The same results, along with levels of an unknown pentabromodiphenyl ether, expressed on a dry sediment weight basis were reported by Sellström (1996) as 2.5 µg/kg dry weight upstream and 490 µg/kg dry weight downstream for 2,2',4,4'-tetrabromodiphenyl ether, 5.9 µg/kg dry weight upstream and 770 µg/kg dry weight downstream for 2,2',4,4',5-pentabromodiphenyl ether and 1.1 µg/kg dry weight upstream and 170 µg/kg dry weight downstream for the unknown pentabromodiphenyl isomer (sum of all three components is 9.5 µg/kg dry weight upstream and 1,400 µg/kg dry weight downstream). A background sediment sample taken from the Bornholm deep in the Baltic Sea was found to contain around 0.52 µg/kg dry weight as the sum of all three congeners (Sellström, 1996).

The levels of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and 2,2'4,4',6-pentabromodiphenyl ether in sediments from Sweden have also been determined by Sellström et al (1998). Surface sediment (0-2 cm) was collected at 8 locations in the River Viskan, its tributary the River Häggån and other nearby water systems. Samples were collected up- and downstream from a number of industries thought to be using flame retardants.

The levels measured ranged between<2-50 µg/kg IG (dry weight ignition loss basis) for 2,2',4,4'-tetrabromodiphenyl ether, <1-53 µg/kg IG for 2,2',4,4',5-pentabromodiphenyl ether and <0.4-19 µg/kg IG for 2,2',4,4',6-pentabromodiphenyl ether, with the highest levels generally being found downstream from industry. The results are shown in **Table 3.16**.

Table 3.13 Levels of commercial pentabromodiphenyl ethers measured in the United Kingdom (Law et al, 1996; Allchin et al, 1999)

Location	Comments[c]	Level (μg/kg dry weight)				
		2,2',4,4'-TetraBDPE	2,2',4,4',5-PentaBDPE	2,2',3,4,4'-PentaBDPE	Approx. total[a]	Product basis[b]
River Tweed at Tweedmouth	Background site	0.4	<0.6	<0.4	0.4	<0.38
River Tweed at Berwick on Tweed bridges	Background site	<0.3	0.6	<0.4	0.6	<0.38
River Nith, upstream of wwtp	Near rubber producer	<0.3	<0.6	<0.4	nd	<0.38
River Nith, downstream of wwtp	Near rubber producer	1.7	3.5	<0.4	5.2	0.6
River Nith at Glencaple	Near rubber producer	0.7	1.0	<0.4	1.7	<0.38
Avonmouth	Near flame retardant producer/user	2.4-3.6	2.9-4.7	<0.4-9.2	7.1-16.6	0.6-1.0
River Tees, upstream of confluence with River Skerne	Near a producer of pentaBDPE[d]	<0.3	<0.6	<0.4	nd	<0.38
River Tees, downstream of confluence with River Skerne	Near a producer of pentaBDPE[d]	8.0	11	2.9	21.9	35
River Skerne at Croft-on-Tees	Near a producer of pentaBDPE[d]	51	85	3.5	139.5	34
River Skerne at Newton Aycliffe	Near a producer of pentaBDPE[d]	239	319	2.7	560.7	130
Howden Beck	Near a producer of pentaBDPE[d]	86	111	1.8	198.8	45
River Skerne, upstream of Howden Beck	Near a producer of pentaBDPE[d]	112	159	<0.4	271	68
River Skerne, upstream of Howden Beck	Near a producer of pentaBDPE[d]	68	126	0.7	194.7	51
Hyndburn Brook, upstream of wwtp	Near to foam manufacturer	7.6	16	<0.4	23.6	6.1
River Calder at Cock Bridge	Near a foam manufacturer	2.3	0.6	4.2	7.1	<0.38
River Calder, downstream of wwtp	Near to foam manufacturer	24	46	0.5	94.1	18
Elstow landfill	Landfill receiving brominated wastes	0.8-2.4	2.9-5.7	<0.4	5.3-6.5	<0.38-1.5
Elstow Brook	Downstream of landfill site	0.4	<0.6	1.2	1.6	<0.38

Table 3.13 continued overleaf

Table 3.13 continued

Location	Comments[c]	Level (μg/kg dry weight)				
		2,2',4,4'-TetraBDPE	2,2',4,4',5-PentaBDPE	2,2',3,4,4'-PentaBDPE	Approx. total[a]	Product basis[b]
Tees Estuary	Portrack wwtp	8.9	16	9.1	34	19
	Bamlett's Bight	368	898	4.8	1,271	366
	No. 23 buoy	49	99	14	162	77
	Phillips approach buoy	103	201	72	372	81
Great Ouse at Kings Lynn	Downstream of landfill site	4.2	4.6	<0.4	8.8	<0.38
River Ribble at Freckleton saltings	Near foam manufacturing site	1.2	1.7	<0.4	2.9	<0.38
River Humber at Paull		21	36	<0.4	57	6.6

[a]Estimated concentration of commercial product based on the sum of the main three components.
[b]Estimated concentration using a commercial pentaBDPE product for quantitation.
[c]The main possible source of polybrominated diphenyl ethers in general were identified – it is not known if pentaBDPE was used at all these sites.
[d]Production has since stopped at this site.

Table 3.14 Levels of pentabromodiphenyl ether in sediment in the UK near to possible sources of release

Location	Comment	Level of pentabromodiphenyl ether
Upstream of a plastics processor	Decabromodiphenyl ether used.	<50 μg/kg (dry weight)
Downstream of a plastics processor	Decabromodiphenyl ether used	<50 μg/kg (dry weight)
Upstream of warehouse	Decabromodiphenyl ether stored	<100 μg/kg (dry weight)
Downstream of warehouse	Decabromodiphenyl ether stored	<100 μg/kg (dry weight)
Industrial area	Upstream of site possibly using pentaBDPE	<100 μg/kg (dry weight)
Industrial area	Downstream of site possibly using pentaBDPE	<100 μg/kg (dry weight)
Mersey estuary	Industrial area, upstream of polymer processing site	<100 μg/kg (dry weight)
Mersey estuary	Downstream of polymer processing site	<100 μg/kg (dry weight)
Upstream of a plastic compounder	Decabromodiphenyl ether used	5.9 μg/kg (dry weight)
Downstream of a plastic compounder	Decabromodiphenyl ether used	<5 μg/kg (dry weight)
Landfill site.	Pentabromodiphenyl ether waste disposed on-site	<100 μg/kg in sediment at the site and nearby stream

Table 3.15 Levels of commercial pentabromodiphenyl ether in sediments in the Netherlands (de Boer and Dao, 1993)

Location	Comments	Level (μg/kg wet weight)		
		2,2',4,4'-TetraBDPE	2,2',4,4',5-PentaBDPE	Approx. total
Haringvliet-east	River sediment from 1992	6.7	7.3	14
Nieuwe Merwede	River sediment from 1992	17		(17)
Meuse	River sediment from 1992	6.9	8.2	15.1
Waal	River sediment from 1992	23	21	44

Table 3.16 Levels of commercial pentabromodiphenyl ether in sediments in Sweden (continued overleaf)

Location	Comments	Level (μg/kg IG)[a]			
		2,2',4,4'-TetraBDPE	2,2',4,4',5-PentaBDPE	Unknown PentaBDPE isomer	Approx. total
Sediments from near a polymer factory, southern Sweden	Upstream	3.5[b]	8.2[b]		11.7
	Downstream	840[b]	1,200[b]		2,000
Lake Marsjön	Upstream from industry	<2[d]	<1[d]	<0.4[d, e]	<3
River Viskan	Downstream from town	12[d]	12[d]	3.5[d, e, f]	27.5
River Viskan	At Moga	13[d]	9.2[d]	3.6[d, e, f]	25.8
River Viskan	Upstream from Skene	23[d]	4[d]	8.9[d, e, f]	74.9
River Viskan	Downstream from Skene	50[d]	53[d]	19[d, e]	122
River Häggån	Upstream from Fritsla	1.3[d]	1.1[d]	0.31[d, e]	2.7
River Häggån	Downstream from Fritsla	2.0	2.7[d]	0.69[d, e]	5.4
Lake Skäresjön		<2[d]	<2[d]	0.63[d, e, f]	<4.6
Sediment core, Baltic Sea	0-5 mm depth	1.6[c]	0.98[c]	0.31[c]	2.89
	5-10 mm depth	0.76[c]	0.20[c]	0.07[c]	1.03
	10-15 mm depth	0.68[c]	0.36[c]	<0.04[c]	1.04
	15-20 mm depth	0.50[c]	0.13[c]	<0.04[c]	1.67
	80-90 mm depth	0.06[c]	<0.04[c]	<0.04[c]	0.06
Lake Öresjö	Downstream from industry	7.4[d]	3.5[d]	1.2[d, e, f]	12.1

[a]Concentrations given on a dry weight ignition loss basis
[b]Data from Sellström et al, 1990.
[c]Data from Nylund et al, 1992.
[d]Data from Sellström et al, 1998.
[e]Identified as 2,2',4,4',6-pentabromodiphenyl ether.
[f]Maximum value due to interferences.

Table 3.17 Levels in sediments (<63 µm fraction) from estuaries in the EU (van Zeijl, 1997)

Estuary/location	% of sediment <63 µm	% organic carbon in <63 µm fraction	% organic carbon in whole sediment	Concentration in the <63 µm fraction (µg/kg dry weight)	
				Tetrabromodiphenyl ether	Pentabromodiphenyl ether
Liffey River	23.4	2.01	0.86	0.61	0.73
Clyde	72.4	3.25	3.13	0.74	1.03
Mersey	42.1	2.44	1.09	2.20	2.27
Southampton	35.7	1.03	0.81	0.19	0.23
Thames	10.0	1.90	0.3	0.64	0.70
Humber	20.3	2.40	1.17	5.80	6.93
Tyne	29.2	1.89	1.01	0.70	0.99
Forth	19.8	2.41	0.78	0.39	0.36
Seine	53.3	2.77	2.92	0.69	0.83
North sea (off Belgium)	38.4	1.48	1.1	<0.17	<0.20
Schelde	5.8	3.53		0.42	0.32
Rijn	51.9	2.83	2.65	1.40	1.30
Noordwijk	7.4	2.91		0.90	1.00
Waddensee	10.2	2.27	0.33	0.19	0.42
Ems	68.9	4.13	4.53	0.38	0.44
Weser	54.7	2.73	2.46	0.17	0.20
Elbe	49.9	1.79	1.59	<0.17	<0.20
Göta	73.1	2.28	2.23	<0.17	<0.20
Glomma	71.2	2.38	2.19	<0.17	<0.20
Skiens	70.3	3.30	3.02	<0.17	<0.20
Otria	61.2	2.68	2.64	<0.17	<0.20
100 km off Terschdling (reference site)	18.7	1.15	0.33	0.18	0.20

A recent unpublished study indicated that the sum of the levels of 2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether in 20 surficial sediments from sites in the Baltic Sea were in the range 0.21 to 1.1 µg/kg dry weight in 8 sites in the southern part (Baltic Proper) and were not detected in samples from the northern part (Bothnian Bay) (de Wit, 1999; Sellström et al, 1999).

van Zeijl (1997) reported the results of the analysis of sediments from 22 estuaries in Western Europe. In the study, the top layer (to a maximum depth of 5 cm) was sampled and the <63 µm fraction was analysed for the presence of tetrabromodiphenyl ether and pentabromodiphenyl ether using a GC-MS technique (electron capture negative ionisation and monitoring the bromide ions formed). No information on the compounds used for calibration of the method was given. The results are shown in **Table 3.17**.

Fernández et al (1992) detected pentaBDPE in sediments taken off the coast of Spain between the Besós River and Barcelona Harbour (no detection limit stated).

3.1.1.2.3 Comparison of measured levels with predicted levels

Water

Very few measured levels in water are available for the constituents of commercial pentaBDPE and so it is not possible to compare the predicted levels with the modelled levels directly. However, since the predicted levels in water are used to derive the predicted levels in sediment, it would be expected that similar comments as given below in the comparison of sediment levels may also apply to the estimated water levels.

Sediment

Components of commercial pentaBDPEs have been measured in sediments in several EU countries, and also Japan. The interpretation of the measured results is complicated by the fact that different bases of measurement have been used in some of the studies, and results are reported for various isomers of the commercial mixtures. Thus the measured results can be used only to obtain an approximate indication of the levels found in the environment.

Levels of commercial pentaBDPE of around 561-1,271 µg/kg dry weight (approximately 215-490 µg/kg wet weight using the Technical Guidance default water content) have been measured in a river and heavily industrialised estuary close to a former pentaBDPE production site in the United Kingdom (production at the site has now ceased). The highest levels were found in the heavily industrialised estuary, which may indicate that sources other than the production site contributed to these levels. No production currently occurs in the EU. Levels of pentaBDPE near to polymer processing sites in the UK are around 94.1 µg/kg dry weight (approximately 36 µg/kg wet weight using the Technical Guidance default water content), although it is not clear if pentaBDPE was used at the site. Higher levels of around 2,000 µg/kg IG or 1,400 µg/kg dry weight (approximately 540 µg/kg wet weight using the Technical Guidance default water content) have been measured near to a factory (unspecified) in Sweden. These measured concentrations are considerably lower than the concentrations of pentaBDPE predicted to occur at a polyurethane processing site (4.49 mg/kg wet weight). These discrepancies could be due to several reasons, such as overestimation of the amounts released, greater removal and dilution than estimated during waste water treatment or overestimation of the amounts adsorbed to sediment (the equations used may not

be valid for substances with very high log K_{ow} values). It is therefore proposed that the measured values relevant to processing sites will be used along with the predicted values in the risk assessment.

At a regional level, the levels measured in rivers (in industrialised countries/areas) of individual isomers are in general around 1-20 µg/kg wet weight for 2,2',4,4'-tetrabromodiphenyl ether and 1-20 µg/kg wet weight for 2,2',4,4',5-pentabromodiphenyl ether, with the levels of other pentabromodiphenyl ether isomers generally being lower. The approximate level of the commercial pentaBDPE measured is up to around 50 µg/kg wet weight. This is in good agreement with the level predicted for the total commercial pentaBDPE in the regional model of 32 µg/kg wet weight for fresh sediment. Lower levels of pentaBDPE, generally <5 µg/kg have been measured in sediments from estuaries.

Industry has indicated that there is a possibility that commercial pentaBDPE may have been used in hydraulic mining fluids as a polychlorinated biphenyl replacement, although it is thought that pentaBDPE is not currently used for this application in the EU. If this use did occur it might account for some of the reported occurrences of the substance in remote areas (for instance, there are many mining areas situated in Sweden). However, after intensive investigation (KEMI, 1999b), this use has not been confirmed in the areas sampled. Similarly, industry indicates that there is a possible (unconfirmed) use in completion fluids used in oil wells/drilling in the North Sea. Again, such a use could explain the occurrence of the substance in marine environments.

3.1.1.3 Summary of PECs for the aquatic compartment

Concentrations of pentaBDPE in the aquatic compartment have been estimated using a variety of assumptions. The concentrations of pentaBDPE estimated for the aquatic compartment are summarised in **Table 3.18**.

The predicted concentrations of pentaBDPE in water are low for all of the scenarios considered. Adsorption onto sediment is predicted to be important and this is where the highest concentrations of pentaBDPE are predicted to occur in the aquatic environment. This is born out by the measured data. The highest reported levels of pentaBDPE (up to around approximately 490-540 µg/kg wet weight) have been found in a heavily industrialised area near to potential sites of release. Pentabromodiphenyl ether is not currently produced in the EU.

Table 3.18 Summary of predicted environmental concentrations for the aquatic compartment

Media	Source	Type	Concentration
Water	Polyurethane production	PEC_{local}	0.37 µg/l
	Regional scale	$PEC_{regional}$	0.0015 µg/l[a]
Sediment (fresh)	Polyurethane production	PEC_{local}	4.5 mg/kg wet weight
		Measured	0.54 mg/kg wet weight
	Regional scale	$PEC_{regional}$	0.032 mg/kg wet weight[a]
		Measured	0.05 mg/kg wet weight

[a]The calculations do not include the contribution from "waste remaining in the environment". When this is included the $PEC_{regional}$ is 0.0053 µg/l for surface water and 0.114 mg/kg wet weight for sediment

3.1.2 Terrestrial compartment

3.1.2.1 Calculation of PECs

The Technical Guidance outlines methods for calculation of soil concentrations as a result of application of sewage sludge to agricultural land and from wet and dry deposition from the atmosphere. The major potential route for pentaBDPE to the atmosphere identified appears to be from volatilisation from polyurethane foam over the lifetime of a product. The concentrations in soil have been estimated using the EUSES programme. Details of the input parameters used in the model are given in Section 3.1.1.1.3 and a printout of the model results is given as Appendix B. The predicted levels obtained are summarised in **Table 3.19**.

Table 3.19 Summary of the predicted concentrations in soil

Scenario	Soil type	PEC
Polyurethane production	Agricultural soil – averaged over 30 days	PEC_{local} = 2.67 mg/kg wet weight
	Agricultural soil – averaged over 180 days	PEC_{lcoal} = 2.67 mg/kg wet weight
	Grassland - averaged over 180 days	PEC_{local} = 1.18 mg/kg wet weight
Regional	Agricultural soil	$PEC_{regional}$ = 0.13 mg/kg wet weight
	Natural soil and industrial/urban soil	$PEC_{regional}$ = 0.16 mg/kg wet weight

The results given in **Table 3.19** do not include the contribution for "waste remaining in the environment". When this is included the regional concentrations are 0.17 mg/kg wet weight for agricultural soil, 0.21 mg/kg wet weight for natural soil and 2.27 mg/kg wet weight for industrial/urban soil. There are large uncertainties in these values (see Section 3.1.1.1.3).

At the regional level, atmospheric deposition appears to make an important contribution to the predicted concentrations in soil. This is because the levels estimated for agricultural and natural are similar but natural soil receives aerial deposition only, whereas agricultural soil receives contributions from both sewage sludge and aerial deposition.

Since pentaBDPE is a persistent substance, the levels in soil might be expected to build up in time. The regional concentration estimated in **Table 3.19** is a "steady state" concentration, and represents the concentration that would build up in the environment over many years assuming a constant input rate. At the local level, the concentrations are estimated after 10 years input via sewage sludge and atmospheric deposition. For pentaBDPE, it is estimated that after 10 years, the concentrations predicted represent around 0.6-0.9% of the "steady state" values. This means that higher concentrations would be predicted if longer application periods were considered for sewage sludge. Also, although atmospheric deposition only makes a small contribution to the predicted local concentrations in soil, it could, over very long periods (probably of the order of hundreds of years), also contribute to a build up in soil (as is seen with the regional modelling).

3.1.2.2 Measured levels

No measured levels of pentaBDPE in soil have been reported.

The levels of polybrominated diphenyl ethers in sewage sludge from 13 municipal wastewater treatment plants in Germany have been determined (Hagenmaier et al, 1992). The sludge from the treatment plants was known to be used on agricultural land. The levels of polybrominated diphenyl ethers were determined using a GC-MS method. The results of the analyses for components of commercial pentaBDPE are shown in **Table 3.20**.

Table 3.20 Levels of polybrominated diphenyl ethers in sewage sludge applied to agricultural land

Component	Level (mg/kg dry weight)
Tribromodiphenyl ether	0.1-0.97
Tetrabromodiphenyl ether	0.17-7.52
Pentabromodiphenyl ether	0.22-7.51
Hexabromodiphenyl ether	0-1.21

Samples of Swedish sewage sludge collected in 1988 were also analysed by Nylund et al (1992) for the polybrominated diphenyl ethers. The levels found [measured on a dry weight ignition loss basis (IG)] were 15 µg/kg IG for 2,2',4,4'-tetrabromodiphenyl ether, 19 µg/kg IG for 2,2',4,4',5-pentabromodiphenyl ether and 3.4-3.7µg/kg IG for the unknown pentabromodiphenyl ether.

Using the percentage ignition losses (57-67%) and dry solid contents (27%) given in the paper, it is possible to convert the sewage sludge values to dry or wet weight values. On a dry weight basis, the measured levels are 8.6-10.1 µg/kg dry weight for 2,2',4,4'-tetrabromodiphenyl ether, 10.8-12.7 µg/kg dry weight for 2,2',4,4',5-pentabromodiphenyl ether and 1.9-2.5 µg/kg dry weight for the unknown pentabromodiphenyl ether. Expressed on a wet weight basis the values are 2.3-2.7 µg/kg wet weight for 2,2',4,4'-tetrabromodiphenyl ether, 2.9-3.4 µg/kg wet weight for 2,2',4,4',5-pentabromodiphenyl ether and 0.52-0.67 µg/kg wet weight for the unknown pentabromodiphenyl ether.

Further levels in digested sewage sludge from Sweden were reported by de Wit (1999) and also (in slightly different form) by Sellström et al (1999).The samples were collected from three sewage treatment plants in Stockholm in 1998 and the levels found were 39-91 µg/kg dry weight for 2,2',4,4'-tetrabromodiphenyl ether, 48-120 µg/kg dry weight for 2,2',4,4',5-pentabromodiphenyl ether and 11-28 µg/kg dry weight for 2,2',4,4',6-pentabromodiphenyl ether.

3.1.2.3 Comparison of predicted and measured levels

No measured levels of pentaBDPE have been reported for soil. There are several data showing that components of commercial pentaBDPEs are present in sewage sludge in the EU, but it is not possible to say how these levels refer to the various scenarios considered in this assessment (i.e. if any of the sewage treatment plants sampled received effluent from a facility using pentaBDPE). Based on the reported data, the level of commercial pentaBDPE in sewage sludge is around 20-250 µg/kg dry weight. This is around 700-8,500 times lower than the values in sewage sludge (171 mg/kg dry weight for polyurethane production) used for predicting the concentration of pentaBDPE in soil in the local scenario. The EUSES printout does not give an estimate of the concentration in sewage sludge in the regional model, but this can be roughly estimated as around 55 µg/kg dry weight (based on a daily

regional emission to the waste water treatment plant (0.086 kg/day; from **Table 3.1.0.3**), the fraction directed to sludge in the waste water treatment plant (90.7%) and the estimated sludge production rate for the size of the regional waste water treatment plant [i.e. approximately $1.42 \cdot 10^6$ kg of dry sludge will be produced each day from treatment plants serving a population of $2 \cdot 10^7$ people)]. This value is in good agreement with the levels found in the various studies. Atmospheric deposition of pentaBDPE may also contribute to the levels in soil and so in the absence of actual measured levels in soil, the predicted concentrations will be used in the assessment.

3.1.3 Air compartment

3.1.3.1 Calculation of PEC_{local} (air)

In Section 3.1.0, the only point source release to air of pentaBDPE identified was from polyurethane foam production. Using the methods outlined in the Technical Guidance Document, the following PEC_{local} in air at 100 m from the source of release can be estimated:

Amount released on each day	= 0.124 kg/day
Standard concentration in air at a source strength of 1 kg/day	= $2.78 \cdot 10^{-4}$ mg/m^3
Concentration of pentaBDPE during emission episode	= 34.5 ng/m^3
Annual average concentration of pentaBDPE	= 28.3 ng/m^3

No significant direct emission of pentaBDPE is thought to occur during production and use or through sewage treatment processes and so it is not possible to calculate a PEC_{local} for these situations.

3.1.3.2 Calculation of $PEC_{regional}$ (air) and $PEC_{continental}$ (air)

The regional and continental concentrations of pentaBDPE have been estimated using EUSES. Details of the input data are given in Section 3.1.1.1.3 and a full print out of the model is shown in Appendix B. The estimated $PEC_{regional}$ is 0.27 ng/m^3 and the $PEC_{continental}$ is 0.1 ng/m^3. These values do not include the contribution from "waste remaining in the environment". When this is included, the $PEC_{regional}$ is 0.35 ng/m^3 and the $PEC_{continental}$ is 0.13 ng/m^3.

3.1.3.3 Measured levels

No measured levels of pentaBDPE in outdoor air appear to be available, and so the predicted levels will be used for the assessment. The concentrations of pentaBDPE in air are expected to be very low. A recent study looked for the presence of

2,2',4,4'-tetrabromodiphenyl ether,
2,2',3,4,4'-pentabromodiphenyl ether,
2,2',4,4',5-pentabromodiphenyl ether,
2,2',4,4',6-pentabromodiphenyl ether,
2,2',4,4',5,5'-hexabromodiphenyl ether,
2,2',4,4',5,6'-hexabromodiphenyl ether and
2,2',3,4,4',5',6'-heptabromodiphenyl ether

in indoor air where office equipment was in use.

Particulates in the air where sampled and 2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether were detected in some samples but no levels were reported. Also, no indication was given in the paper as to whether these substances were found in control environments (e.g. outdoor air or offices without business equipment) (Bergman et al, 1997a).

The levels of commercial pentaBDPE have recently been measured in air from within a television set from Israel. The television had been used for 13 years and the inside of the housing was heated to temperatures of 42-110^{o}C to simulate operating temperatures. Air samples were taken from inside the television set and from the surrounding laboratory air. No brominated compounds were found in the laboratory air (no detection limit given), but very low levels of one tetrabromodiphenyl ether isomer (39 ng/m^3), three pentaBDPE isomers (10 ng/m^3, 26 ng/m^3 and 51 ng/m^3) and one hexabromodiphenyl ether isomer (52 ng/m^3) were found. The same compounds were found at very low levels in the circuit board (tetrabromodiphenyl ether isomer at 46 µg/kg, pentaBDPE isomers at <0.02-<0.4 µg/kg and hexabromodiphenyl ether isomers at 3.1-14 µg/kg) indicating that this may have been the source of these substances. Wipe samples from the television back indicated that decabromodiphenyl ether was present in this component (de Boer et al, 1998a).

Watanabe et al (1992) measured the levels of various polybrominated diphenyl ethers in air from the vicinity of recycling/incineration plants in Taiwan and an urban area in Japan. In the samples from Taiwan, the levels measured were 30-34 pg/m^3, 48-55 pg/m^3, 13-34 pg/m^3 and 5.6-81 pg/m^3 for the tri-, tetra-, penta- and hexabromodiphenyl ether congeners respectively. The levels found in Japan were 4.7-10 pg/m^3, 10-39 pg/m^3, 4.7-18 pg/m^3 and 12-33 pg/m^3 for the tri-, tetra-, penta- and hexabromodiphenyl ether congeners respectively.

Bergander et al (1995) measured levels of tetra- and pentaBDPE congeners in air samples from two areas of Sweden. The areas sampled were Ammarnäs (located on approximately N 65^{o} on the eastern rim of the mountain ridge separating Norway and Sweden) in January 1991, and Hoburgen (located on the southernmost tip of the island Gotland in the central Baltic) in July 1990. Both sampling sites are considered to be in areas remote from industry. In the sampling, the substances in the particulate phase were collected on glass fibre filters and substances in the gas phase were adsorbed onto polyurethane foam plugs The results of the analysis are shown in **Table 3.21**. The total polybrominated diphenyl ether levels measured in the samples were around 1-8 pg/m^3. Indications of the presence of hexabromodiphenyl ether was found in the particulate phase samples.

Levels of polybrominated diphenyl ethers in air in computer rooms have been reported (Kemmlein, 2000). The level found was 165 pg/m^3 in a room containing a main frame computer, six personal computers and several printers and copy machines (volume 100 m^3) and 314 pg/m^3 in a room containing eight personal computers and several printers (volume 30 m^3). The dominant congeners found were 2,2',4,4'-tetrabromodiphenyl ether (~60-64% of total) and 2,2',4,4'5-pentaBDPE (~20% of total).

Table 3.21 Levels of pentaBDPE in air from remote locations in Sweden (Bergander et al, 1995)

Sampling site	Sample type	Concentration (pg/m^3)		
		2,2',4,4'-TetraBDPE	2,2',4,4',5-PentaBDPE	2,2',4,4',6-PentaBDPE
Ammarnäs	PUF	4.1	0.3	0.1
	Filter	2.2	1.3	0.3
Hoburgen	PUF	0.5	0.15	0.04
	Filter	0.2	0.2	0.04

PUF = polyurethane foam plug - gas phase concentration
Filter = filter sample - particulate phase concentration

The concentration of 2,2',4,4'-tetrabromodiphenyl ether has been reported to be 1.2-2.1 ng/m^3 in ambient air at a plant for dismantling electronic equipment in Sweden, but was not detected in office air (Sjödin et al, 1999).

Preliminary results for the levels of 13 polybrominated diphenyl ether congeners in air from two locations (rural areas) in the United Kingdom are available. In these samples, the mean annual concentration of the 13 congeners (ranging from tri- to heptabromodiphenyl ethers) were 120 pg/m^3 and 100 pg/m^3 at two sites respectively (DETR, 1999).

3.1.3.4 Comparison of predicted and measured levels

The database of measured levels in air is relatively small and not directly comparable with the local release scenarios. The highest total levels measured are associated with indoor air, e.g. in computer rooms (up to 314 pg/m^3) and at sites where electronic equipment is being dismantled/recycled (up to 2,100 ng/m^3). The significance of these results, in terms of elevated exposure at the sites, is uncertain due to a lack of control or background samples. The limited data available on background levels indicates a concentration of around 1-8 pg/m^3 from remote areas of Sweden and 100-120 pg/m^3 from rural areas in the United Kingdom. These values are comparable with the predicted regional and continental concentrations of 270 and 100 pg/m^3 respectively.

3.1.4 Non-compartment specific exposure relevant for the food chain

3.1.4.1 Predicted concentrations in biota

According to the Technical Guidance Document, two secondary poisoning scenarios may be considered. These are water $\Rightarrow$ fish $\Rightarrow$ fish-eating bird or mammal and soil $\Rightarrow$ earthworm $\Rightarrow$ worm-eating birds or mammals. In both scenarios, a PEC(oral) in food is determined.

For fish-eating birds and mammals, the PEC(oral, fish) can be calculated from the PEC(water) and a fish bioconcentration factor (BCF). For pentaBDPE, a BCF of around 14,350 l/kg (wet fish) has been determined, and re-analysis of this data leads to a BCF of 27,400 l/kg (wet fish) (see Section 3.1.0.5.3). Using these values for the BCF, estimated PEC(oral, fish) are shown in **Table 3.22** for the various scenarios considered. For the local scenarios, the annual average water concentrations are used, as recommended in the Technical Guidance.

Table 3.22 Estimated PEC(oral, fish) for pentabromodiphenyl ether

Source	Estimated water concentration	Estimated concentration in fish	
		BCF = 14,350 l/kg	BCF = 27,400 l/kg
Polyurethane production	PEC_{local}(water) = 0.305 µg/l (annual average)	PEC_{local}(oral, fish) = 4.38 mg/kg (wet fish)	PEC_{local}(oral, fish) = 8.36 mg/kg (wet fish)
Regional	$PEC_{regional}$ = 1.5 ng/l	$PEC_{regional}$ (oral, fish) = 0.022 mg/kg (wet fish)[a]	$PEC_{regional}$ (oral, fish) = 0.041 mg/kg (wet fish)[a]
Continental	$PEC_{continental}$ = 0.6 ng/l	$PEC_{continental}$(oral, fish) = 0.008 mg/kg (wet fish)	$PEC_{continental}$(oral, fish) = 0.016 mg/kg (wet fish)

[a]The calculations do not include the contribution from "waste remaining in the environment". If this is included the resulting $PEC_{regional}$(oral, fish) becomes 0.076 or 0.145 mg/kg wet fish

For the terrestrial food chain, a bioconcentration factor for earthworms is needed. No measured value exists for pentaBDPE and so a value has to be estimated from the log K_{ow} value as $K_{earthworm\text{-}porewater} = 1.26 \cdot 10^5$ l (porewater)/kg (wet earthworm) (this is the maximum value set by EUSES). It should be noted that the QSAR used to estimate the $K_{earthworm\text{-}porewater}$ is valid only for log K_{ow} values between 1 and 6.5 and so may not be valid for this substance. Using the porewater concentrations estimated in soil (Section 3.1.2.1), the estimated concentrations in earthworms are shown in **Table 3.23**.

Table 3.23 Estimated PEC(oral, earthworm) for pentabromodiphenyl ether

Source	Estimated soil porewater concentration	Estimated concentration in earthworms
Polyurethane production	PEC_{local}(soil, porewater) = $2.72 \cdot 10^{-4}$ mg/l (agricultural soil)	34.3 mg/kg (wet weight)
Regional	$PEC_{regional}$(soil, porewater) = $1.35 \cdot 10^{-5}$ mg/l (agricultural soil)[a]	1.7 mg/kg (wet weight)[a]

[a]The calculations do not include the regional contribution from "waste remaining in the environment"

If this is included the estimated regional soil pore water concentration would be $1.7 \cdot 10^{-5}$ mg/l for agricultural soil and the estimated concentration in earthworms would be 2.14 mg/kg wet weight. Higher concentrations would result in earthworms in urban soil, but the calculations are highly uncertain

For the food chains considered, the Technical Guidance suggests that the PEC(oral) used in the risk assessment should be calculated assuming 50% of the dose comes from local sources and 50% from regional doses. Thus the following value is obtained for the water ⇒ fish ⇒ fish-eating bird or mammal scenario:

> PEC(oral, fish) = 2.2 mg/kg (wet fish) or 4.2 mg/kg (wet fish) from polyurethane foam production

For the soil ⇒ earthworm ⇒ worm-eating bird or mammal the values are:

> PEC(oral, earthworm) = 18.0 mg/kg (wet weight) from polyurethane foam production.

3.1.4.2 Predicted levels in human food intake

The concentrations in food for human intake have been estimated using EUSES (see Appendix B) based on the release rates derived in Section 3.1.1. The results are shown in **Table 3.24**.

Table 3.24 Estimated concentrations of pentabromodiphenyl ether in food for human intake

Food/media	Concentration in food/media	
	Polyurethane foam production	Regional sources
Fish	4.38 mg/kg wet weight or 8.36 mg/kg wet weight	0.022 mg/kg wet weight or 0.041 mg/kg wet weight
Root crops	6.78 mg/kg wet weight	0.34 mg/kg wet weight
Leaf crops	0.031 mg/kg wet weight	$2.9 \cdot 10^{-4}$ mg/kg wet weight
Drinking water	$2.7 \cdot 10^{-4}$ mg/l	$1.4 \cdot 10^{-5}$ mg/l
Meat	0.208 mg/kg wet weight	0.0065 mg/kg wet weight
Milk	0.066 mg/kg wet weight	0.0021 mg/kg wet weight
Air	28.3 ng/m^3	0.27 ng/m^3

Based on the data given in **Table 3.24**, the daily human intake of pentaBDPE through food can be estimated as:

polyurethane foam production	0.046-0.053 mg/kg bw/day
regional sources	0.0019-0.0020 mg/kg bw/day

These figures do not include the regional contribution from "waste remaining in the environment". If this were included, the resulting regional daily human intake would be 0.0025-0.0027 mg/kg bw/day.

In all cases, around 70-95% of the total daily intake arises from the concentrations in root crops. No measured data is available on the concentrations of pentaBDPE in root crops or indeed soil from which uptake could occur, and so it is not possible to comment on the validity of these figures. There are some limited data that appear to show that the uptake of pentaBDPE from soil by sugar beet, although occurring, is around 20-40 times less than is predicted by the methods given in the Technical Guidance Document (see Section 3.1.0.5.3). Therefore, the above calculations may overestimate the contribution from root crops in general by a similar factor. However, few details of the test are currently available.

3.1.4.3 Measured levels in biota

In most analyses of pentaBDPE in biota, the commercial compound Bromkal 70 was used as reference for identification and quantification. This substance has been shown to consist mainly of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and an unknown pentabromodiphenyl ether and the levels are sometimes reported for the individual components and sometimes reported in terms of the commercial formulation. Although the commercial compound Bromkal 70 is no longer supplied in the EU, the current pentaBDPE products appear to have very similar compositions to this compound (see Section 1.2) and so,

although the results are often expressed as Bromkal 70, they are likely to represent the total concentrations of all commercial pentaBDPEs in the environment, not just that particular product. The levels measured of the various components of commercial pentaBDPE are discussed below. Wherever possible details of the actual component measured are given.

The components of commercial pentaBDPEs have been measured extensively in the biota in Europe. In almost all cases, 2,2',4,4'-tetrabromodiphenyl ether is the dominant component of the commercial formulations found (typically >70% of the total). Since this isomer makes up around 35-40% of the commercial product, the levels found in biota indicate preferential uptake of this isomer over the pentabromodiphenyl ether isomers. This would be expected based on the fish bioconcentration data given in Section 3.1.0.5.3, where BCFs for tetrabromodiphenyl ethers were determined at around 35,100-66,700 l/kg compared with values of 11,700-17,700 l/kg for one pentabromodiphenyl ether isomer and 73-1,440 l/kg for another pentabromodiphenyl ether. This means that results of analyses given on a commercial formulation basis should be treated with caution since the distribution of isomers found in the organisms is unlikely to be the same as in the commercial formulation.

A survey of levels of commercial pentaBDPEs in marine species has recently been carried out in the United Kingdom (see **Table 3.25**). The highest levels measured were in fish from the Tees estuary, downstream from a pentaBDPE production site and in an area where there is a large chemical industry in general. Levels in fish liver (up to 1.3 mg/kg wet weight for 2,2',4,4'-tetrabromodiphenyl ether) were generally higher than in muscle (up to 22 µg/kg wet weight for 2,2',4,4'-tetrabromodiphenyl ether). On a lipid basis, the highest levels of the tetrabromodiphenyl ether isomer are up to around 9.5 mg/kg in liver and 1.8 mg/kg in muscle.

Sellström et al (1993) measured the concentrations of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and an unidentified pentabromodiphenyl ether (all are components of the commercial brominated flame retardant Bromkal 70-5DE) in biota samples from in and around Sweden (see **Table 3.26**). The concentration of the brominated diphenyl ethers in biota were found to be lowest in samples from the west coast and the highest concentrations were found in samples from the southern part of the Baltic. The concentrations (on a lipid weight basis) of brominated diphenyl ethers in herring were found to be higher in fish caught in the spring than fish caught in the autumn. This was thought to be due to the lower fat content of the spring fish. Generally low levels were measured in terrestrial mammals. In this study the highest levels were generally found in freshwater fish, with the highest levels being reported as 24 mg/kg lipid for 2,2',4,4'-tetrabromodiphenyl ether and 9.4 mg/kg lipid for 2,2',4,4',5-pentabromodiphenyl ether in muscle of perch. Levels in marine fish were generally lower than freshwater fish. Levels in seal blubber were similar to those in fish, indicating that little accumulation through the food chain was occurring. In contrast to this, levels in fish-eating birds and their eggs were much higher than levels in starlings, indicating that fish may be a significant source of exposure for these species. Similar conclusions can be drawn from the results reported in **Table 3.27**, where levels of up to 88 mg/kg lipid in liver and 24 mg/kg lipid in muscle have been determined in freshwater fish (Pike).

Table 3.25 Levels of commercial pentabromodiphenyl ethers in marine species from the United Kingdom (Law et al 1996; Allchin et al, 1999)

Species	Location/Comment	Level (mg/kg wet weight)			
		2,2',4,4'-TetraBDPE[a]	2,2'4,4',5-PentaBDPE[a]	2,2',3,4,4'-PentaBDPE[a]	Product basis[b]
Dab (*Limandalimanda)* liver	Off River Tees; 12% lipid	129	9.4	<1	13
	Off Wash; 31% lipid	117	23	<1	34
	Tees Bay; 23.6% lipid	601	29	55	236
	Bideford Bay; 33.6% lipid	37	11	11	33
Dab *(Limanda limanda) m*uscle	Bideford Bay; 1% lipid	<1	<1	<1	1
	Tees Bay; 1.2% lipid	7.0	1.0	1.6	11
Whiting (*Merlangius Merlangus)* liver	Bristol Channel; 45% lipid	102	21	<1	48
Flounder (*Platichthys flesus*) liver	Off Lune/Wyre; 12% lipid	49	6.5	<1	12
	Off River Humber; 14% lipid	217	22	<1	16
	Nith Estuary; 18.8% lipid	19	3.6	<1	9
	Nith Estuary; 19.2% lipid	14	3.1	<1	9
	Bideford Bay; 18.8% lipid	69	4.9	22	22
	Tees Bay; 13.6% lipid	1,294	108	130	169
Plaice (*Pleuronectes platessa*) muscle	Bideford Bay, 0.6% lipid	0.6	<1	<1	1
	Tees Bay; 1.6% lipid	8.3	1.6	2.2	15
Plaice (*Pleuronectes platessa*) liver	Bideford Bay; 16% lipid	15	3	3.6	15
	Tees Bay; 3.3% lipid	161	12	14	35
Winkles (*Littorina littorea*)	River Tweed; 2.6% lipid	1.9	1.8	1.5	25
Mussels (*Mytilus edulis*)	Gat Sand/Hunstanton, the Wash; 1.8% lipid	3.5	3.9	2.0	18
Flounder (*Platichthys flesus*) muscle	Nith Estuary; 1% lipid	1.4	<1	<1	1.2
	Nith Estuary; 1% lipid	1.2	<1	<1	1
	Bideford Bay; 0.8% lipid	1.4	<1	<1	0.8
	Tees Bay; 1.2% lipid	22	4.4	1.1	13

[a]Concentrations based on standards of each isomer
[b]Concentrations based on a commercial pentaBDPE standard

Similar to Sellström et al (1993) above, Andersson and Wartanian (1992) also found that the levels in seal blubber samples were slightly higher in animals from the Baltic compared to the west coast of Sweden. The results are reported in **Table 3.28**.

In the Sellström et al (1993) study, a time-trend analysis of the levels of the main components of commercial pentaBDPE found in guillemot egg samples was carried out. The samples analysed covered the years 1970 to 1989 and included 1 guillemot egg in each of 6 years (1970, 1975, 1979, 1983, 1986 and 1989), pooled samples of 10 guillemot eggs in each of 5 years

(1974, 1976, 1982, 1987 and 1989) and pooled samples of 8 guillemot eggs in 1978. The authors concluded that there was no statistically significant difference between the levels found in 1976 and 1989, based on the separate analysis of 10 eggs representing each year. Single egg samples did indicate an increasing trend in the levels over the period 1970-1989. The authors concluded that, based on the statistical results (taking into account the individual variation between individual egg samples) for two years, although the levels found in guillemot eggs had increased over the period 1976-1989, this increase was not statistically significant. Sellström (1996) extended the scope of the time-trend study in guillemot eggs by analysing further pooled samples (covering 1969-1992) and individual samples of 10 eggs/year (covering 1992-1994). Using this larger data set, the results indicated that the levels found in the eggs had increased significantly since the 1970's, but a decline in the levels had been seen in recent years (since 1990).

In a later study by Sellström et al (1998), levels of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and 2,2'4,4',6-pentabromodiphenyl ether were determined in pike (muscle) from the River Viskan and nearby water systems. The results are shown in **Table 3.26**. The range of levels found (sum of all three isomers) were generally in the range 100-700 µg/kg lipid, with one individual found to contain higher levels of 4,600 µg/kg lipid.

The substances were found in fish both upstream and downstream from industry, indicating a possible contribution of these substances from diffuse sources. A very extensive study of the levels of 2,2',4,4'-pentabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether has been carried out in the Netherlands over the years 1977-1992 (de Boer and Dao, 1993; see **Table 3.29**). In all, 325 samples, from 106 locations, representing 25 species were analysed. It was found that the concentration of 2,2',4,4'-tetrabromodiphenyl ether was generally below 100 µg/kg wet weight in fish and shell fish and that most 2,2',4,4',5-pentabromodiphenyl ether concentrations were below 10 µg/kg in these organisms. However, high concentrations of both compounds were found in the organs of a cormorant (up to 25 mg/kg and 4 mg/kg wet weight (in the liver) of the two substances respectively). This was thought to represent bioaccumulation of the substances through the food chain.

High levels of 2,2',4,4'-tetrabromodiphenyl ether were also detected in marine mammals (e.g. dolphin and porpoise), again indicating possible bioaccumulation. In general, the data showed a decreasing trend in the concentration with time, however, an increasing trend was noted in eels from the River Roer and this was thought to be due to possible (unconfirmed) use of polybrominated diphenyl ethers in mining equipment in Germany (de Boer, 1990). One sample of human milk was taken and this was found to contain 0.4 µg/kg wet weight of 2,2'4,4'-tetrabromodiphenyl ether. Again, generally levels in marine fish were less than those in freshwater fish, particularly eels. Levels in invertebrates were generally very low.

Table 3.26 Concentrations of commercial pentabromodiphenyl ethers in biota around Sweden (Sellström et al, 1993 and 1998; Jansson et al, 1993)

Species	Location/Comment	Level (µg/kg lipid weight)		
		2,2',4,4'-TetraBDPE	2,2',4,4',5-PentaBDPE	PentaBDPE[a]
Mammals				
Rabbit (*Oryctolagus cuniculus*)	Pooled muscle samples, 1986 1.1% lipid.	<1.8	<0.34	<0.21
Moose (*Alces alces*)	Pooled muscle samples, 1985-1986. 2.0% lipid	0.82	0.64	0.24
Reindeer (*Rangifer tarandus*)	Pooled suet samples, 1986 56% lipid.	0.17	0.26	0.04
Marine species				
Whitefish (*Coregonus* sp.)	Pooled muscle samples, 1986 0.66% lipid	15	7.2	3.9
Arctic char (*Salvelinus alpinus*)	Pooled muscle samples, 1987 5.3% lipid.	400	64	51
Herring (*Clupea harengus*)	Pooled and individual samples, 1986-1987 3.2-5.4% lipid.	12-450	3.4-46	1.6-32
Ringed seal (*Pusa hispida*)	Pooled blubber samples, 1981. 88% lipid.	47	1.7	2.3
Grey seal (*Halichoerus grypus*)	Pooled blubber samples, 1979-1985 74% lipid.	650	40	38
Birds				
Osprey (*Pandion haliaetus*)	Pooled muscle samples, 1982-1986 4% lipid.	1,800	140	200
Starling (*Sturnus vulgaris*)	Muscle samples, 1988	2.7-7.8	2.3-4.2	0.62-1.1
Guillemot (*Uria aalge*) eggs	Pooled and individual samples, 1970-1989	130-1,500	24-330	4.2-79
Freshwater fish				
Bream (*Abramis brama*)	Muscle samples, 1987.	250-750	2.3-2.4	11-37
Pike (*Esox lucius*)	Pooled and individual muscle samples 1987-1988.	94-6,500	60-1,100	25-640
	Muscle samples, Lake Marsjön, 1995 0.46-0.56% lipid.	40-63[b]	<52-<70[b]	9.3-16[b]
	Muscle samples, Lake Öresjö, 1995 0.46-0.75% lipid.	240-2,000[b]	68-1,600[b]	60-1,000[b]
	Muscle samples, River Viskan, downstream from Borås 1995 0.49-0.57% lipid	330-510[b]	<48-<59[b]	65-98[b]
	Muscle samples, River Viskan at Moga, 1995. 0.53-0.79% lipid.	150-200[b]	<37-<56[b]	24-43[b]
	Muscle samples, Lake Skäresjön, 1995 0.65-1.09% lipid.	130-190[b]	<37-58[b]	20-49[b,c]
Perch (*Perca fluviatilis*)	Muscle samples, 1987	2,200-24,000	380-9,400	230-3,500
Trout (*Salmo trutta*)	Pooled and individual muscle samples 1988.	120-460	64-590	33-150

[a]Unknown pentabromodiphenyl ether isomer
[b]Identified as 2,2',4,4',6-pentabromodiphenyl ether
[c]Maximum value due to interferences

Table 3.27 Levels of commercial pentabromodiphenyl ethers in biota from the Baltic area (Jansson et al, 1987; Andersson and Blomkvist, 1981)

Species	Comment	PentaBDPE[c] concentration (mg/kg lipid)
Marine species		
Harbour seal (*Phoca vitulina*) from the Baltic	Blubber sample[a]	90
Harbour seal (*Phoca vitulina*) from the Kattegat	Blubber sample[a]	10
Ringed seal (*Pusa hispida*) from the Arctic Ocean	Blubber sample[a]	40
Birds		
Guillemot (*Uria aalge*) from the Baltic	Pectoral muscle sample[a]	370
Guillemot (*Uria aalge*) from the North Sea	Pectoral muscle sample[a]	80
Guillemot (*Uria lomvi*) from the Arctic Ocean.	Pectoral muscle sample[a]	130
Sea eagle (*Halichoerus albicilla*)	Pectoral muscle sample[a]	350
Freshwater fish		
Pike (*Esox lucius*) muscle from the Viskan River system	Mean levels, 1979-1981[b]. 0.52-0.63% lipid.	nd-24,000
Pike (*Esox lucius*) liver from the Viskan River system	Mean levels, 1979-1981[b]. 5.8-11% lipid.	nd-88,000
Bream (*Abramis brama*) muscle from the Viskan River system	Mean levels, 1979-1981[b]. 1.5% lipid.	9,700
Tench (*Tinca tinca*) muscle from the Viskan River system	Mean levels, 1979-1981[b]. 5.3% lipid.	950
Eel (*Anguilla anguilla*) muscle from the Viskan River system	Mean levels, 1979-1981[b]. 4.7-10% lipid.	900-16,000
Sea trout (*Salmo ocla*) muscle from the Viskan River system	Mean levels, 1979-1981[b]. 1.1% lipid.	1,400

[a]Concentration on a commercial formulation basis (Bromkal 70-5).
[b]Concentration on a commercial formulation basis (Bromkal 70-5-DE)
[c]2,2',4,4'-tetrabromodiphenyl ether was found to be the major component (70-80% of the total polybrominated diphenyl ethers present), pentabromodiphenyl ether isomers made up the rest

Table 3.28 Levels of commercial pentabromodiphenyl ether in seals from around Sweden (Andersson and Wartanian, 1992)

Species	Comment	PentaBDPE[a] concentration (mg/kg lipid)
Harbour seal (*Phoca vitulina*) from the Skagerrak	Composite blubber samples from 5 juveniles	160-190
	Composite blubber samples from 5 juveniles collected during the epizootic, 1988	240-250
	Composite blubber sample from 4 adult males	230
Harbour seal (*Phoca vitulina*) from the Kattegat	Composite blubber samples from 5 juveniles	210-390
Harbour seal (*Phoca vitulina*) from the Baltic, Kalmarsund	Composite blubber samples from 5 juveniles	450-570
Harbour seal (*Phoca vitulina*) from the Baltic, Måkläppen	Composite blubber samples from 4 and 3 juveniles collected during the epizootic, 1988	620-650
Grey seal (*Halichoerus grypus*) from the Baltic	Composite blubber samples from 5 juveniles	300-310
	Composite blubber sample from 5 adult males	280
	Composite blubber samples from 3 female unstarved, non-occluded specimens	280-450
	Composite blubber samples from 3 and 4 female unstarved, occluded specimens	1,000-1,100
	Composite blubber sample from 4 female starved, occluded specimens	1,500
Ringed seal (*Pusa hispida*) from the Baltic	Composite blubber samples from 5 juveniles	190-310
Ringed seal (*Pusa hispida*) from the Baltic	Composite blubber sample from 5 adult males	320

[a]Concentration on a commercial formulation basis (Bromkal 70-5). 2,2'4,4'-tetrabromodiphenyl ether was found to constitute 66 - 82% of the total polybrominated diphenyl ethers found

Table 3.29 Levels of commercial pentabromodiphenyl ethers in biota from the Netherlands and the North Sea (de Boer and Dao, 1993)

Species	Location/Comment	Level (mg/kg wet weight)	
		2,2',4,4'-TetraBDPE	2,2'4,4',5-PentaBDPE
Marine fish			
Hake	Atlantic, 1987	0.8	0.4
	Bay of Biscay, 1983	69	
Hake liver	Atlantic, 1986	<20	<10
	Bay of Biscay, 1983	70	
	English Channel, 1982	11	<10
	Irish Sea, 1982	18	<10
Cod (*Gadus morhua*)	Central North Sea, 1985-1991	0.2-1	<0.1
	Northern North Sea, 1986	0.4	<10
	Southern North Sea, 1984-1991	0.3-1	<0.1
Cod liver	Central North Sea, 1983-1989	12-73	3.9-13
	Northern North Sea, 1983-1989	14-30	1.3-5.1
	Southern North Sea, 1981-1991	45-460	1.7-17
Herring (*Clupea harengus*)	Central North Sea, 1985	1	<10
	Northern North Sea, 1985	0.7	<10
	Skagerrak, 1991	4.3	1.7
	Southern North Sea, 1985-1991	1.6-11	<10
	Southern North Sea (Vlaamse Bank), 1992	28	17
	Straits of Dover, 1985	0.9-7.6	<10
Herring liver	Southern North Sea (Vlaamse Bank), 1992	2.4	1.3
Plaice	Danish West Coast, 1989	<0.1	
	English Channel, 1989	0.4	
	English East Coast, 1989	<0.1	
	German Bight, 1989	0.1	
	Skagerrak, 1989	0.1	
Plaice liver	Danish West Coast, 1989	1.1	
	English Channel, 1989	4.5	
	English East Coast, 1989	6.6	
	German Bight, 1989	2.1	
	Skagerrak, 1989	1.3	
	Straits of Dover, 1989	0.2	

Table 3.29 continued overleaf

Table 3.29 continued

Species	Location/Comment	Level (µg/kg wet weight)	
		2,2',4,4'-TetraBDPE	2,2'4,4',5-PentaBDPE
Sprat	English Channel, 1982	1.8	
Blenny	Southern North Sea, 1992	1	0.2
Brill	Southern North Sea, 1992	0.4	<0.1
Brill liver	Southern North Sea, 1992	13	0.7
Dab	German Bight, 1991	0.19	<0.1
	North Sea (IJmuiden), 1990	3.5	<0.3
	Wadden Sea, 1991	0.4	<0.1
Dab liver	German Bight, 1991	3	
	Wadden Sea, 1991	11	<1
Whiting	Southern North Sea, 1992	0.4	0.1
Twaite shad	Southern North Sea, 1987	77	<4
Twaite shad liver	Southern North Sea, 1987	15	1.7
Turbot	Southern North Sea, 1992	0.2	<0.1
Turbot liver	Southern North Sea, 1992	7	1
Sole	German Bight, 1990	<0.1	<0.1
	Southern North Sea, 1991-1992	0.1-0.5	<0.1
Sole liver	German Bight, 1990	2	<2
Mackerel	Shetland Islands, 1991	3.1	<1
Smelt	Southern North Sea, 1992	1.2	0.2
Marine mammals			
Dolphin blubber	Atlantic, 1983	590	<10
Dolphin muscle	Atlantic, 1983	18	
	Southern North Sea, 1990	57	12
Dolphin liver	Southern North Sea, 1990	45-180	5.3-30
Dolphin kidney	Southern North Sea, 1990	44	7.9
Dolphin spleen	Southern North Sea, 1990	43	8.7
Porpoise blubber	Southern North Sea, 1990	830	79
	Southern North Sea, 1990	2,600-3,000	220

Table 3.29 continued overleaf

Table 3.29 continued

Species	Location/Comment	Level (µg/kg wet weight)	
		2,2',4,4'-TetraBDPE	2,2'4,4',5-PentaBDPE
Freshwater fish			
Silver Eel	Ketelmeer, 1987	7.4-81	4.3-14
	Waal, 1987	55	4.4
Yellow Eel (*Anguilla anguilla*)	Aar Kanaal (Ter Aar), 1992	6.2	<1
	Amstel Drecht Kanaal, 1991	<1	0.5
	Amsterdam-Rijnkanaal, 1992	3.5	
	Apeldooms Kanaal, 1991	5	1.3
	Bergsche plas, 1991	1.6	1
	Binnen Liede, 1983	<10	<10
	Boven Merwede (Gorinchem), 1989	9.7-120	1.8-11
	Buiten Liede, 1983	<10	<10
	Callandkanaal, 1985	9.7	<10
	Delfzijl, 1984	3.5 and <10	
	Diemerzeedijk, 1985	<10	<10
	Geul (Meersen), 1992	6.8	0.7
	Haringvliet-east, 1977-1992	6.7-190	<2-7.3
	Haringvliet-west, 1989-1992	22-62	<2-2.1
	Hollands Diep, 1979-1992	32-190	1-4
	Hollandse Ijssel (Gouderak), 1984-1987	52-91	<10
	IJ, Amsterdam, 1992	4.3	
	Ketelmeer, 1977-1992	16-120	<2-7.9
	Lek, 1988-1992	34-97	2.4-3.8
	Linge (Rhenoij), 1991	12	0.6
	Maas-Waalkanaal (Malden), 1992	40	2.2
	Markermeer, 1991-1992	4-6.2	<1
	Meuse, 1983-1992	1.3-110	<1-2.8
	Niers, 1984	<10	
	Nieuwe Maas, 1989	18-55	1.1-4.3
	Nieuwe Merwede, 1987-1992	40-97	2.4-8.7
	Lauwersmeer, 1988-1992	1.7-3.4	<1-2.2

Table 3.29 continued overleaf

Table 3.29 continued

Species	Location/Comment	Level (µg/kg wet weight)	
		2,2',4,4'-TetraBDPE	2,2'4,4',5-PentaBDPE
Yellow Eel (continued)	Nieuwe Waterweg, 1991	25	1.3
	Noordhollands kanaal, 1992	2.4	
	Noordzeekanaal, 1992	3.3-5.2	<0.5-1.1
	Oostvaardersplassen, 1984	<10	<10
	Oude Rijn Sprangen, 1986	3.9	<4
	Oude Maas, 1989-1990	77-110	<5
	Paterswoldermeer, 1991	1.9	<4
	Prinses Margrietkanaal, 1992	1.1	<1
	Rhine (Lobith), 1984-1992	18-250	0.9-7.5
	Ringvaart (Haarlemmermeer), 1983	<10	<10
	Roer (Vlodrop), 1983-1992	68-260	<4-32
	Rottige Meenthe, 1988	1.1	<1
	Tjeukemeer, 1988-1991	<2-5.3	<2
	Tongelreep (Bruggerhuizen), 1992	7.6	<2
	Twentekanaal, 1987-1992	4.7-49	<1-2.9
	Vecht (Ommen), 1991-1992	6.6-7.7	0.5
	Vliet (Rijswijk), 1988	<3	<5
	Volkerak, 1986-1992	4.9-14	<1-3.4
	Wadden Sea-east (Eems), 1992	1.5	1.5
	Wadden Sea (Steendiep), 1991-1992	5.5-9.7	0.68
	Western Scheldt, 1983-1992	3.5-6.3	0.8
	Yssel (Deventer), 1988-1992	33-110	<3-5.4
	Yssel Lake, 1984-1992	4.8-40	<1-2.1
	Zoommeer, 1987-1992	3.1-3.8	<4
	Zuid-Willemsvaart, 1989-1992	3-3.7	0.6-1.5
	Zuidlaardermeer, 1992	1.5	1.3
Yellow Eel liver	Nieuwe Merwede, 1989	5.7	0.61
	Waal, 1983-1992	43-340	6.1-22

Table 3.39 continued overleaf

Table 3.29 continued

Species	Location/Comment	Level (µg/kg wet weight)	
		2,2',4,4'-TetraBDPE	2,2'4,4',5-PentaBDPE
Sea Trout	Meuse, 1989	1.8-2.1	0.2-0.6
	Waal, 1989	2.9-3.3	0.5-0.7
Roach	Boven Merwede (Gorinchem), 1990	2.8	
	Haringvliet-east, 1990	16	
	Ketelmeer, 1990	1.8	
	Rhine (Lobith), 1990	2.4	
	Twentekanaal, 1987	15	<1
	Waal, 1990	2.1	
Pike-perch	Hollands Diep, 1990-1991	5.1-5.5	1.3
	Hollandse Ijssel, 1990	5.6-25	1-4.7
	Yssel Lake, 1991	1.1	
Pike-perch liver	Hollands Diep, 1990	61	19
Invertebrates			
Mussel	Eastern Scheldt, 1984-1991	0.3-0.7	<1
	Wadden Sea-east, 1984	0.4	<10
	Wadden Sea, 1984	0.4	<10
	Western Scheldt, 1984	1.5	<10
Oyster	Eastern Scheldt, 1991	0.7	0.7
Shrimp	Eastern Scheldt, 1984	0.3	<10
	Egmond, 1984	0.7-1.5	<10
	IJmond, 1991	0.1	
	Maasvlakte, 1984	1	<10
	Rijnmond, 1984	2.5	<10
	Southern North Sea, 1989-1992	<0.1-0.4	<0.1-0.1
	Wadden Sea-east, 1984	<10	<10
	Wadden Sea, 1984	0.6	<10
	Western Scheldt, 1984	1	<10
Shrimp liver	Southern North Sea, 1985	4	<4
	Hollandse Ijssel, 1990	25	4.7

Levels of tetra- and pentabromodiphenyl ethers have been reported in cod liver from the North Sea from the years 1977-1987 (de Boer, 1989).
The levels found were 2,2',4,4'-tetrabromodiphenyl ether at 26-170 μg/kg wet weight, 2,2',4,4',5-pentabromodiphenyl ether at 1.9-22 μg/kg wet weight and an unknown pentabromodiphenyl ether at 3-26 μg/kg wet weight. Similar levels were reported by de Boer and Dao (1993) in **Table 3.29**.

A recent study has looked at the levels commercial pentaBDPE in various whales, dolphin, seals and fish from around the coast of the Netherlands around 1995 (de Boer et al, 1998b). The results are shown in **Table 3.30**. The authors concluded that the presence of the substances in sperm whales indicated that they had reached deep ocean waters, since sperm whales do not usually occur in shelf seas and usually feed in deep waters. The highest levels of total polybrominated diphenyl ethers were found in samples of dolphins (up to 7.7 mg/kg wet weight) and seals (up to 1.46 mg/kg wet weight), which had been feeding in the North Sea and the Wadden Sea.

Table 3.30 Levels of commercial pentabromodiphenyl ether in marine mammals and fish from around the coast of the Netherlands (de Boer et al, 1998b)

Sample	Comment	Measured level (μg/kg wet weight)		
		2,2',4,4'-TetraBDPE	Unknown PentaBDPE	2,2'4,4'5-PentaBDPE
Sperm whale (*Physeter macrocephalus*)	Blubber – 72.2% lipid	95	15	26
	Blubber – 23.4% lipid	58	8.1	15
	Blubber – 31.7% lipid	61	7.5	10
	Liver - 2.3% lipid	2.7	0.54	0.91
Whitebeaked dolphin (*Lagenorhynchus albirostris*)	Blubber – 99% lipid	5,500	1,200	1,000
	Liver - 2.7% lipid	22	5.8	3.0
Minke whale (*Balaenoptera acutorostrata*)	Blubber – 14% lipid	88	11	23
Harbour seal (*Phoca vitulina*)	Blubber - 24.4 % lipid	1,200	110	160
	Blubber - 96.3% lipid	1,200	100	40
	Blubber - 72.2% lipid	280	18	140
	Liver - 3.5% lipid	21	0.93	0.85
	Liver - 5.1% lipid	12	0.33	5.1
	Liver - 3.0% lipid	20	0.07	0.53
Mackerel (*Scomber scombrus*)	Muscle - 15.2% lipid	5.4	1.8	1.9

A study of levels of commercial pentaBDPE in biota samples from the Baltic has been reported (Haglund et al, 1997). Samples of seal and herring were collected between 1981 and 1988 from along the Swedish coastline and were analysed for several components of commercial pentaBDPE. Other samples included in the study were a salmon sample from the Umeå River, four commercial fish oil samples and a human adipose tissue[5] sample from a healthy 74 year old male. The component found at the highest concentrations was generally 2,2',4,4'-pentabromodiphenyl ether. In general, the concentrations found increased with the age of fish and the levels found where higher in seals than in fish. These results indicate that bioaccumulation through the food chain may be occurring. The study also detected the presence of methoxy-polybrominated diphenyl ethers in some samples. The levels found are reported in **Table 3.31**.

Longanathan et al (1995) analysed 48 carp (*Cyprinus carpio*) for the presence of polybrominated diphenyl ethers (see **Table 3.32**). The carp were collected in July 1991 from the Buffalo River, New York. Before analysis, the carp were split into 3 classes (young, middle-aged and old) depending on length and girth and all fish in each class (15 in each) were pooled and the muscle tissue was analysed by a GC/MS method. It is not clear how the substances were quantified. Tetrabromodiphenyl ethers accounted for 94-96% of the polybrominated diphenyl ethers detected, with pentabromodiphenyl ethers and hexabromodiphenyl ethers accounting for 3-5% and 1% respectively.

[5] Reference to human adipose tissue in this section is given as supporting evidence of general levels in biota. It is not carried through to the human health assessment unless indicated otherwise.

Table 3.31 Levels of commercial pentabromodiphenyl ether in biota from around the Baltic (Haglund et al, 1997)

Species	Comment	Concentration (µg/kg lipid)						
		Tetra-BDPE-1	2,2',4,4'-TetraBDPE	PentaBDPE-1	2,2',4,4',5-PentaBDPE	HexaBDPE-1	HexaBDPE-2	2,2',4,4',5,5'-HexaBDPE
Herring (*Clupea harengus*)	2 year old	0.4	3.2	<0.1	<0.1	<0.1	<0.1	<0.1
	3 year old	1.4	10	1.3	1.0	<0.1	<0.1	<0.1
	4 year old	2.0	13	<0.1	<0.1	<0.1	<0.1	<0.1
	5 year old	4.6	27	1.9	2.9	<0.1	<0.1	<0.1
Grey seal (*Halichoerus grypus*)	liver	<0.1	16	0.8	1.3	<0.1	<0.1	<0.1
	blubber	<0.1	308	57	54	11	27	11
Ringed seal (*Phoca hispida botnica*)	liver	<0.1	33	2.9	3.0	<0.1	1.2	2.5
	blubber	<0.1	256	61	33	2.6	17	9.6
Salmon (*Salmo salar*)	muscle	18	167	44	52	1.7	11	4.2
Fish oil	sample 1	<0.1	3.9	2.3	2.8	<0.1	<0.1	<0.1
	sample 2	0.1	0.7	0.1	0.1	<0.1	<0.1	<0.1
	sample 3	<0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1
	sample 4	<0.1	23	3.8	1.3	<0.1	<0.1	<0.1
Human	adipose tissue	0.3	8.8	1.8	1.1	<0.1	<0.1	1.7

TetraBDPE, PentaBDPE and HexaBDPE are unidentified tetra-, penta- and hexabromodiphenyl ether congeners respectively

Table 3.32 Levels of commercial pentabromodiphenyl ether in biota from Japan (Watanabe et al, 1987a) and the United States (Longanathan et al, 1995; Kuehl et al, 1991)

Species	Location/Comments	Level (mg/kg wet weight)	
		Tetrabromodiphenyl ether	Pentabromodiphenyl ether
Mussels	Japan, 1981-1985 Detection limit 0.1 μg/kg wet weight	nd-14.6	nd-2.8
Mullet	Japan, 1981-1985 Detection limit 0.1 μg/kg wet weight	nd	nd
Goby	Japan, 1981-1985 Detection limit 0.1 μg/kg wet weight	nd	nd
Sardine	Japan, 1981-1985 Detection limit 0.1 μg/kg wet weight	nd-0.8	nd
Sea bass	Japan, 1981-1985 Detection limit 0.1 μg/kg wet weight	0.1	nd
Horse Mackerel	Japan, 1981-1985 Detection limit 0.1 μg/kg wet weight	nd	nd
Mackerel	Japan, 1981-1985. Detection limit 0.1 μg/kg wet weight	0.3	nd
Hairtail	Japan, 1981-1985 Detection limit 0.1 μg/kg wet weight	0.1	nd
Carp	Buffalo River, United States, 1991. Young fish	12.3	0.63
	Buffalo River, United States, 1991. Middle aged fish	19.3	0.65
	Buffalo River, United States, 1991. Old fish	21.3	1.17
Bottlenose dolphin (*Tursiops truncatus*) blubber	Three beach-stranded animals, 1987 Concentration is sum of tetra- to hexa-bromodiphenyl ether components	180, 200 and 220 μg/kg lipid	

nd = not detected

A recent study by Burreau et al (1999) investigated the levels of the main components of commercial pentaBDPE in sprat (*Sprattus sprattus*), herring (*Clupea harengus*) and salmon (*Salmo salar*) from the central and northern part of the Baltic proper in the summer and autumn 1998. As well as determining the concentrations of the polybrominated diphenyl ethers present, the samples were also analysed for their isotopic nitrogen composition. The authors used the $^{15}N/^{14}N$ ratio to define the trophic position of the organism (^{15}N is enriched compared to ^{14}N with increasing trophic position of an organism) and used this to look at whether the concentrations of the polybrominated diphenyl ethers were increasing or decreasing with trophic level. Tri-, tetra-, penta- and hexabromodiphenyl ethers were found in the samples and the results are shown in **Table 3.33**. The authors concluded that the levels of all the congeners detected were increasing with increasing trophic level, with the effect being most marked with the tetra- and pentabromodiphenyl ether congeners, being slightly less with the tribromodiphenyl ether congeners and being considerably less with the hexabromodiphenyl ether congeners.

Table 3.33 Levels of polybrominated diphenyl ethers in fish representing different trophic levels from the Baltic (Burreau et al, 1999)

Congener	Measured level (µg/kg lipid)		
	Sprat (*Sprattus sprattus*)	Herring (*Clupea harengus*)	Salmon (*Salmo salar*)
2,2',4-tribromodiphenyl ether + 2,3',4-tribromodiphenyl ether	0.18	0.04	0.79
3,3',4-tribromodiphenyl ether	0.22	0.12	0.52
2,4,4'-tribromodiphenyl ether	0.60[a]	0.85[a]	4.39[a]
2,2',4,5'-tetrabromodiphenyl ether	1.85[a]	2.18[a]	15.19[a]
2,2',4,4'-tetrabromodiphenyl ether	4.32	6.21	46.29
2,3',4,4'-tetrabromodiphenyl ether	0.18	0.22	1.42
2,2',4,4',6-pentabromodiphenyl ether	0.80	0.81	6.37
2,2',4,4',5-pentabromodiphenyl ether	0.71	0.62	7.27
2,2',4,4',6,6'-hexabromodiphenyl ether	0	0.06	0.33
2,2',4,4',5,6'-hexabromodiphenyl ether	0.12	0.47	1.98
2,2',4,4',5,5'-hexabromodiphenyl ether	0	0	0.95
Total	8.98	11.58	85.5

[a]Quantification of these congeners is uncertain

Several polybrominated diphenyl ethers with between 2 and 6 bromine atoms have been detected in a sample of trout from Lake Ontario and Pacific herring. Samples of 24 reference brominated diphenyl ether congeners were used to aid identification of the congeners present in the sample. Several heptabromodiphenyl ether isomers were also reported to be present, although the chromatographic retention times did not correspond with the reference material (2,3,3',4,4',5,6-heptabromodiphenyl ether). Levels up to around 100 ng/kg were reported for the penta- and hexa- congeners in the trout sample, with lower levels around 10 ng/kg for the tetra- and penta- congeners being found in the herring (Sergeant et al, 1998).

A further study on the time-trends in levels of 2,2',4,4'-tetrabromodiphenyl ether in Swedish biota has been carried out (Kierkegaard et al, 1999).

The samples included in the study were pike (*Esox lucius*) muscle tissue from Lake Bolmen (a mesotrophic lake situated in woodland with minor agricultural and industrial activities nearby) and roach (*Rutilus rutilis*) muscle tissue from Lake Krankesjön (a eutrophic lake located in an agricultural region). For pike, the time-trend data showed an increase in the concentration of 2,2',4,4'-tetrabromodiphenyl ether from 1967 to the early 1980s. Between 1984 and 1997, the concentration of 2,2',4,4'-tetrabromodiphenyl ether was relatively constant at around 60-110 µg/kg lipid.

The concentration of 2,2',4,4'-tetrabromodiphenyl ether was reported to be around 1.8 times higher than the level in 2,2',4,4',5-pentabromodiphenyl ether in the samples, although no data on the levels of the latter congener were reported.

The concentration of 2,2',4,4'-tetrabromodiphenyl ether in roach (up to around 22 µg/kg lipid) were generally lower than in pike. As with pike, the variation in concentration between years was quite large, and, although the highest concentration found was in samples from 1988, no significant time-trend in the concentration was seen over the period 1980-1997. The congener profile found in roach differed somewhat from that seen in pike, with 2,2',4,4'-tetrabromodiphenyl ether dominating and little or 2,2',4,4',5-pentabromodiphenyl ether being found.

Levels of commercial pentaBDPE in fish and human adipose tissue from Finland have also been reported (Strandman et al, 1999). In this study, ten human adipose tissue samples and ten fish homogenates [Baltic herring (*Clupea harengus*) and sprat (*Sprattus sprattus*) from the Baltic sea; whole fish samples were pooled from individuals of the same age] were analysed for the presence of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and 2,2',4,4',5,5'-hexabromodiphenyl ether. The results are shown in **Table 3.34**. The levels in fish were found to increase with age.

van Bavel et al (1999) used a supercritical fluid extraction method to determine the concentration of commercial pentaBDPE in long-finned pilot whales (*Globicephala melas*) from the Faroe Islands in 1997. The whales sampled were categorised as adults or juveniles and divided into males and females, with three individuals being sampled within each group. The concentrations found are shown in **Table 3.35**.

Table 3.34 Levels of commercial pentabromodiphenyl ether in marine fish and human adipose tissue from Finland (Strandman et al, 1999)

Sample	Age (years)	Measured level (µg/kg lipid)			
		2,2',4,4'-TetraBDPE	2,2'4,4'5-PentaBDPE	2,2',4,4',5,5'-HexaBDPE	Sum of congeners
Herring (*Clupea harengus*)	1	7.64	4.28	0.95	12.87
	2	10.43	4.26	0.73	15.42
	3	23.76	3.89	0.60	28.25
Sprat (*Sprattus sprattus*)	3	17.54	4.13	0.92	22.59
	4	17.48-25.10	2.91-3.00	0.07-0.92	21.18-28.93
	5	30.77	4.26	0.92	35.95
	6	53.33	9.51	1.27	64.31
	8	109.15	4.16	1.26	114.57
	10	107.66	4.80	1.12	113.58
	13	82.73-140.84	1.89-6.07	0.57-2.36	85.19-149.27
Human adipose	36	3.07	0.80	3.05	6.92
	45	6.17	2.77	2.88	11.82
	47	8.76	5.51	3.74	18.01
	54	3.94	0.74	1.47	6.15
	57	6.55	1.55	3.25	11.35
	62	16.75	3.27	1.68	21.70
	64	6.23	1.31	1.26	8.80
	69	14.46	2.45	1.81	18.72
	82	3.48	1.40	1.61	6.49
	84	3.39	0.88	2.54	6.81

Another survey of levels of polybrominated diphenyl ethers in long-finned pilot whales from off the coast of the Faroe Islands has been carried out by Lindström et al (1999). The whales in this study were sampled in either 1994 or 1996. The results are shown in **Table 3.36**.

Table 3.35 Concentration of polybrominated diphenyl ethers in blubber of long-finned pilot whales in 1997 (van Bavel et al, 1999)

Congener		Concentration (µg/kg lipid)			
		Adult males (52-78% lipid)	Adult females (71-85% lipid)	Juvenile males (69-85% lipid)	Juvenile females (78-81% lipid)
2,2',4,4'-tetrabromodiphenyl ether		271.0-486.6	66.0-211.7	249.4-557.1	247.1-749.1
Unknown tetrabromodiphenyl ether isomers (6 isomers)	1	1.6-1.7	0.5-1.5	1.2-3.5	2.0-3.9
	2	nd-0.3	nd-0.4	nd-0.4	nd-0.4
	3	0.8-1.4	nd-0.8	0.8-1.8	1.1-2.7
	4	1.9-3.4	2.1-3.4	1.7-3.2	2.6-2.8
	5	1.0-2.6	nd-1.3	1.0-2.5	1.6-4.2
	6	7.1-9.6	3.2-7.8	5.9-15.0	11.0-17.5
2,2',4,4',5-pentabromodiphenyl ether		54.5-92.9	23.9-51.1	67.1-112.5	67.3-169.3
2,2',3,4,4'-pentabromodiphenyl ether		nd	nd	nd	nd
Unknown pentabromodiphenyl ether isomers (7 isomers)	1	1.5-3.3	0.9-1.5	2.5-4.5	2.0-5.9
	2	nd	nd	nd	nd
	3	nd	nd-0.6	nd-1.2	nd-1.5
	4	28.2-50.4	12.4-26.0	34.0-59.9	33.5-97.7
	5	nd	nd	nd	nd
	6	nd-0.4	nd-0.7	nd-1.0	nd-1.1
	7	1.0-1.7	nd-0.3	nd-2.5	2.4-3.8
2,2',4,4',5,5'-hexabromodiphenyl ether		6.4-10.9	2.1-3.7	5.3-9.7	6.5-13.5
2,2',3,4,4',5-hexabromodiphenyl ether		nd	nd	nd	nd
Unknown hexabromodiphenyl ether isomers (3 isomers)	1	4.2-13.4	2.7-4.7	4.5-10.1	5.9-17.3
	2	14.9-35.0	6.9-11.8	20.3-25.9	16.5-42.4
	3	nd	nd	nd	nd
Total		397.2-669.2	125.6-326.3	411.2-795.2	401.9-1,246

nd = not detected

Table 3.36 Concentration of polybrominated diphenyl ethers in blubber of long-finned pilot whales in 1994 and 1996 (Lindström et al, 1999)

Congener		Mean concentration (µg/kg lipid)				
		9 Females from Hvannasund, 1994 (82% lipid)	19 Females from Vestmanna, 1996 (79% lipid)	8 Males from Vestmanna, 1996 (66% lipid)	4 Young females from Vestmanna, 1996 (72% lipid)	13 Young males from Vestmanna, 1996 (76% lipid)
2,2',4,4'-tetrabromodiphenyl ether		411.9	529.4	862.4	1,727.4	1,782.1
Unknown tetrabromo-diphenyl ether isomers (6 isomers)	1	2.3	2.9	3.9	8.5	5.8
	2	0.7	0.8	0.8	1.4	1.0
	3	1.5	2.4	3.5	7.9	7.8
	4	4.7	7.5	8.7	11.2	6.1
	5	2.2	2.9	3.9	8.5	8.1
	6	13.4	21.9	28.2	61.5	40.2
2,2',4,4',5-pentabromodiphenyl ether		164.1	209.0	292.0	562.2	603.6
Unknown pentabromo-diphenyl ether isomers (7 isomers)	1	3.5	4.6	6.8	12.1	13.1
	2	nd	nd	0.2	0.4	0.5
	3	1.5	1.9	2.8	6.3	6.4
	4[a]	87.1	104.4	153.6	281.1	280.5
	5	2.0	2.4	3.4	6.3	6.4
	6	0.8	nd	1.7	3.3	3.6
	7	6.3	4.8	12.4	19.1	25.2
2,2',4,4',5,5'-hexabromodiphenyl ether		32.0	35.2	53.2	77.4	90.0
Unknown hexabromodiphenyl ether isomers (3 isomers)	1	27.8	29.2	43.9	54.6	67.2
	2	77.9	85.1	123.3	178.6	203.7
	3	3.5	3.4	5.8	10.4	9.0
Total		843.2	1,048	1,610	3,038	3,160

nd = not detected

[a]This isomer was tentatively identified as 2,2'4,4'6-pentabromodiphenyl ether

Alaee et al (1999) determined the levels of commercial polybromobromodiphenyl ethers in biota from the Canadian environment. The average concentrations found in lake trout were 545 µg/kg lipid in trout from Lake Ontario, 237 µg/kg lipid in trout from Lake Huron and 135 µg/kg lipid in trout from Lake Superior. The predominant congeners found were 2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether. Tri-, hexa- and heptabromodiphenyl ethers were also detected in some samples. Samples of ringed seal and beluga blubber were also analysed. The average concentrations found were 25.8 µg/kg blubber in female ringed seals, 50.0 µg/kg blubber in male ringed seals, 81.2 µg/kg in female beluga and 160 µg/kg in male beluga. Again 2,2',4,4'-tetrabromodiphenyl ether was

the predominant congener found, followed by 2,2',4,4',5-pentabromodiphenyl ether. Tri- and hexabromodiphenyl ethers were also detected.

Asplund et al (1999a) reported the results of a detailed investigation of the levels of polybrominated diphenyl ethers in Baltic salmon (*Salmo salar*) from the River Daläven sampled in November 1995 as part as an investigation of possible causes of M74 syndrome in salmon. In this paper, levels were reported in muscle, eggs and blood of 31 fish collected, 17 of which later produced offspring with M74 syndrome.

The levels found by GC-ECD analysis are shown in **Table 3.37**. Some samples were also analysed by GC-MS analysis [monitoring the bromide ions (m/z=79 and 81)]. These showed similar levels for the 2,2'4,4'-tetrabromodiphenyl ether as reported in **Table 3.37**, but the levels of 2,2',4,4'5-pentabromodiphenyl ether and 2,2',4,4',6-pentabromodiphenyl ether were around half of those found by the GC-ECD method. The presence of polybrominated phenoxyanisols and polybrominated phenoxyphenols (i.e. derivatives of polybrominated diphenyl ethers containing a methoxy or hydroxy group on the aromatic ring) containing 4 or 5 bromine atoms was also detected in the analysis.

Table 3.37 Comparison of levels in Baltic salmon from River Daläven (Asplund et al, 1999a)

Congener	Mean concentration if fish whose offspring did not develop M74 syndrome (µg/kg lipid)			Mean concentration if fish whose offspring did develop M74 syndrome (µg/kg lipid)		
	Muscle (4.7% lipid)	egg (8.6% lipid)	blood (2.0% lipid)	muscle (5.0% lipid)	egg (8.6% lipid)	blood (2.0% lipid)
2,2',4,4'-tetrabromodiphenyl ether	200	63	200	180	66	180
2,2',4,4',5-pentabromodiphenyl ether	54	16	64	50	16	45
2,2',4,4',6-pentabromodiphenyl ether	47	18	65	45	19	52
Total	301	97	329	275	101	277

Asplund et al (1999b) carried out a comparison of the levels of polybrominated diphenyl ethers in muscle of six steelhead trout (*Oncorhynchus mykiss*) collected from Lake Michigan 1995 (and held in a fish hatchery prior to being sampled in February 1996) and eight Baltic salmon (*Salmo salar*) from River Daläven sampled in November 1995 (these may be part of the same sampling as reported in Asplund et al, 1999a above).

The results are shown in **Table 3.38**. The mean lipid content of the fish was 1.4% in the trout and 3.7% in the salmon. The fish were collected just before spawning and so had a lower lipid level than would be normal for most of the year. The 2,2'4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and 2,2',4,4',6-pentabromodiphenyl ether congeners account for around 90% of the total concentrations.

Table 3.38 Comparison of muscle levels in steel head trout from Lake Michigan and Baltic salmon from River Daläven (Asplund et al, 1999b)

Congener	Mean concentration in steelhead trout muscle		Mean concentration in Baltic salmon muscle	
	µg/kg fresh weight	µg/kg lipid	µg/kg fresh weight	µg/kg lipid
2,4,4'-tribromodiphenyl ether	1.5	110	0.13	3.5
2,2',4,4'-tetrabromodiphenyl ether	23	1,700	4.2	110
2,2',4,4',5-pentabromodiphenyl ether	7.9	600	1.3	35
2,2',4,4',6-pentabromodiphenyl ether	4.8	360	0.95	26
2,2',4,4',5,5'-hexabromodiphenyl ether	1.5	110	0.12	3.2
2,2',4,4',5,6'-hexabromodiphenyl ether	2.7	200	0.22	6.0
Total	41.4	3,080	6.92	183.7

Ikonomou et al (1999) determined the levels of total polybrominated diphenyl ethers in 25 samples of resident species from the Strait of Georgia, British Columbia. The analytical method used 23 polybrominated diphenyl ether congeners as standards, and all 23 congeners were analysed for in each sample.The samples analysed included Dungeness crab hepatopancreas, sturgeon muscle and liver, blubber of porpoises, seals and killer whales, Pacific sockeye salmon, pacific herring and lake trout. The samples were collected in harbours, the Fraser River estuary and near to pulp and paper mills. In all samples, no monobromodiphenyl ethers were detected and the di-, tri-, hexa- and heptabromodiphenyl ethers were found to account for <10% of the total levels found. The most abundant congener found was 2,3',4',6-tetrabromodiphenyl ether, followed by 2,2',4,4',5-pentabromodiphenyl ether and other pentabromodiphenyl ethers. The actual levels were only reported in graphical form and so it is difficult to determine the precise values measured. However, from the graph, it is possible to estimate that the highest concentration was found in a porpoise sample which contained approximately 1,450 µg/kg lipid 2,3',4',6-tetrabromodiphenyl ether and 500 µg/kg lipid 2,2',4,4',5-pentabromodiphenyl ether. This study is notable in that the most abundant congener found is not 2,2',4,4'-tetrabromodiphenyl ether, as is found in almost all other studies of biota. The reason for this is unknown since other researchers in Canada have found that 2,2',4,4'-tetrabromodiphenyl ether is the dominant congener in biota (e.g. Alaee et al (1999) – this paper also indicated that preliminary results had found that 2,2',4,4'-tetrabromodiphenyl ether was the main constituent in samples similar to those analysed here).

Components of commercial pentaBDPE have also been determined in fish samples from Virginia Rivers, USA (Hale et al, 2000). In the study 253 muscle tissue samples from 30 species of fish were analysed for the presence of polybrominated diphenyl ethers. The 2,2'4,4'-tetrabromo congener was found in 85% of the samples analysed and accounted for ~70% of the total concentration of polybrominated diphenyl ethers found in the samples (tetra- to hexabromodiphenyl ethers were found in the samples). The total polybrominated diphenyl ether concentrations were found to be >1 mg/kg (lipid weight) in fish from 9 out of 50 sites sampled, with the highest concentrations (up to 57 mg/kg lipid in carp) being found in an area with textile and furniture industries.

There are several studies that have looked at levels of polybrominated diphenyl ethers in human blood, adipose and milk samples. These are summarised below.

Levels of brominated diphenyl ether of 2.1±1.4 ng/g lipid have been detected in 40 blood samples randomly selected from the Swedish population. The dominant compound found was 2,2',4,4'-tetrabromodiphenyl ether (Örn, 1997; Meironyté et al, 1998). Another study in Sweden looked at the levels of 2,2',4,4'-tetrabromodiphenyl ether in human adipose tissue (77 samples collected between 1995 and 1997). The compound was detected in all samples and the range of levels measured was 0.6-98.2 µg/kg lipid. The levels found were generally higher in males than females (Lindström et al, 1998).

Unpublished information from Germany indicated that the levels of the main components of commercial pentaBDPE have increased in human blood samples over the years 1985 to 1999, with levels being generally higher in males than in females (Schröter-Kermani et al, 2000). The levels found were similar to, but slightly higher than in those reported above in blood samples from the Swedish population.

Samples of milk from mothers living in the Stockholm region have recently been analysed for the presence of polybrominated diphenyl ethers. The samples analysed covered the years 1972-1997. The main congener found in the samples was 2,2',4,4'-tetrabromodiphenyl ether (60-70% of total), but other congeners found were 2,4,4'-tri-, 2,3',4,4'-tetra-, 2,2',4,4',5-penta, 2,2',4,4',6-penta, 2,2',3,4,4'-penta-, 2,2',4,4',5,5'-hexa and 2,2',4,4',5,6'-hexabromodiphenyl ether. The levels of polybrominated diphenyl ether were shown to increase exponentially over the time period, with a doubling time of around 5 years. The total levels found in the 1997 samples were 4 µg/kg lipid compared with 0.072 µg/kg in 1972 (Norén and Meironyté, 1998; Meironyté et al, 1998).

In another study from Sweden (Darnerud et al, 1998), 39 breast milk samples were analysed for the presence of polybrominated diphenyl ethers. The mean and median levels found were 4.4 µg/kg lipid and 3.4 µg/kg lipid respectively for the sum of the five dominant congeners (tetra- to hexabrominated). On a fresh weight basis, the mean and median levels were 0.14 and 0.10 µg/kg respectively. No correlation was found in this study between the levels found and the mothers age, computer usage frequency or consumption of fish. The dominant congener found was 2,2',4,4'-tetrabromodiphenyl ether.

The levels of the components of commercial pentaBDPE have been measured in adipose tissue and blood of a 21 year old Israeli male, and also in cows milk and poultry fat from Israel (de Boer et al, 1998a).

The levels found in adipose tissue (71.6% fat) were: 2,2',4,4'-tetrabromodiphenyl ether 2 µg/kg wet weight; 2,2',4,4'5-pentabromodiphenyl ether 4µg/kg wet weight and an unknown pentabromodiphenyl ether 1µg/kg wet weight. The substances were not detected in blood (0.15% fat; detection limits <0.01-<0.02 µg/kg wet weight), cows milk (1.9 % fat; detection limits <0.01-<0.02 µg/kg wet weight) or poultry fat (93% fat; detection limit <0.1-<0.8 µg/kg wet weight).

Meironyté Guvenius and Norén (1999) reported the results of a pilot study to analyse the concentrations of polybrominated diphenyl ethers with between 4 and 6 bromine atoms/molecule in paired samples of human liver and adipose tissue. The samples were taken from two Swedish males age 78 and 66. The pattern of congeners found was similar in both liver and adipose and 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and 2,2',4,4',5,5'-hexabromodiphenyl ether were the predominant congeners found, with lower levels of 2,4,4'-tribromodiphenyl ether, 2,2',4,4',6-pentabromodiphenyl ether,

2,2',3,4,4'-pentabromodiphenyle ether and 2,2',4,4',5,6'-hexabromodiphenyl ether also being found. The sum of the polybrominated diphenyl ethers found were 19 and 24 µg/kg lipid in liver and 18 and 17 µg/kg lipid in adipose in the two individuals respectively.

Pentabromodiphenyl ether has been detected in cows milk and human breast milk from Germany in an unpublished study (reported in de Wit, 1999). The levels found (referring to the sum of the main components of the commercial product) were 2.5-4.5 µg/kg lipid in cows milk and 0.6-11 µg/kg lipid in 25 samples of human breast milk. The same source indicated that the levels found in several species of freshwater fish from North-Rhine Westphalia were 18-939 µg/kg lipid. Similar levels (possibly from the same study) of polybrominated diphenyl ethers (probably tetra- and penta- congeners) of 0.6-11 µg/kg lipid have been reported in human breast milk from Germany by de Boer et al (1998a).

Recently, the levels of commercial pentaBDPE have been measured in 13 samples of human adipose tissue from Spain (Meneses et al, 1999). Tetrabromodiphenyl ether, pentabromodiphenyl ether and hexabromodiphenyl ethers were detected in all samples at average levels of 1.36 µg/kg lipid, 0.93 µg/kg lipid and 1.83 µg/kg lipid respectively.

The main congeners found were identified as 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether, an unidentified pentabromodiphenyl ether isomer and 2,2',4,4',5,5'-hexabromodiphenyl ether. The paper also reports unpublished data by Nordström et al (1999) indicating that the mean level of tetrabromodiphenyl ether in 121 samples of human adipose tissue from Sweden was 3.6 µg/kg lipid.

3.1.4.3.1 Summary of measured levels in biota

There is a consistent pattern in the levels of commercial pentaBDPEs measured in biota in Europe. The major isomer detected is 2,2',4,4'-tetrabromodiphenyl ether which typically makes up >70% of the total components detected. Levels in freshwater fish are generally slightly higher than marine fish, possibly reflecting the proximity to likely sources of pentaBDPE. There is evidence of bioaccumulation through the fish ⇒ fish-eating bird food chain, and also some evidence that bioaccumulation may also be occurring in marine mammals, as the substance has been detected at mg/kg levels in lipids of marine mammals such as whales, dolphins and seals. On a lipid basis, levels of up to 88 mg/kg on a formulation basis have been measured in fish liver in Sweden. High levels have been measured in marine fish in the United Kingdom in industrialised areas near to a pentaBDPE production site. Recent information on levels in the United States and Canada is consistent with the pattern found in Europe. However, one study (Ikonomou et al, 1999) found that the isomer 2,3',4',6-tetrabromodiphenyl ether was the dominant species present in biota samples from certain areas around Canada. The explanation for this finding is unknown as other data from Canada and the United States showed that 2,2',4,4'-tetrabromodiphenyl ether was the dominant species found, similar to the situation in Europe.

In human samples, the presence of the various components of commercial pentaBDPE has been shown in many samples of adipose tissue and milk. The levels found, when expressed on a lipid weight basis show a remarkably consistent picture between the various surveys and samples (the levels in milk and adipose tissue are similar), with the levels generally being around 2-4 µg/kg lipid in both milk and adipose tissue with up to around 100 µg/kg lipid in adipose tissue and 11 µg/kg in human milk being measured in some samples. The dominant congener found in the surveys is 2,2',4,4'-tetrabromodiphenyl ether (usually around 60-70%

of the total), which is consistent with the pattern of bioaccumulation found in laboratory experiments and the environmental monitoring data. The time trend data indicate that the levels in human tissue have increased markedly over the period 1972-1997 and may still be increasing.

3.1.4.4 Comparison of predicted and measured data

The predicted regional concentration in fish of 22-41 µg/kg wet weight is consistent with the levels found in fish in industrialised areas of the United Kingdom and the Netherlands, and so will be used for the risk assessment. Most of the levels from Sweden are reported on a lipid weight basis, making direct comparison difficult. However, Jansson et al (1993) measured total levels (i.e. sum of the three individual components measured) of around 528 µg/kg lipid in herring (% lipid = 4.4) and 515 µg/kg lipid in arctic char (% lipid = 5.3%) from around Sweden (**Table 3.26**), which, when converted to whole body weight basis (23 and 27 µg/kg wet weight) are again consistent with the predicted regional concentration.

High levels were also measured in fish samples from the industrial Viskan River system from Sweden (**Table 3.27**). The highest levels reported for total pentaBDPE were 24,000 µg/kg lipid for pike muscle, 9,700 µg/kg lipid for bream and 16,000 µg/kg lipid for eel. Using the mean lipid contents of the fish sampled (0.52%, 1.5% and 8.6% for pike muscle, bream and eel respectively), these values are equivalent to 125 µg/kg wet weight, 146 µg/kg wet weight and 1,376 µg/kg wet weight respectively.

Although it is not possible to compare the measured data directly with the local scenarios, the local concentration from polyurethane production of 4,360-8,330 µg/kg wet weight seems to be a reasonable value based on the measured data but is slightly higher than levels measured in the Tees Estuary (a heavily industrialised area, downstream of a pentaBDPE production plant) and from the industrial Viskan River system. Given the generally good agreement between the predicted and measured concentrations, the predicted PEC(oral, fish) will be used in the assessment.

It is not possible to compare the predicted levels in earthworms with the measured data and so the predicted levels will be used later in the assessment. However, the values predicted may not be reliable.

Industry has indicated that there is a possibility that commercial pentaBDPE may have been used in hydraulic mining fluids (as a polychlorinated biphenyl replacement). If this use did occur it might account for some of the reported occurrences of the substance in remote areas (for instance, there are many mining areas situated in Sweden). However, after intensive investigation (KEMI, 1999b), this use has not been confirmed in the areas sampled and the use no longer occurs. Similarly, industry indicates that there is a possible (unconfirmed) use in completion fluids used in oil wells/drilling in the North Sea. Again, such a use could explain the occurrence of the substance in marine environments.

3.1.5 Summary of PECs for risk assessment

Table 3.39 summarises the PECs that will be used in the risk assessment. In cases where there is a large discrepancy between the predicted and measured concentrations in the environment, both will be used in the risk assessment.

Table 3.39 Summary of PECs used in Risk Assessment

Media	Release source	Concentration	Predicted/measured
Surface water	Polyurethane production	PEC_{local} = 0.37 µg/l	Predicted
	Regional sources	$PEC_{regional}$ = 0.0015 µg/l	Predicted
Sediment	Polyurethane production	PEC_{local} = 4.5 mg/kg wet weight	Predicted
	Local sources	0.54 mg/kg wet weight	Measured data
	Regional sources	$PEC_{regional}$ = 32 µg/kg wet weight	Predicted
	Regional sources	50 µg/kg wet weight	Measured data
Air	Polyurethane production	PEC_{local} = 34.5 ng/m^3	Predicted
	Regional sources	$PEC_{regional}$ = 0.27 ng/m^3	Predicted
Fish (secondary poisoning)	Polyurethane production	PEC(oral, fish) = 2.2 mg/kg wet weight or 4.2 mg/kg wet weight	Predicted
	Local sources	PEC(oral, fish) = 1.4 mg/kg wet weight	Measured data
Earthworms (secondary poisoning)	Polyurethane production	PEC(oral, earthworm) = 18.1 mg/kg wet weight	Predicted
Agricultural soil	Polyurethane production	PEC_{local} = 2.68 mg/kg wet weight	Predicted
	Regional sources	$PEC_{regional}$ = 0.13 mg/kg wet weight	Predicted

These PECs do include the contribution from waste remaining in the environment. This contribution is discussed in the risk characterisation (Section 3.3) where appropriate

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

3.2.1 Aquatic compartment

3.2.1.1 Toxicity to fish

A 48-hour toxicity test on adult orange-red killifish (*Oryzias latipes*) has been carried out as part of a bioaccumulation study on a commercial pentaBDPE (CITI, 1982). The substance tested was known to be a mixture of tetra-, penta and hexabromodiphenyl ethers (see **Table 3.5**, Section 3.1.0.5.3 for the approximate composition). In the test, pentaBDPE was dispersed in water with dimethyl sulphoxide (DMSO) and a dispersing agent such that a 1,000 mg/l dispersion of pentaBDPE contained around 10 g/l of DMSO and 20 g/l of dispersing agent. The test was carried out at 25±1^{o}C using fish with an average body weight of 0.13 g. The dissolved oxygen concentration during the test was 7.1 mg/l and the pH was 7.5. Few other details of the test were reported. The 48h-LC_{50} was reported to be >500 mg/l (i.e. no deaths occurred at 500 mg/l). It should be noted that the concentration of DMSO and the dispersing agent in the test solution (i.e. 500 mg/l of pentaBDPE) must have been around

5 g/l and 10 g/l respectively, which is well above the recommended values for solubilising agents of 100 mg/l, given in the EU test methods.

The toxicity of pentaBDPE to rainbow trout (*Oncorhynchus mykiss)* has been determined over 96 hours using a flow-through test system (GLP study based on OECD 203 method). The substance tested was a composite sample from two current suppliers and had the following composition: 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether. Dimethylformamide at a concentration of 0.1 ml/l was used as a cosolvent. The concentrations of the test substance were measured at the start of the test and after 48 and 96 hours. The mean test concentrations measured were 1.1, 2.3, 3.9, 7.8 and 21 µg/l. No mortalities or overt signs of toxicity were seen at any exposure concentration and the 96h-LC_{50} and NOEC were greater than the water solubility of the substance (Palmer et al, 1997c).

In this test, stock solutions of the test substance were prepared by dissolving it in dimethylformamide, with one stock solution being prepared for each concentration tested. These stock solutions were then injected into the diluter mixing chambers to give the desired test concentrations, with the solvent concentration being 0.1 ml/l in all cases (Palmer et al, 1997c). This method ensures that the composition of the substance in solution is as close as possible to that in the commercial preparation, providing all the test substance enters into solution.

The analytical method used in the test was gas chromatography with electron capture detection (GC-ECD) (Palmer et al, 1997c). Quantification involved summing the peak areas in the chromatograph corresponding with the two main peaks (not identified in the report but probably one pentabromodiphenyl ether and one tetrabromodiphenyl ether), using standard solutions of the commercial pentaBDPE (prepared in solvent) to construct a calibration curve. Such a calibration method requires the composition of the substance in the test water to be the same as it is in the calibration standards in order for the method to accurately reflect the concentration of the commercial substance. Example chromatographs are given in the report and these allow the following ratios for the peak heights for the two main components (e.g. penta- and tetrabromodiphenyl ether) to be estimated: low-level calibration standard penta:tetra 2.4:1; high-level calibration standard penta:tetra 2.0:1; 30 µg/l matrix fortification standard (prepared in same way as test solutions) penta:tetra 2.0:1; 6.5 µg/l nominal test solution penta:tetra 2.5:1. From these ratios it can be seen that the relative concentrations of the two components of the commercial pentaBDPE used for quantification are the same in the standards and the test solutions, giving some degree of confidence to the analytical results.

A fish early life stage toxicity study (OECD 210) has been carried out using rainbow trout (*Oncorhynchus mykiss*) (Wildlife International, 2000a). The substance tested had the following composition: 0.23% tribromodiphenyl ether, 36.02% tetrabromodiphenyl ether, 55.10% pentabromodiphenyl ether and 8.58% hexabromodiphenyl ether, based on GC areas (Wildlife International, 2000b).

In the test, trout embryos were exposed to 5 concentrations of the test substance under flow-through conditions (6.4 volume additions every 24 hours) at 12^{o}C. Stock solutions of the test substance were prepared by dissolving in dimethylformamide (DMF). The concentration of DMF in all test solutions was 0.10 ml/l, and controls (no test substance or DMF) and solvent controls (DMF at 0.1 ml/l) were also run. Four replicate test chambers were maintained in each treatment and control group. At the start of the test, each test chamber contained two

incubation cups, with each cup containing 15 embryos (giving a total of 30 embryos per replicate and 120 embryos per test concentration). After hatching, the larvae from all test concentrations were counted and released into the appropriate test chamber. When >90% of the control group had reached the swim-up stage the number of larvae in all replicates were reduced to 15 (i.e. 60 larvae per test concentration) to prevent overcrowding.

The total exposure period was 87 days, which consisted of a 27-day hatching period followed by a 60-day post hatch period. The mean percentage fertilisation was determined as 98% in the test. The nominal concentrations of pentaBDPE tested were 1.6, 3.3, 6.5, 13 and 26 µg/l. Mean measured test concentrations were determined from samples of test water collected from each treatment group at test initiation and at weekly intervals. Analysis was carried out by HPLC with UV detection, with the sum of the peak area responses of the major components of the commercial product being used for quantification. The mean measured concentrations determined over the test period for the 5 treatments respectively were 1.2, 2.5, 4.0, 8.9 and 16 µg/l. All results are reported based on the mean measured concentrations.

The following endpoints were determined in the test: embryo survival (hatching success); time to hatch; time to swim-up of larvae; post-hatch growth (weight and length); and post hatch survival. No statistically significant differences ($p>0.05$) were seen between the control group and the solvent control group in any of these endpoints, and so the data from these two groups were pooled for comparison with the effects seen in the exposed populations. All organisms in the control and test populations appeared normal and healthy during the entire test.

Time to hatch and hatching success

No statistically significant differences ($p>0.05$) were seen in time to hatch between the control groups and any treatment. All embryos emerged on day 27 of the experiment. The hatching success in the control and solvent control groups was 93% and 92% respectively. The hatching success in all treatments was ≥89%, and was not statistically significantly different ($p>0.05$) from the controls at any concentration. The NOEC for these endpoints is therefore ≥16 µg/l.

Time to swim up

Swim up began on day 14 post-hatch and by day 15 post-hatch 90% of control fish had attained swim up (at this time all chambers were thinned to 15 fish). No statistically significant differences ($p>0.05$) were seen between controls and any treatment in the time to swim. The NOEC for this endpoint is therefore ≥16 µg/l.

Larvae and fry survival

This was analysed over two time periods: day 1 post-hatch to thinning on day 15 post-hatch; and day 15 to day 60 post-hatch. The mean control survival prior to thinning was 99%. The mean survival prior to thinning in all treatments was ≥96%, which was not statistically significantly different ($p>0.05$) from controls at any concentration. After thinning, the mean survival was 99% in controls and ≥95% in all treatments, again indicating no statistically significant differences ($p>0.05$) between the controls and any treatment concentration. The overall NOEC for these endpoints is ≥16 µg/l.

Growth

Growth was evaluated at day 30 post-hatch (fish length) and day 60 post-hatch (fish length and wet and dry weight). At day 30, the mean fish length was found to be statistically significantly reduced ($p<0.05$) in the 4 µg/l treatment group when compared with controls, however this did not appear to be treatment related due to the lack of statistically significant ($p>0.05$) effects at 8.9 and 16 µg/l.

At day 60, the mean length, wet weight and dry weight of fish exposed to 16 µg/l was statistically significantly reduced ($p<0.05$) compared to controls. The mean lengths (given in mm) found were 48.8±0.49 in the control group, 48.8±0.31 in the solvent control group and 49.4±0.28, 48.9±1.04, 48.9±1.21, 48.2±0.72 and 47.2±0.53 in the 1.2 µg/l, 2.5 µg/l, 4.0 µg/l, 8.9 µg/l and 16 µg/l treatment groups respectively. Similarly the mean wet weights (given in g) were 0.983±0.055 in the control group, 0.983±0.018 in the solvent control group and 0.983±0.028, 0.987±0.069, 0.995±0.078, 0.948±0.022 and 0.856±0.028 in the five treatment groups respectively. The mean dry weights (given in g) were 0.209±0.09 in the control group, 0.211±0.004 in the solvent control group and 0.215±0.010, 0.212±0.016, 0.214±0.016, 0.201±0.004 and 0.183±0.008 in the five treatment groups respectively. Thus the NOEC for the growth endpoint is 8.9 µg/l and the LOEC is 16 µg/l.

In summary therefore, the overall NOEC from the study was determined to be 8.9 µg/l, with statistically significant effects being seen on juvenile fish length and weight by day 60 post-hatch at a concentration of 16 µg/l.

A study has been carried out to examine the effects of pentaBDPE on the liver morphology and cytochrome P450 activity in fry of rainbow trout (*Oncorhynchus mykiss*). The commercial pentaBDPE Bromkal 70 was used in the tests. One week prior to hatching, 100-200 trout embryos in each exposure group were injected with a solution of the polybrominated diphenyl ether in dimethyl sulphoxide (DMSO). Three concentrations were used, 0.08, 0.8 and 4 µg/egg (equivalent to 1, 10 and 50 µg/g fresh weight at the start of the experiment). Two control groups were used, one receiving no treatment and one being injected with DMSO alone. Six weeks after the embryos were exposed the morphology and the EROD activity of the liver of the fry was examined. Cumulative mortality in the 4 µg/egg group (54% mortality) was slightly higher than that seen in the DMSO control group (33% mortality) but both were significantly higher than the untreated control group (<5% mortality), indicating that at least some of the mortality seen in the treated groups could be due to the method of administration. Some changes in liver morphology (introcytoplasmic myelin figures and sporadically occurring intranuclear mitocondria) were noted at 4 µg/egg and a slight increase (2-3 times) in EROD activity was found at 0.8 µg/egg, but not at 0.08 or 4 µg/egg. These effects were much less than those produced by known P450 inducers using the same test system (e.g. a dose related increase of up to 35 times the control hepatic EROD activity was seen for polychlorinated diphenyl) (Norrgren et al, 1993).

Hornung et al (1996) used a rainbow trout (*Oncorhynchus mykiss*) early lifestage mortality bioassay to compare the potency of individual polybrominated diphenyl ether isomers with that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The compounds studied in the test were 2,2'4,4'-tetrabromodiphenyl ether, 2,2',3,4,4'-pentabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether. All isomers were >98% purity.

In the experiment, the test substance was dissolved in chloroform and then incorporated into phosphatidylcholine lioposomes using a thin-film hydration method. The test substance was then injected into eggs 24-50 hours after fertilisation, and the eggs were then placed in flowing water at 11°C. The eggs and fry were observed 3 times/week and mortality was scored as either positive or negative for signs of TCDD-like toxicity. The polybrominated diphenyl ethers tested did not cause sac-fry mortality or signs of TCDD-like toxicity at concentrations up to 12 µg/g egg (the highest concentration tested).

The effect of food contaminated with pentaBDPE (Bromkal 70-5DE) on reproduction has been studied using the three-spined stickleback (*Gasterosteus aculeatus*). Female fish (20 per group; initial weight 0.9±0.1g; salinity of water 6‰) were fed freeze-dried chironomids (at around 2% of body weight/day) contaminated with pentaBDPE for three months. Two exposure concentrations were used, 6.29 and 10.39 mg of the substance in food (this was total amount of pentaBDPE fed to the exposed fish over approximately 100 days). These concentrations are equivalent to initial exposure concentrations (doses) in food of 3.5 mg/kg food/day and 5.77 mg/kg food/day. After this initial exposure the temperature was gradually increased from 10°C to 15°C over 8 days. After a further week (i.e. 3.5 months total exposure), 8-11 females from each group were transferred to spawning aquaria containing unexposed males. The spawning aquaria contained sand and *Cladophora* sp. Each aquaria contained 1 pair of fish. Spawning was considered to be successful if it occurred within 24 hours. After spawning the eggs were collected and the temperature was increased gradually to 21±1°C. One week after hatching the number of fry and non-hatched eggs were counted. No changes in feeding patterns or behaviour were noted during the exposure period and no dose related mortality was seen from the start of exposure until spawning. There was no significant difference in the mean liver somatic index of exposed and control fish but a slight but not statistically significant ($p<0.05$) increase (around 3-5 times) in mean EROD activity was noted in exposed fish over control fish. On examination of the livers, exposed fish showed intracellular lipid accumulation. No significant difference between exposed fish and controls was seen in spawning success (Holm et al, 1993)

3.2.1.2 Toxicity to aquatic invertebrates

The toxicity of the substance to *Daphnia magna* has been determined over 48 hours using a flow-through system (GLP study, based on OECD 202 method). The substance tested was a composite sample from two current suppliers and had the following composition: 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether. Dimethylformamide at a concentration of 0.1 ml/l was used as a cosolvent. The concentrations of the test substance were measured at the start and end of the test and the results are based on the mean measured concentrations (1.2, 2.4, 4.9, 9.1 and 20 µg/l). Mortality was seen at concentrations of 9.1 µg/l and above within 24 hours and by 48 hours, 45% of daphnids in the 9.1 µg/l treatment and 65% in the 20 µg/l treatment were dead or immobile. The 48-hour EC_{50} was determined to be 14 µg/l and the NOEC was 4.9 µg/l, based on the mean measured concentrations. It was stated in the test report that the effects seen could have been due to physical impairment (undissolved test substance adsorbing onto the daphnids and adversely affecting respiration, swimming etc.) rather than a direct toxic effect (Palmer et al, 1997b).

In the test, stock solutions of the test substance were prepared by dissolving it in dimethylformamide, with one stock solution being prepared for each concentration tested. These stock solutions were then injected into the diluter mixing chambers to give the desired

test concentrations, with the solvent concentration being 0.1 ml/l in all cases (Palmer et al, 1997b). This method ensures that the composition of the substance in solution is as close as possible to that in the commercial preparation, providing all the test substance enters into solution.

Similar to the fish test (see Section 3.2.1.1) analysis was carried out by GC-ECD using the sum of the main peak areas. Example chromatographs are given in the report and these allow the following ratios for the main peak heights (e.g. the penta- and tetrabromodiphenyl ether components) to be estimated: low-level calibration standard penta:tetra 2.3:1; high-level calibration standard penta:tetra 2.1:1; 10 µg/l matrix fortification standard (prepared in same way as test solutions) penta:tetra 1.8:1; 6.5 µg/l nominal test solution penta:tetra 1.9:1. From these ratios it can be seen that the relative concentrations of the two components of the commercial pentaBDPE used for quantification are the same in the standards and the test solutions, giving some degree of confidence to the analytical results. The effects of pentaBDPE has also been studied in a 21-day life-cycle study (method OECD 202) (Drottar and Krueger, 1998).

A similar flow-through procedure as in the 48 hour study reported above was used. The test substance was a composite sample from two suppliers and had the following composition: tetrabromodiphenyl ether 33.7%; pentabromodiphenyl ether 54.6%; hexabromodiphenyl ether 11.7%. Stock solutions of the test substance were prepared in dimethylformamide, and were added directly to the diluter of the flow-through system. The rate of flow through the test system was such that 5 volume additions occurred every 24 hours. The concentration of dimethylformamide in the test chambers was 0.08 ml/l, and a solvent control using the same concentration, as well as a control without solvent, was also run. The test was carried out at $20\pm1^{o}C$ using filtered well water (parameters during test: pH=7.9-8.3, dissolved oxygen >76% of saturation; hardness 128-136 mg/l as $CaCO_3$). Five test concentrations were used: 1.4, 2.6, 5.3, 9.8 and 20.0 µg/l, based on the mean measured concentration during the test. No significant ($p>0.05$) differences between the control and solvent control daphnids were seen for any endpoint studied and so effects in the exposed daphnids were compared against the pooled effects seen in the controls and solvent controls. No significant ($p>0.05$) mortality was seen in the 1.4, 2.6, 5.3 and 9.8 µg/l treatments when compared to controls. However, by day 7 of the test, 100% mortality of the daphnids in the 20 µg/l treatment was seen (32.5% mortality after 48 hours; 72.5% mortality by 96 hours).

The EC_{50} for mortality/immobilisation was found to be 17 µg/l after 96 hours and 14 µg/l between days 7-21. No significant effects ($p>0.05$) on reproduction (as determined by the number of young per reproductive day) were seen in the 1.4, 2.6, 5.3 and 9.8 µg/l treatments (average young per reproductive day 7.48, 5.68, 5.22 and 6.11 respectively) compared to controls (average young per reproductive day 6.04 in control and 6.22 in solvent control). No young were produced in the 20 µg/l treatment as all test organisms had died before the first brood was produced (day 8). The EC_{50} for this endpoint was estimated as 14 µg/l at days 14 and 21. The final endpoint considered in the study was growth of the first generation organisms. Here a small but significant ($p<0.050$) reduction in mean length of the organisms was found in the 9.8 µg/l treatment group. A slight reduction in mean dry body weight was also found but this was not statistically significant ($p>0.05$) when compared to controls. Overall, the NOEC from the study was found to be 5.3 µg/l and the LOEC was found to be 9.8 µg/l.

In this long-term study, the concentrations of pentaBDPE in solution were determined by HPLC using UV detection. As before (see Section 3.2.1.1) the sum of the peak area responses for the two major components of the mixture was used for quantification. Example chromatographs are given in the report and these allow the following ratios for the two main peak heights to be estimated: low-level calibration standard 1.58:1; high-level calibration standard 1.58:1; matrix fortification standard 1.59:1; 1.4 µg/l test solution 1.5:1. From these ratios it can be seen that the relative concentrations of the two components of the commercial pentaBDPE used for quantification are approximately the same in the standards and the test solutions, giving some degree of confidence to the analytical results.

3.2.1.3 Toxicity to algae

The toxicity of pentaBDPE has been determined over 96 hours using the freshwater alga (*Selenastrum capricornutum*) (GLP study, based on OECD 201 method). The test substance used was a composite sample from two current suppliers and had the following composition: 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether. A static test system was used and dimethylformamide (DMF) at a concentration of 0.1 ml/l was used as cosolvent. The concentrations of the test substance were measured at the start and end of the test. At the start of the test, the exposure concentrations were 1.7, 3.1, 5.9, 12 and 26 µg/l, but by the end of the test the concentration of the test substance was below the detection limit (<0.8 µg/l) in all exposures (presumably the substance had adsorbed onto or was taken up by the biomass). Over the 96 hour exposure period, no statistically significant ($p<0.05$) differences between treatment and control groups were seen in either cell densities or areas under growth curves. However, at 24 hours a slight, but statistically significant, inhibition of growth was seen in the higher exposure groups and a 24-hour EC_{10} of 3.1 µg/l based on cell density and 2.7 µg/l based on area under the growth curve was calculated. By 48 hours and longer, no significant difference was seen between controls and any exposure group (Palmer et al, 1997a).

In the test, stock solutions of the test substance were prepared by dissolving it in dimethylformamide. One stock solution was prepared for each concentration tested. These stock solutions were then injected into the diluter mixing chambers to give the desired test concentrations, with the solvent concentration being 0.1 ml/l in all cases (Palmer et al, 1997a). This method ensures that the composition of the substance in solution is as close as possible to that in the commercial preparation, providing all the test substance enters into solution.

Similar to the fish test (see Section 3.2.1.1) analysis was carried out by GC-ECD using the sum of the main peak areas. Example chromatographs are given in the report and these allow the following ratios for the peak heights for the two main peaks (e.g. penta- and tetrabromodiphenyl ether components) to be estimated: low-level calibration standard penta:tetra 1.8:1; high-level calibration standard penta:tetra 2.1:1; 30 µg/l matrix fortification standard (prepared in same way as test solutions) penta:tetra 2.0:1; 13 µg/l nominal test solution penta:tetra 1.9:1. From these ratios it can be seen that the relative concentrations of the two components of the commercial pentaBDPE used for quantification are the same in the standards and the test solutions, giving some degree of confidence to the analytical results.

The results of the algal toxicity test are difficult to interpret since the test concentration declined during the test, presumably by adsorption onto the algae. Although this itself does not invalidate the test (OECD, 1993), it does make it difficult to determine a) if the effects

seen over 24 hours were real and b) at what concentrations effects may occur through continuous exposure over longer periods. The results (based on both cell density and area under the growth curve, compared with that of the controls) from the test do indicate that at 24 hours there was a slight stimulation of algal growth at an initial concentration of 1.6 µg/l, around a 10-13% inhibition of algal growth at an initial concentration of 3.3 and a 11-15% inhibition of algal growth at an initial concentration of 6.5 µg/l. Higher, but not dose related, inhibition of algal growth was seen at initial concentrations of 13 and 26 µg/l, with the maximum inhibition seen being 33% (cell density) and 45% (area under growth curve). The statistical significance of these % inhibition values was not given in the report (however these were used to estimate the 24h-EC_{10} value in the report). Thus, although no significant effects on algal growth were seen over the whole 96 hour period under the conditions of the test, the available data do not rule out the possibility that the substance may have the potential to cause effects on algal growth at concentrations above around 3.3-6.5 µg/l if these concentrations are maintained.

3.2.1.4 Microorganisms

No data are available on the toxicity of pentaBDPE to microorganisms.

3.2.1.5 QSAR data

The high octanol-water partition coefficient of pentaBDPE (log K_{ow} = 6.46-6.97) means that it is not ideally suited for QSAR predictions (generally only valid for substances with log K_{ow} between -1 and 6). Aquatic toxicity predictions have been obtained using the equations given in Chapter 4 in the Technical Guidance Document.

The results are shown below:

Fish:

96h-LC_{50}		
Pimephales promelas	$= 4.85 \cdot 10^{-8}$-$9.25 \cdot 10^{-8}$ mole/l =	27.3-52.2 µg/l
28-32d-NOEC		
Brachidanio rerio and *Pimephales promelas*	$= 2.67 \cdot 10^{-9}$-$5.30 \cdot 10^{-9}$ mole/l =	1.5-3.0 µg/l

***Daphnia magna*:**

48h-EC_{50}	$= 1.14 \cdot 10^{-8}$-$2.36 \cdot 10^{-8}$ mole/l =	6.4-13.3 µg/l
16d-NOEC	$= 6.78 \cdot 10^{-10}$-$1.51 \cdot 10^{-9}$ mole/l =	0.38-0.85 µg/l

Algae:

72-96h-EC_{50}		
Selenastrum capricornutum	$= 6.31 \cdot 10^{-9}$-$1.35 \cdot 10^{-8}$ mole/l =	3.6-7.6 µg/l

As can be seen from these results, the QSAR estimates are generally in good agreement with the experimental results obtained in the studies.

3.2.1.6 Sediment organisms

The substance used in the following sediment toxicity tests had the composition: 0.23% tribromodiphenyl ether, 36.02% tetrabromodiphenyl ether, 55.10% pentabromodiphenyl ether and 8.58% hexabromodiphenyl ether, based on GC areas (Wildlife International, 2000b). These tests were all carried out as a result of the initial risk assessment for this substance.

3.2.1.6.1 *Hyalella azteca*

A prolonged sediment toxicity test using spiked sediment has been carried out with the amphipod *Hyalella azteca* using a flow-through system (Wildlife International, 2000c). The test protocol was based on the ASTM E 1706-95b Guideline and USEPA Series 850 Ecological Effects Test Guidelines (OPPTS No. 850.1735).

The sediment used in the test was an artificial sediment consisting of 1% humic acid and dolomite, 5% alpha cellulose, 14% silt and kaolin and 80% industrial quartz sand. The sediment had a mean organic matter content of <2%, a water holding capacity of 11%, a pH of 6.6 and a particle distribution of 83% sand, 6% silt and 11% clay. The test substance was added to the sediment as a solution in DMF (final concentration of DMF was 0.1 ml/kg dry sediment), which was mixed into approximately 150 ml of moist sediment before dilution water was added. The test system consisted of 52 litre diluter tanks (one per treatment group) equipped with a siphoning system to allow the dilution water to flow through the system. The flow rate of the dilution water was set so that each tank received approximately 2 volume additions of water per day. At this flow rate the depth of water in the tank was 9.3 cm. The test compartments used in the tanks were 300 ml glass beakers with two nylon mesh-covered holes to allow water to flow through the compartment. Each compartment contained approximately 100 ml of sediment and 75-150 ml of overlying water (the sediment:overlying water ratio was therefore around 1:0.75-1.5 in each test compartment, but the actual overall volume of water present in the test tank would be higher than this). The test system was left for 48 hours to equilibrate before introduction of the test organisms.

In the test, groups of 12-day old amphipods were exposed to a series of 5 test concentrations, a solvent control and control sediment for 28 days at 23±2°C. Eight replicate test compartments, each containing 10 amphipods, were maintained in each treatment and control group, giving a total of 80 amphipods per treatment group. The nominal concentrations tested were 3.1, 6.3, 13, 25 and 50 mg/kg dry weight. Additional replicates were added to the highest and lowest treatment and control groups to allow for analytical sampling of water and sediment during the test. The amphipods were fed throughout the test. The overlying water used in the test had the following properties: dissolved oxygen 6.3-8.5 mg/l, pH 8.2-8.6, hardness 129 mg/l as $CaCO_3$. During the test the amphipods were fed 1.5 ml per day of a mixture of yeast, Cerophyll® and trout chow.

Analysis of the concentration of the test substance in sediment, pore water and overlying water was carried out at two test concentrations at days 0, 7 and 28 of the test. The results are shown in **Table 3.40**. Based on the analysis of the solid phase, it is clear that the concentrations were well maintained throughout the test (approximately 81% of nominal at 3.1 mg/kg dry weight and 74% of nominal at 50 mg/kg dry weight; mean is 77% of nominal – substance is also present in the pore water which means exact comparison of the measured and nominal concentrations is difficult).

As the measured concentrations indicate that approximately 80% of the nominal concentration were maintained throughout the test, the results are reported based on the nominal concentrations.

Table 3.40 Results of analysis of test concentrations during the test

Nominal Concentration	Measured concentrations											
	Solid phase (mg/kg dry weight)				Pore water (µg/l)				Overlying water (µg/l)			
	day 0	day 7	day 28	mean	day 0	day 7	day 28	mean	day 0	day 7	day 28	mean
3.1 mg/kg dry weight	2.35 & 2.37[a]	2.42 & 2.65[a]	2.68 & 2.82[a]	2.5	17.0	17.0	9.64	14.5	nd	nd	nd	nd
50 mg/kg dry weight	37.9 & 38.8[a]	35.2 & 25.3[a]	46.8 & 38.9[a]	37.1	89.0	45.1	20.1	51.4	nd	nd	nd	nd

[a]Replicate sample
nd – not detected (<1 µg/l)

The endpoints determined in the study were: percent mortality; and growth (dry body weight).

No statistically significant differences ($p>0.05$) were observed between the control and solvent control groups and so the two groups were pooled for comparison with the responses seen in the treatment groups.

Mortalities at 28 days were 30% in the controls, 34% in the solvent controls, and 37%, 30%, 56%, 41% and 44% in the 3.1, 6.3, 13, 25 and 50 mg/kg dry weight treatment groups respectively. Mortalities were reported to be variable within and between treatment groups and in the controls. From these results it was determined that a slight increase in mortality relative to controls was seen at the three highest concentrations tested, but that this increase was only statistically significant ($p<0.05$) compared to the pooled controls in the 13 mg/kg dry weight treatment group.

The average individual dry weights determined at the end of the test were 0.063 mg in the control group, 0.116 mg in the solvent control group and 0.123, 0.148, 0.260, 0.074 and 0.110 mg respectively in the 3.1, 6.3, 13, 25 and 50 mg/kg dry weight treatments respectively. Again the weights of individuals within and between treatment groups, including the controls, were highly variable, but any reduction in weight in comparison with the pooled controls was not concentration-dependent or statistically significant ($p>0.05$).

Due to the variability of responses seen in this study it is not possible to derive exact values for the NOEC and LOEC. The report indicates that the 28-day EC_{50} is >50 mg/kg dry weight and that the LOEC is ≥13 mg/kg dry weight, based on the general increase in mortality seen at and above this concentration. The NOEC is therefore around 6.3 mg/kg dry weight.

3.2.1.6.2 *Chironomus riparius*

A prolonged sediment toxicity test using spiked sediment has been carried out with the midge *Chironomus riparius* (Wildlife International, 2000d). The test protocol was based on the OECD draft test guideline (May 1998 version). The sediment used in the test was an artificial sediment consisting of 1% humic acid and dolomite, 5% alpha cellulose, 14% silt and kaolin

and 80% industrial quartz sand. The sediment had a mean organic matter content of <2%, a water holding capacity of 11%, a pH of 6.6 and a particle distribution of 83% sand, 6% silt and 11% clay. The test substance was added to the sediment as a solution in DMF (final concentration of DMF was 0.1 ml/kg dry sediment), which was mixed into approximately 150 ml of moist sediment before 600 ml of dilution water was added (i.e. the sediment:overlying water ratio was 1:4). The test system was allowed to equilibrate for 48 hours before the midge larvae were introduced.

In the test, groups of midge larvae were exposed to a series of 5 test concentrations, a solvent control and control sediment for 28 days at 20±2°C using a static system. The larvae used in the test were first-instar larvae, approximately 3 days old. Four replicate chambers, each containing 20 larvae, were maintained in each treatment and control group, giving a total of 80 larvae per treatment group. The nominal concentrations tested were 3.1, 6.3, 13, 25 and 50 mg/kg dry weight. Additional replicates were added to the highest and lowest treatment and control groups to allow for analytical sampling of water and sediment during the test. The larvae were fed throughout the test. The overlying water used in the test had the following properties: dissolved oxygen 6.0-8.5 mg/l, pH 8.1-8.4, hardness 130 mg/l as $CaCO_3$. Gentle aeration was used throughout the test, with the vessels being covered to minimise evaporation. The larvae were fed on a suspension of flake food during the test. This was added at a rate of 0.5 mg per larvae per day by adding 1 ml of suspension to each test chamber on every other day. After 10 days, a slightly lower feeding rate was used every other day to discourage fungal growth.

Analysis of the concentration of the test substance in sediment, pore water and overlying water was carried out at two test concentrations at days 0, 7 and 28 of the test. The results are shown in **Table 3.41**.

Table 3.41 Results of analysis of test concentrations during the test

Nominal Concentration	Measured concentrations											
	Solid phase (mg/kg dry weight)				Pore water (µg/l)				Overlying water (µg/l)			
	day 0	day 7	day 28	mean	day 0	day 7	day 28	mean	day 0	day 7	day 28	mean
3.1 mg/kg dry weight	2.16 & 2.82[a]	2.12 & 2.00[a]	3.04 & 1.81[a]	2.3	12.5 & 9.74[a]	18.5 & 33.9[a]	14.6 & 12.9[a]	17.0	7.28	2.98	3.73	4.7
50 mg/kg dry weight	21.3 & 30.9[a]	19.3 & 25.8[a]	20.6 & 51.7[a]	28	19.6 & 19.2[a]	22.6 & 32.2[a]	26.8 & 17.1[a]	22.9	7.78	3.09	7.78	6.2

[a]Replicate sample

Based on the analysis of the solid phase, it is clear that the concentrations were reasonably well maintained throughout the test (approximately 74% of nominal at 3.1 mg/kg dry weight and 56% of nominal at 50 mg/kg dry weight; mean is 65% on nominal – substance is also present in the pore water and overlying water which means exact comparison of the measured and nominal concentrations is difficult). As the measured concentrations indicate the actual concentration was slightly lower than the nominal concentration in the test, the results are reported in terms of both the nominal and measured (where appropriate) concentrations.

The data reported in **Table 3.41** also allows a sediment-water partition coefficient to be estimated for pentaBDPE for the sediment used in this study. Based on the ratio of the measured concentration in the solid phase/measured concentration in overlying water, the

Kp_{sed} is ~490 l/kg for the low exposure concentration and ~4,516 l/kg for the high exposure concentration.

The endpoints determined in the study were: percent mortality (percentage of unemerged organisms), mean development time (the mean time span between application of the test substance and emergence of the experimental cohort of midges), emergence rate (defined as sum of midges emerged per test chamber/number of larvae introduced) and development rate (the portion of larval development that took place per day).

All emerged midges appeared normal during the test. Emergence was first seen on day 16 of the test and continued until test termination on day 28. At test termination, the mean percentage emergence in the control and solvent control groups was 96% and 95% respectively. The mean percentage emergence in the 3.1, 6.3, 13, 25 and 50 mg/kg dry weight treatment groups was 96%, 84%, 98%, 86% and 76% respectively at test termination (no indication is given in the report as to the statistical significance of these reductions in emergence). The 28 day-EC_{50} was therefore >50 mg/kg dry weight.

The mean development time for each replicate and treatment group for the 3.1, 6.3, 13 and 25 mg/kg dry weight treatments was comparable to controls (22-24 days). There was a slight delay in the mean development time in the 50 mg/kg treatment group (26 days) compared to controls (22 days), but this difference was not statistically significant ($p>0.05$).

No statistically significant differences were seen in the mean development rates between controls and the 3.1, 6.3, 13 and 25 mg/kg dry weight treatments. However, a statistically significant ($p<0.05$) decrease in the mean development rate of the 50 mg/kg dry weight treatment groups compared to controls was seen. The values for the mean development rate (which represents the proportion of larval development which takes place each day) were 0.048 in the control group, 0.047 in the solvent control group, and 0.048, 0.042, 0.047, 0.044 and 0.040 in the five treatment groups respectively.

The overall NOEC from this study is therefore 25 mg/kg dry weight (nominal), and the LOEC is 50 mg/kg dry weight (nominal). The actual measured concentrations appear to be slightly lower than the nominal concentrations in this study, and the same results based on the mean measured concentration would give the LOEC to be around 28 mg/kg dry weight and the NOEC to be around 16 mg/kg dry weight (assuming that the actual concentration in the 25 mg/kg treatment is 65% of the nominal value).

3.2.1.6.3 *Lumbriculus variegatus*

A prolonged sediment toxicity test using spiked sediment has been carried out with the oligochaete *Lumbriculus variegatus* using a flow-through test system (Wildlife International, 2000e). The test protocol was based on the ASTM E 1706-95b Guideline and USEPA Series 850 Ecological Effects Test Guidelines (OPPTS No. 850.1735). The sediment and test system used was the same as in the *Hyalella azteca* test (see Section 3.2.1.6.1).

In the test, groups of adult oligochaetes were exposed to a series of 5 test concentrations, a solvent control and control sediment for 28 days at 23±2°C using a flow-through system. Eight replicate test compartments, each containing 10 oligochaetes, were maintained in each treatment and control group, giving a total of 80 oligochaetes per treatment group. The nominal concentrations tested were 3.1, 6.3, 13, 25 and 50 mg/kg dry weight. Additional

replicates were added to the highest and lowest treatment and control groups to allow for analytical sampling of water and sediment during the test. The oligochaetes were fed throughout the test with salmon starter. During the first 6 days of the test, 20 mg of food was added to each test compartment every 3 days, but this was reduced to 10 mg of food every 3 days from day 9 onwards to discourage fungal growth. The overlying water used in the test had the following properties: dissolved oxygen 6.0-8.2 mg/l, pH 7.9-8.6, hardness 130 mg/l as $CaCO_3$.

Analysis of the concentration of the test substance in sediment, pore water and overlying water was carried out at two test concentrations at days 0, 7 and 28 of the test. The results are shown in **Table 3.42**.

Table 3.42 Results of analysis of test concentrations during the test

Nominal Concentration	Measured concentrations											
	Solid phase (mg/kg dry weight)				Pore water (µg/l)				Overlying water (µg/l)			
	day 0	day 7	day 28	mean	day 0	day 7	day 28	mean	day 0	day 7	day 28	mean
3.1 mg/kg dry weight	2.50 & 2.31[a]	2.54 & 2.63[a]	2.73 & 2.95[a]	2.6	29.2	15.6	11.5	18.8	nd	nd	nd	nd
50 mg/kg dry weight	46.4 & 67.0[a]	39.1 & 59.2[a]	34.2 & 75.6[a]	53.6	35.7	24.8	39.0	33.2	nd	nd	1.06	nd

[a]Replicate sample
nd – not detected (<1 µg/l)

Based on the analysis of the solid phase, it is clear that the concentrations were well maintained throughout the test (approximately 84% of nominal at 3.1 mg/kg dry weight and 107% of nominal at 50 mg/kg dry weight; mean is 96% of nominal – substance is also present in pore water which means exact comparison of the measured and nominal concentrations is difficult). As the measured concentrations indicate that approximately 96% of the nominal concentration was maintained throughout the test, the results are reported base on the nominal concentrations.

The endpoints determined in the study were: survival/reproduction (total number of organisms present at end of study; as it is not possible to distinguish between adults and young this is a combination of parent survival and number of young produced); and growth (dry body weight).

Statistically significant differences ($p<0.05$) in the mean dry weight data of individuals were observed between the control and solvent control groups and so the two groups were not pooled. The solvent control group was used for comparison with the responses seen in the treatment groups.

During the test, no observations of mortality or abnormal behaviour of oligochaetes were seen in any of the replicates or control groups. At the end of the test, an increase in the numbers of oligochaetes was found in each replicate (experiment started with 10/replicate) indicating that reproduction had occurred. The mean number of oligochaetes/replicate found at the end of the test was 38.3 in the control group, 37.4 in the solvent control group and 33.4, 24.0, 27.5, 32.4 and 27.9 in the 3.1, 6.3, 13, 25 and 50 mg/kg treatments respectively. The

reduction in the number of worms/replicate in the 6.3, 13 and 50 mg/kg treatments was statistically significantly different ($p<0.05$) from the solvent controls.

The average individual dry weights determined at the end of the test were 1.59 mg in the control group, 1.40 mg in the solvent control group and 1.38, 1.46, 1.39, 1.36 and 1.74 mg respectively in the 3.1, 6.3, 13, 25 and 50 mg/kg dry weight treatments respectively. Any reduction in weight in comparison with the solvent controls was not concentration-dependent or statistically significant ($p>0.05$). The report indicates that the 28-day EC_{50} is >50 mg/kg dry weight and that the LOEC is 6.3 mg/kg dry weight, based on the survival/reproduction. The NOEC is therefore 3.1 mg/kg dry weight.

3.2.1.6.4 Observations on sediment studies

Two of the test methods used a flow-through system. Here water was slowly pumped through the test vessels over the 28-day test period. Since the substance was added to the sediment at the start of the test, and was not present in the influent water, this test system has the potential to cause loss of test substance during the test. However, the concentrations in the overlying water were generally very low (<1 µg/l) and the monitoring data from the sediment itself indicated that the concentrations were well maintained throughout the test and so the actual loss in the flow-through water was probably small and unlikely to affect the results of the test.

The second observation concerns the organic carbon content of the sediment. The draft OECD guideline for the *Chironomus* study indicates that the organic carbon content of the sediment should be 2±0.5%, and this was indicated in the test protocols for all three sediment tests. The draft OECD guideline also indicates that sphagnum moss peat is recommended to make up the artificial sediment. In these tests, alpha cellulose was used instead of sphagnum moss peat as it is stated in the reports that this is a more standardised source of organic matter than peat moss. The organic matter content of the sediments used in the tests is given as <2%, which indicates that the actual organic carbon content may have been lower than recommended in the test guidelines. The result of this is to maximise the availability of the substance in the pore-water phase. Since the test substance is highly adsorptive, the majority of the substance is still mainly found on solid phase (as indicated by the analytical measurements) and so could still contribute to the toxicity if direct ingestion of sediment-bound substance is an important route. Thus the test system appears to have maximised the potential for exposure through both pore water and direct ingestion of sediment.

In all these studies, the organisms were fed on clean food. Thus the major source of exposure of the organisms to the substance in these tests would be from pore water and/or ingestion of sediment. It is also possible that the test substance would adsorb onto the food added to the test system, particularly if this was not eaten immediately, and this may provide another mechanism for exposure (e.g. exposure via the food chain) of the organisms during the test. The actual influence of this on the results is unknown.

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

3.2.1.7.1 Surface water

Long-term NOECs are available for fish, *Daphnia* and algae. The lowest NOEC is 5.3 µg/l for *Daphnia*. The available algal data are difficult to interpret but indicate that the substance may have the potential to cause effects at a similar concentration to that found in the *Daphnia* study. An assessment factor of 10 is appropriate for this data set. The PNEC for water is estimated at 0.53 µg/l.

3.2.1.7.2 Sediment

A PNEC for sediment can be estimated using the equilibrium partitioning method:

$$PNEC_{sed} = \frac{K_{susp-water}}{RHO_{susp}} \cdot PNEC_{water} \cdot 1{,}000$$

where $K_{susp\text{-}water} = 13{,}921\ m^3/m^3$
$RHO_{susp} = 1{,}150\ kg/m^3$

The $PNEC_{sed}$ = 6.42 mg/kg wet weight by this method. This value is equivalent to around 16.7 mg/kg dry weight using the default water content for sediment given in the Technical Guidance Document (sediment is approximately 62% by weight water).

Sediment toxicity data are also available. The lowest NOEC from the three long-term sediment toxicity tests is 3.1 mg/kg dry weight. An assessment factor of 10 is appropriate for this data set, in accordance with the sediment assessment strategy agreed by the ESR Technical Meeting in December 1998. Thus the $PNEC_{sed}$ = 0.31 mg/kg dry weight.

According to the Technical Guidance Document (TGD), for soil organisms the NOEC should be normalised to the standard organic matter (or organic carbon content) of soil as used in the TGD (i.e. $NOEC_{standard} = NOEC_{experimental} \cdot Fom_{soil(standard)}/Fom_{soil(experimental)}$; where Fom = fraction of organic matter). This normalisation is not suggested in the TGD for NOECs from sediment tests, but, in principle, it seems sensible to carry out such a normalisation so that the test results and PECs are compared on the same basis. However, this normalisation assumes that the toxicity seen is due to the chemical present in porewater of the soil or sediment. For this substance, one of the reasons for carrying out the sediment test was to determine if the substance also exerts toxicity from the adsorbed fraction, and so it is questionable if such a correction should be applied here. For this reason, both the standardised NOEC and the NOEC from the test directly will be considered.

The actual organic carbon contents of the sediments used in the tests are unknown. The test protocols themselves indicate that the organic carbon content should be 2±0.5% in these tests. However, the test reports indicate that the organic matter content used was <2% in each test. Since organic matter contents are usually very approximately two times higher than the organic carbon contents, this would imply that the organic carbon contents of the sediments used were very low at <1%. Assuming this value and the standard organic carbon content of sediment to be 5% (from the TGD), the lowest NOEC of 3.1 mg/kg dry weight is equivalent

to a $NOEC_{standard}$ of 15.5 mg/kg dry weight. Thus the $PNEC_{sed(standard)}$ = 1.55 mg/kg dry weight. Given that there are some uncertainties over the organic carbon contents of the test sediments, this value indicates that the substance may be more toxic to sediment organisms than indicated by the equilibrium partition method above using the aquatic toxicity data.

The other piece of information that is useful for this discussion is that the mean pore water concentration of the substance in the 3.1 mg/kg dry weight test sediments was measured as 14.5, 17.0 and 18.8 µg/l in the three test systems used (similar sediments were used in each test). These values are slightly higher than, but broadly comparable with, the NOECs obtained in the standard aquatic tests and indicate that the effects seen in the sediment tests could be due solely to the substance presence in the pore water, and that the equilibrium partitioning method adequately accounts for the sediment toxicity seen without the need to apply an extra factor of 10 to account for direct ingestion of sediment-bound substance (i.e. direct ingestion does not contribute significantly to the toxicity).

From the above discussion it is apparent that there is some uncertainty over whether or not the equilibrium partitioning method adequately describes the toxicity of pentaBDPE to sediment organisms. The pore water concentrations measured during the study are similar to those found to cause effects in the aquatic toxicity tests, and indicate that the equilibrium partitioning approach is appropriate. However, the PNECs based on the dry sediment weights derived directly from the test are lower than those derived using the equilibrium partitioning method using the aquatic toxicity data. This difference could be due to a lower sediment-water partition coefficient for the substance in this sediment than would be predicted from the data used in the risk assessment report. For example, a Kp_{sed} of around 490-4,516 l/kg was estimated in Section 3.2.1.6.2 from the data reported in the *Chironomus* test. Assuming a 1% organic carbon content in this sediment, this is equivalent to a K_{oc} of 49,000-451,600 l/kg; this compares with the K_{oc} value used in the Risk Assessment of 556,801 l/kg.

The PNECs derived from the sediment test data rather than the equilibrium partitioning method will be considered in the risk characterisation.

3.2.1.7.3 Sewage treatment processes

It is not possible to estimate a PNEC for microorganisms in sewage treatment processes due to a lack of data.

3.2.2 Terrestrial compartment

The substance used in the following terrestrial toxicity tests had the following composition: 0.23% tribromodiphenyl ether, 36.02% tetrabromodiphenyl ether, 55.10% pentabromodiphenyl ether and 8.58% hexabromodiphenyl ether, based on GC areas (Wildlife International, 2000b). These tests were all carried out as a result of the initial risk assessment for this substance.

3.2.2.1 Microorganisms

The toxicity of commercial pentaBDPE to soil microorganisms was studied in the OECD 216 Soil Microorganisms, Nitrogen Transformation Test (Inveresk, 1999). The soil used was a sandy loam of pH 6.8 and 1.0% organic carbon content. The moisture content of the soil was 11.4% as supplied, and the maximum water holding capacity (MWHC) was 41.9%. Before

use in the test, the soil moisture content was adjusted to ~40% of the MWHC (i.e. the soil water content was around 17%), and this level was maintained throughout the test. The soil samples were treated with the test material using quartz sand as carrier. The test substance was added to sand as an acetone solution, and once the acetone had evaporated, the sand was thoroughly mixed into the soil samples. The concentrations tested were 0.01, 0.03, 0.10, 0.33 and 1.00 mg/kg dry soil weight. Lucerne meal (0.5% w/w) was then added to the soil and the samples were incubated at 20±2^{o}C for 28 days under aerobic conditions. Nitrate production was determined after 0-3 hours and 28 days incubation. Increasing concentrations of test material were found to have no effect on the levels of nitrate produced. The variation in nitrate concentration between replicate control samples was <15% at 0-3 hours and 28 days (actual variation was 1.7% and 0.4% respectively), indicating a valid test. The NOEC from this test is therefore >1 mg/kg dry weight.

3.2.2.2 Plants

The toxicity of pentaBDPE to six species of plants has been determined using OECD Guideline 208 (the protocol is based on the 1998 proposal for revision for this test guideline) (Wildlife International, 2000g). The soil used in the test was an artificial sandy soil produced by mixing kaolinite clay, industrial quartz sand and peat in the weight ratio 4:50:5 respectively. Crushed limestone and a slow-release fertiliser were also added. The particle size distribution of the soil was 92% sand, 0% silt and 8% clay, and the soil had a pH of 7.5 and an organic matter content of 2.9%.

The test soils were prepared by dissolving a known weight of the test substance in 85 ml of DMF and mixing this with a subsample of around 500 g of the soil. This soil was then mixed with the bulk of the soil (total 50 kg) for 20 minutes to produce the soil for use in the test. After mixing, 3 subsamples of the soil were collected for analysis to confirm the initial concentration of the test substance within the treated soil, and also to check on the homogeneity of the treated soil.

The following six plant species were tested: monocots; corn (*Zea mays*), onion (*Allium cepa*), rye grass (*Lolium perenne*): dicots; cucumber (*Cucumis sativa*), soybean (*Glycine max*), tomato (*Lycopersicon esculentum*). For each species, a control group, solvent control group and 5 treatment groups were run. Each group consisted of 4 replicate pots each containing 10 seeds (giving 40 seeds per control or treatment group). The nominal concentrations tested were 62.5, 125, 250, 500 and 1000 mg/kg dry soil. Analysis by HPLC with UV detection (quantitation by summing the peak areas of the main components of the commercial product) of the two lowest and two highest concentrations indicated that the mean measured concentrations at day 0 were 98.9-105% of the nominal value and that the samples were homogeneous.

During the 21-day test, weekly observations of emergence were made (number of emerged seedlings per pot). In addition, a qualitative assessment of the condition of each seedling was made (i.e. presence or absence of signs of phytoxicity such as colour changes, necrosis, leaf curling, plant lodging or plant stunting). At the termination of the test, the growth of the emerged seedlings was evaluated in terms of the mean shoot height and mean shoot fresh weight.

Corn

No statistically significant differences ($p>0.05$) were found between the control and solvent control groups and so these were pooled for comparison with the treatments. No statistically significant effects ($p>0.05$) on the emergence of seedlings were noted in any treatment group compared with the control group. The emerged seedlings generally appeared normal throughout the test (there were isolated individuals which displayed signs of phytotoxicity such as stunting, necrosis or death but none of these conditions appeared to be dose-responsive and so were not attributed to the treatments). Effects were, however, seen on the mean shoot height and mean shoot weight after 21-days compared with the control group. The mean shoot height was statistically significantly reduced ($p<0.05$) in the 250, 500 and 1,000 mg/kg dry weight groups over the controls (mean shoot height was 52.6 cm in the pooled control group, and 46.7 cm, 46.8 cm, 41.1 cm, 41.4 cm and 44.5 cm in the 62.5, 125, 250, 500 and 1,000 mg/kg dry weight treatment groups respectively). The EC_{25} for this endpoint was estimated to be >1,000 mg/kg dry weight. The mean shoot fresh weights were found to be statistically significantly reduced ($p<0.05$) in all treatment groups compared with the controls (mean shoot fresh weight was 6.32 g in the pooled control group, and 5.09 g, 5.03 g, 3.51 g, 3.55 g and 4.30 g in the 62.5, 125, 250, 500 and 1,000 mg/kg dry weight treatment groups respectively). Based on the dose-response seen an EC_{25} of 154 mg/kg dry weight was calculated. Since significant effects were seen at the lowest concentration tested, it is not possible to obtain a NOEC directly from the results, however, an EC_5 of 16 mg/kg dry weight was calculated in the test report and this can be considered as the NOEC.

Cucumber

In this test there were differences in the mean shoot heights and weights between the control group and solvent control group that were statistically significant ($p<0.05$) and so the solvent control group was used for comparison with the treatments. No statistically significant differences ($p>0.05$) were seen between treatments and the solvent control in the emergence of seedlings, mean shoot heights or mean shoot fresh weights in this experiment. The emerged seedlings generally appeared normal (isolated individuals appeared stunted in growth but this was not dose-responsive and also appeared in the control and solvent control groups and so was not treatment related). The NOEC for this species is therefore ≥1,000 mg/kg dry weight.

Onion

No statistically significant differences ($p>0.05$) were found between the control and solvent control groups and so these were pooled for comparison with the treatments. No statistically significant differences ($p>0.05$) were seen between treatments and the controls in the emergence of seedlings, mean shoot heights or mean shoot fresh weights [weight reductions of >25% compared to controls were observed but these were not statistically significant ($p>0.05$)] in this experiment. The emerged seedlings generally appeared normal (isolated incidences of necrosis or death were seen but these were not dose-responsive and so were not considered treatment related). The NOEC for this species is therefore ≥1,000 mg/kg dry weight.

Ryegrass

No statistically significant differences ($p>0.05$) were found between the control and solvent control groups and so these were pooled for comparison with the treatments. No statistically significant differences ($p>0.05$) were seen between treatments and the controls in the emergence of seedlings, mean shoot heights or mean shoot fresh weights (a statistically significant increase in weight was seen in the 62.5 mg/kg dry weight treatment compared with controls but this was not considered an adverse effect; weight reductions of >25% compared to controls were observed in some treatments but these were not statistically significant ($p>0.05$)) in this experiment. The emerged seedlings generally appeared normal (isolated incidences of stunting, chlorosis or necrosis were seen but these were not dose-responsive and so were not considered treatment related). The NOEC for this species is therefore ≥1,000 mg/kg dry weight.

Soybean

There was a small, but statistically significant difference, between the mean shoot fresh weights in the solvent control group compared to the control group but this was not clearly attributable to the solvent and so the two control groups were pooled for comparison with the treatments. In addition, for the mean shoot fresh weight endpoint, the treatment groups were also compared to the solvent control group alone. No statistically significant differences ($p>0.05$) were seen between treatments and the appropriate control groups in the emergence of seedlings, mean shoot heights or mean shoot fresh weights in this experiment (mean shoot fresh weights were statistically significantly reduced in the 250 and 500 mg/kg dry weight treatments when compared to the pooled controls, but not when compared to the solvent control). The emerged seedlings generally appeared normal (isolated incidences of stunting, stem curl or death were seen but these were not dose-responsive and so were not considered treatment related). The NOEC for this species is therefore ≥1,000 mg/kg dry weight.

Tomato

In this test a statistically significant difference ($p<0.05$) was seen in emergence on day 21 between the control group and solvent control groups. However, the emergence in the solvent group was higher than in the control group (i.e. the solvent did not cause a negative effect) and so the two control groups were pooled for comparison with the treatment groups. No statistically significant differences ($p>0.05$) were seen in emergence in the treatment groups compared with the control groups. The emerged seedlings generally appeared normal throughout the test (several seedlings failed to shed their seed coats upon emergence, one seedling was slightly chlorotic and there was one mortality observed on day 21 - however these conditions were not dose-responsive and were not thought to be treatment related). Effects were seen on the mean seedling height and mean seedling fresh weight. A dose-responsive decrease in the mean seedling height was observed, but this was only statistically significantly different ($p<0.05$) from the control group in the 500 mg/kg dry weight treatment group (the mean seedling height was 4.0 cm in the pooled control group, and 4.1 cm, 3.7 cm, 3.1 cm, 2.5 cm and 3.2 cm in the 62.5, 125, 250, 500 and 1,000 mg/kg dry weight treatment groups respectively). The EC_{25} for this endpoint was calculated as 369 mg/kg dry weight. The mean shoot fresh weights were found to be statistically significantly ($p<0.05$) reduced in the 250, 500 and 1,000 mg/kg treatment groups when compared to controls (the mean shoot fresh weight was 515 mg in the pooled control group, and 498 mg, 404 mg, 204 mg, 138 mg and 275 mg in the 62.5, 125, 250, 500 and 1,000 mg/kg dry weight treatment groups

respectively). The EC_{25} was calculated to be 136 mg/kg dry weight and the EC_{50} was calculated to be 217 mg/kg dry weight for this endpoint. Overall, the NOEC for this species was 125 mg/kg dry weight.

3.2.2.3 Earthworms

An OECD 207 toxicity test has been carried out with earthworms (*Eisenia fetida*) (Wildlife International, 2000f). The soil used in the test was an artificial soil prepared by mixing sand (70%), kaolin (20%) and sphagnum peat (10%). The pH of the soil was adjusted to 6. The test soils were prepared by adding a small volume of the test substance dissolved in DMF to a small portion of the artificial soil, which was then added to the bulk of the soil to be used. The water content of the soil was adjusted to 33% by weight and then mixed for 20 minutes to allow the solvent to evaporate. A solvent control soil was also prepared in the same way by adding DMF alone to the soil. Around 750 g of soil was added to each of 4 replicate test chambers per treatment group or control and the test chambers were covered with perforated plastic wrap (to allow for some air exchange). At the start of the test, worms (10 per replicate or 40 per concentration) were placed on the surface of the soil and observed for burrowing behaviour. The chambers were maintained at 20^{o}C throughout the test, and the worms were not fed during the test. On day 7 of the test (total duration of test was 14 days), the content of each test chamber was removed to determine the number of surviving worms and to observe any behavioural or pathological abnormalities. Following these observations, the test soil was returned to the chambers and worms replaced on the soil surface in order to observe burrowing behaviour. At the end of the test, the number of surviving worms, and also the average body weight of the worms was determined.

The test was carried out over two phases. In the first phase, earthworms were exposed to concentrations of 3.1, 6.3, 13, 25 and 50 mg/kg dry weight over 14 days. In the second phase, higher concentrations of 100, 300 and 500 mg/kg dry weight were tested.

Soil samples were analysed at the start of the test to determine the homogeneity of the test soils (done for the 3.1, 50 and 500 mg/kg dry weight treatments) and to verify the concentrations used (done for all treatments). At the end of the test, samples were again analysed for each test concentration to investigate the stability of the test substance in the soil over the period of the test. The mean measured concentrations over the 14 days were determined as 3.3, 6.1, 12, 22, 42, 99, 270 and 456 mg/kg dry weight for the nominal treatments of 3.1, 6.3, 13, 25, 50, 100, 300 and 500 mg/kg dry weight respectively, indicating that the nominal concentrations were achieved and maintained during the test. The pH of the test soil ranged from 6.6 to 7.6 at day 0 and 7.7 to 8.7 at day 14.

The earthworms were monitored for signs of mortality and toxicity after 7 and 14 days exposure. In the first phase of the test, the mortality seen in the control and solvent control was 5% and 10% respectively after 14 days. In the second phase, the mortality seen in the control and solvent control was 10% and 12.5% (the test guideline indicates that mortality in controls should not exceed 10%). The mortality seen in the treatment groups was 2.5, 0, 0, 2.5, 5, 7.5, 12.5 and 10% at 3.1, 6.3, 13, 25, 50, 100, 300 and 500 mg/kg dry weight respectively. These mortalities were comparable to those observed in the control groups and were not considered treatment related.

Some behavioural/physiological effects were noted in the first phase of the experiment in the 25 and 50 mg/kg dry weight treatment groups but these were limited to a few worms that

were thin in appearance. Similar effects were seen in the solvent control group. Similar effects were also seen in the second phase of the experiment but the effects were again few in number and not concentration-dependent. It was therefore concluded that these effects were not treatment related. A slight delay in burrowing was observed in the three highest treatments on day 0 of the second phase of the experiment, but these effects were not considered to be treatment related.

A reduction in the mean body weight occurred in all worms (treatment groups and controls) over the 14 day test, as the worms were not fed during the test. There was no statistically significant ($p>0.05$) differences in the body weight loss between any treatment group and the controls.

A reference substance (chloroacetamide) was tested using the same procedure. The 14-day LC_{50} for this substance was determined to be 19.4 mg/kg dry weight, which is reported to be consistent with results previously observed for this substance.

As no significant treatment-related effects were observed in this study, the NOEC is determined to be >500 mg/kg dry weight.

3.2.2.4 Predicted no effect concentration (PNEC) for the terrestrial compartment

A PNEC for soil can be estimated using the equilibrium partitioning method.

$$PNEC_{soil} = \frac{K_{soil-water}}{RHO_{soil}} \cdot PNEC_{water} \cdot 1{,}000$$

where $K_{soil\text{-}water} = 16{,}704\ m^3/m^3$
$RHO_{soil} = 1{,}700\ kg/m^3$

The $PNEC_{soil}$ = 5.21 mg/kg wet weight by this method. This value is equivalent to 5.91 mg/kg dry weight, using the default water content of soil from the Technical Guidance Document of 20% by volume or 11.8% by weight.

Terrestrial toxicity data are also available. The lowest NOEC from the three soil toxicity tests is >1 mg/kg dry weight from the soil nitrification study. However, the soil nitrification study did not use very high test concentrations (i.e. the highest concentration tested is lower than the PNEC predicted by the equilibrium partitioning method), and so in this respect it could be considered to be invalid due to use of an inappropriate concentration range. The two other soil toxicity tests appear to have used a more realistic concentration range (up to 500 and 1,000 mg/kg dry weight) and effects were seen in the plant study. Therefore, an alternative PNEC for soil could be derived from the results of the plant study. From the data set available, an assessment factor of 50 is appropriate in accordance with the TGD. (However, the same conclusion would be reached in the risk characterisation even if an assessment factor of 10 was used).

Based on the NOEC of 16 mg/kg dry weight from the plant study, the $PNEC_{soil}$ can be estimated at 0.32 mg/kg dry weight, using an assessment factor of 50. This is equivalent to

0.28 mg/kg wet weight using the default water contents for given in the TGD for sediment (soil is approximately 11.8% by weight water).

According to the TGD, for soil organisms it is indicated that the NOEC should be normalised to the standard organic matter content of soil as used in the TGD (i.e. $NOEC_{standard} = NOEC_{experimental} \cdot Fom_{soil(standard)}/Fom_{soil(experimental)}$; where Fom = fraction of organic matter; see Section 3.2.2 above). This was 2.9% in the plant study compared to the standard value of 3.4%. Therefore, the $NOEC_{standard}$ is 18.8 mg/kg dry weight. Thus the $PNEC_{soil(standard)}$ is set at 0.38 mg/kg dry weight.

This PNEC is derived using an assessment factor of 50. In terms of comparison with the PNEC derived from equilibrium partitioning then an assessment factor of 10 could be used in order that both PNECs are based on the same assessment factor. If this factor is used, the PNECs derived would be 5 times higher than the value given (i.e. around 1.9 mg/kg dry weight. This PNEC is similar, but slightly lower, than the PNEC derived from equilibrium partitioning above (this small difference could be due to a slightly lower soil-water partition coefficient for the substance in the soil used in the test than would be predicted from the data in the risk assessment report) and indicates that the toxicity may be adequately explained by the equilibrium partitioning approach. This would be expected to be the case for plants, for which it is hard to envisage an alternative route of exposure to that via pore water (i.e. direct uptake of soil-bound substance by plants is highly unlikely in these tests).

The PNEC derived from the soil data rather than the equilibrium partitioning method will be used in the risk characterisation.

3.2.3 Atmosphere

No biotic effects data are available.

Although volatilisation to the atmosphere from foams containing pentaBDPE is predicted, only very low concentrations in the atmosphere are expected. Removal is likely to be mainly via wet and dry deposition, although photodegradation may also occur to some extent. Thus, abiotic effects such as global warming, ozone depletion in the stratosphere and acidification are unlikely to occur.

Transport via the atmosphere could occur for this substance and may explain the widespread occurrence in the environment of the substance, particularly in areas remote from sources. Industry has indicated that there is a possibility that commercial pentaBDPE may have been used in hydraulic mining fluids (as a polychlorinated biphenyl replacement). If this use did occur it might account for some of the reported occurrences of the substance in remote areas (for instance, there are many mining areas situated in Sweden). However, after intensive investigation (KEMI, 1999b), this use has not been confirmed in the areas sampled and the use no longer occurs in the EU. Similarly, industry indicates that there is a possible (unconfirmed) use in completion fluids used in oil wells/drilling in the North Sea. Again, such a use could explain the occurrence of the substance in marine environments.

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

The information available, both from laboratory studies and monitoring data in the field, indicates that pentaBDPE has the potential to bioaccumulate in the environment.

No toxicity data are available for birds.

Based on the mammalian toxicity data (Chapter 4) the main effects of repeated dose exposure to pentaBDPE appear to be on the liver. The NOAEL level determined for these effects was 1 mg/kg bw/day in a 30 day study and this is the most sensitive toxicological end-point for pentaBDPE. In developmental toxicity studies no effects were seen on foetal development at doses of 200 mg/kg bw/day. Several studies have investigated certain polybrominated biphenyl ethers and metabolites for possible effects on the thyroid hormonal system. Some of these studies are summarised below, but a more detailed discussion in terms of effects on human health is given in Section 4.

In a recent (and ongoing) study certain lower brominated diphenyl ethers (including 4,4'-dibromodiphenyl ether; 2,4',6-tribromodiphenyl ether and 3,3',4,4'-tetrabromodiphenyl ether) have been shown to undergo competitive binding with thyroxin (T_4) to transtyretine (TTR) after metabolism using phenobarbital induced rat liver microsomes. No competitive binding of the parent brominated diphenyl ether was seen in the study, indicating that metabolites were responsible for the effects seen (Bergman et al, 1997b). Similar results were reported by Meerts et al (1998b), where 9 (including 2,2',4,4'-tetrabromodiphenyl ether and 2,2',4,4',6-pentabromodiphenyl ether) out of 17 di- to heptabrominated congeners tested were found to undergo strong (>60% inhibition) competitive binding, with 4 other congeners (including 2,2',3,4,4'-penta- and 2,2',4,4'5-pentabromodiphenyl ether) showing slight competitive binding, to human TTR after incubation with phenobarbital induced rat liver microsomes. No competitive binding was seen with any of the 17 parent congeners or by most of the 17 congeners after incubation with beta-naphthaflavone or clofibrate induced rat liver microsomes.

Another study has looked at the competitive effect of 2,2',4,4'-tetrabromodiphenyl ether on the binding of ^{125}I-thyroxin (T4) to brain chloroid plexus of male and female rats in both *in vivo* and in vitro experiments. In *in vitro* experiments, the tetrabromodiphenyl ether was found to have no inhibitory effect on the ^{125}I-T4 binding to site in chloroid plexus. However, chloroid plexus homogenate from animals dosed orally with 6 and 18 mg/kg body weight of 2,2'4,4'-tetrabromodiphenyl ether showed 80% and 63% respectively of the ^{125}I-T4 binding of controls. Competitive binding of hydroxylated metabolites of the tetrabromodiphenyl ether were thought to account for the reduction of ^{125}I-T4 binding seen (Sinjari et al, 1998).

In a further study using 2,2',4,4'-pentabromodiphenyl ether (Hallgren and Darnerud, 1998) a significant ($p<0.05$) reduction in plasma levels of free thyroxin when compared to controls was seen rats given a daily oral dose of 18 mg/kg body weight.

In addition, a significant induction of EROD (ethoxyresorufin-O-deethylase) activity, MROD (methoxyresorufin-O-deethylase) activity and PROD (pentoxyresorufin-O-deethylase) activity was seen at 6 and 18 mg/kg body weight/day doses.

The competitive binding seen with thyroxin indicates that metabolites of some of the lower brominated diphenyl ethers may have a potential to cause endocrine disturbing effects in wildlife (Bergman et al, 1997b). However, some of the studies have used compounds (or metabolites of compounds) that are not present in the commercial product, and there are insufficient data currently available to assess the significance of the effects in terms of the commercial pentaBDPE.

The $PNEC_{oral}$ will be estimated from the NOAEL of 1 mg/kg bw/day. Using the conversion factors given in Appendix VII to the Technical Guidance Document, this NOAEL is equivalent to a daily concentration in food of 10-20 mg/kg food.

According to the Technical Guidance Document, an assessment factor of 100 is appropriate for determining the PNEC from the results of a 30 day repeated dose study. However, this is the most sensitive toxicological end point seen in a range of repeated dose studies (no effects were seen on reproduction), and so an assessment factor of 10 may be more appropriate. Thus the $PNEC_{oral}$ is 1 mg/kg food. However, it should also be noted that the available mammalian data set may be inadequate to take into account possible effects from continuous long-term exposure (see also the Human Health assessment). In addition, it has also been reported that behavioural effects have been seen in mice exposed to 2,2',4,4',5-pentabromodiphenyl ether concentrations of 0.8 mg/kg body weight and above (using the conversion factors given in the Technical Guidance Document, this is equivalent to a dose of around 6.6 mg/kg food). The significance of these effects is uncertain.

Another area of concern with regard to secondary poisoning (and also direct toxicity) is the possible formation of brominated dibenzo-*p*-dioxins and dibenzofurans during combustion or other high temperature processes (e.g. incineration, landfill (where fires could occur) or accidental fires) involving articles containing pentaBDPE. The available information is discussed in Appendix A. The consequences are discussed qualitatively in the risk characterisation section.

3.3 RISK CHARACTERISATION

The principal PECs used for the following risk characterisation are those derived for the commercial product, as estimated in the previous sections of this report. However, commercial pentaBDPE is a mixture of congeners, each with slightly different physico-chemical properties. Appendix E considers the environmental modelling and PECs for each of the main components of the commercial product. The PECs arising from this congener-specific analysis, expressed as the sum of the individual component PECs, are also used in the following sections for comparison. These lead to conclusions similar to those based on the PECs for the commercial product itself.

The risk assessment considers releases of the substance from local point sources and also regional diffuse source releases occurring during the service life of the product (taking into account the possible amount of pentaBDPE present in finished articles in the EU - allowance is made for the fact that higher amounts of pentaBDPE may have been used in the EU in the past than at present, and polyurethane foam products containing pentaBDPE may be imported into - or exported from - the EU). At the regional level, releases to the environment are predicted to be dominated by volatilisation losses to the atmosphere from foam articles over their service life.

3.3.1 Aquatic compartment (including sediment)

3.3.1.1 Water

A $PNEC_{water}$ of 0.53 µg/l has been estimated. The resulting PEC/PNEC ratios are shown in **Table 3.43**.

Table 3.43 PEC/PNEC ratios for surface water

Scenario	PEC (µg/l)	PEC/PNEC
Polyurethane production	0.37	0.69
Regional sources	0.0015	0.003

The PEC/PNEC ratio is <1 for local release from polyurethane production and regional sources (this is also the case when the regional contribution from "waste remaining in the environment" is also taken into account; the $PEC_{regional}$ becomes 0.0053 µg/l and the PEC/PNEC becomes 0.01).

The PECs (sum of main components of the commercial formulation) estimated using the congener specific analysis given in Appendix E are 0.28 µg/l for the local concentration from polyurethane production and $2.6 \cdot 10^{-4}$ µg/l for the regional concentration. This leads to similar results to those shown in **Table 3.43**.

It should be noted that the $PEC_{regional}$ for water does not include any contribution from the products containing the substance after they have been disposed of in landfills, etc. Any emissions from this phase would lead to an increase in the $PEC_{regional}$. However, these potential emissions are likely to be mainly to the air due to volatilisation (e.g. in landfills the potential for leaching is probably low because the substance adsorbs strongly to soils and other organic matter), and so only a small proportion would be expected to reach surface water (in the regional model, surface water makes up only a small fraction (3%) of the total area available for wet or dry deposition from the atmosphere). Therefore, such releases would not be expected to increase the $PEC_{regional}$ for surface water to levels where the PEC/PNEC>1 and hence would probably not affect the conclusion with regard to surface water.

Result

For local and regional sources:

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

3.3.1.2 Sediment

For sediment, a $PNEC_{sed}$ of 0.31 mg/kg dry weight and a $PNEC_{sed(standard)}$ of 1.55 mg/kg dry weight have been determined. As these PNECs are based on actual sediment toxicity tests it is not necessary to increase the PEC/PNEC ratio by a factor of 10 to take into account possible uptake via ingestion of sediment, as would normally be applied to the equilibrium partitioning method for high log K_{ow} substances. The resulting PEC/PNEC ratios are shown in **Table 3.44**.

Table 3.44 PEC/PNEC ratios for sediment

Scenario	PEC		PEC/PNEC
	mg/kg wet weight	mg/kg dry weight	
Polyurethane production	4.5 (predicted)	11.7 (predicted)	37.7[a] or 7.5[b]
	0.54 (measured)	1.4 (measured)	4.5[a] or 0.9[b]
Regional sources	0.033 (predicted)	0.084 (predicted)	0.3[a] or 0.05[b]
	0.050 (measured)	0.13 (measured)	0.42[a] or 0.08[b]

[a]Based on $PNEC_{sed}$ estimated directly from sediment tests
[b]Based on $PNEC_{sed(standard)}$, normalised to the organic carbon content given in the TGD

The PEC/PNEC ratios indicate concern based on the predicted and measured concentrations at the local level for polyurethane production.

The PECs (sum of main components of the commercial formulation) estimated using the congener specific analysis given in Appendix E are 5.3 mg/kg wet weight for the local concentration from polyurethane production and 0.01 mg/kg wet weight for the regional concentration. This leads to similar results to those shown in **Table 3.44**.

When the regional contribution from "waste remaining in the environment" is considered the regional PEC would increase to 0.114 mg/kg wet weight (= 0.30 mg/kg dry weight). This would still lead to a PEC/PNEC <1 for regional sources.

As indicated in Section 3.3.1.1, the $PEC_{regional}$ for water, and hence sediment, does not include any contribution from the products containing the substance after they have been disposed of in landfills, etc. For sediment, a similar argument as for surface water could also apply, but in this case there are also monitoring data available (which will include contributions from all sources, including disposal) which are consistent with the estimated PECs. It is possible that in the long term levels in sediment may build up as a result of releases from waste sites. This could be considered further in any future revision of this risk assessment report.

Result

For regional sources:

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

For local sources (polyurethane foam production):

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

3.3.1.3 Sewage treatment processes

It is not possible to carry out the PEC/PNEC comparison for sewage microorganisms since no toxicity data are available.

Result

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

There is a data gap for toxicity to sewage microorganisms. However, a risk reduction strategy has been developed which proposes a restriction on the marketing and use of pentaBDPE under Directive 76/769/EEC. If this strategy is adopted, then this testing requirement should be adjourned unless expert advice is provided which indicates that a test may be relevant to the controls which emerge from negotiations under Directive 76/769/EEC. A test on sewage treatment plant microorganisms would be required if this data gap were to be filled.

3.3.2 Terrestrial compartment

A $PNEC_{soil(standard)}$ of 0.38 mg/kg dry weight has been estimated for pentaBDPE. As this PNEC is based on actual terrestrial toxicity tests it is not necessary to increase the PEC/PNEC ratio by a factor of 10 to take into account possible uptake via ingestion of soil, as would normally be applied to equilibrium partitioning method for high log K_{ow} substances. The estimated PECs and the resulting PEC/PNEC ratios for agricultural soil (averaged over 30 days) are shown in **Table 3.45**.

Table 3.45 PEC/PNEC ratios for soil

Scenario	PEC		PEC/PNEC
	mg/kg wet weight	mg/kg dry weight	
Polyurethane production	2.68	3.03	7.1
Regional sources	0.13	0.15	0.39

For local sources (polyurethane production), the PEC/PNEC ratio is >1. The PNEC used is based on an assessment factor of 50 and so could in theory be refined further. However, the lowest assessment factor that can be used is 10, and even if this was used on the currently available data set, the PEC/PNEC would still be >1 for this endpoint. Therefore a risk to the environment from local sources is concluded.

For the regional compartment, the PEC/PNEC is <1. When the regional contribution from "waste remaining in the environment" is included the PEC becomes 0.168 mg/kg wet weight (= 0.19 mg/kg dry weight) for agricultural soil and 2.27 mg/kg wet weight (= 2.6 mg/kg dry weight) for industrial/urban soil. The resulting PEC/PNEC is <1 for agricultural soil, but would be >1 for industrial/urban soil. As there are a large number of uncertainties involved in the estimation and modelling of the "waste remaining in the environment", the result for the regional industrial/urban soil compartment is on its own not sufficient to recommend risk reduction measures, but is supportive of the conclusion to recommend risk reduction measures at a regional level as part of the secondary poisoning risk characterisation (see Section 3.3.4).

At the local level, the main source of pentaBDPE on soil is predicted to be from application of sewage sludge. At a regional level, volatilisation of pentaBDPE from foams and subsequent deposition is predicted to be an important route to soil. The concentrations predicted at the local level assume 10 years continuous application of sewage sludge. However, since pentaBDPE is a persistent substance, concentrations in soil could build up over longer periods. The percentage of the steady-state concentration estimated after 10 years continuous application is around 0.6-0.9%. This provides further support for the conclusion of a risk from local sources.

The PECs (sum of main components of the commercial formulation) estimated using the congener specific analysis given in Appendix E are 2.5 mg/kg wet weight for the local concentration from polyurethane production and 0.028 mg/kg wet weight for the regional concentration. This leads to similar results to that shown in **Table 3.45**.

It should be noted that the $PEC_{regional}$ for soil does not include any contribution from the products containing the substance after they have been disposed of in landfills, etc. These potential emissions are likely to be mainly to the air due to volatilisation (e.g. in landfills the potential for leaching is probably low because the substance adsorbs strongly to soils and other organic matter), so a significant proportion could be expected to reach soil by wet or dry deposition (in the regional model, soil makes up a major fraction (60% for natural soil; 27% for agricultural soil) of the total area available for wet or dry deposition from the atmosphere). Therefore, such releases could lead to an increase in the $PEC_{regional}$ for soil. It is not currently possible to quantify this possible increase. It is also possible that in the long term levels may increase as a result of releases from waste sites. This could be considered further in any future revision of this risk assessment report.

Result

For local sources (polyurethane foam production):

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

For regional sources:

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

3.3.3 Atmosphere

Very low concentrations of pentaBDPE (≤35 ng/m^3) are predicted for the atmospheric compartment. Removal is likely to be mainly via wet and dry deposition, although photodegradation may also occur to some extent. Thus, pentaBDPE can be considered to present a negligible risk of adding to effects such as global warming, ozone depletion in the stratosphere and acidification.

In view of its properties, transport via the atmosphere could occur for this substance and may explain its widespread occurrence in the environment, particularly in areas remote from sources. Industry has suggested that there is a possibility that commercial pentaBDPE may have been used in hydraulic mining fluids (as a polychlorinated biphenyl replacement). If this

use did occur it might account for some of the reported occurrences of the substance in remote areas (for instance, there are many mining areas situated in Sweden). However, after intensive investigation (KEMI, 1999b), this use has not been confirmed in the areas sampled and the use does not currently occur in the EU, so this explanation is at best speculative. Similarly, industry indicates that there is a possible (unconfirmed) use in completion fluids used in oil wells/drilling in the North Sea. Again, such a use could explain the occurrence of the substance in marine environments, although this is also speculative. Such speculation can not be considered further without substantiation.

A further contribution to the atmospheric levels could come from the disposal phase of products containing the substance. It is not currently possible to quantify this contribution, but it is considered unlikely that it would raise the concentrations predicted in air to levels where effects may be expected to occur. This is also supported by the available monitoring data which, although limited, indicates that the concentrations of this substance in air are low. Nevertheless, the possible long-term increase in levels as a result of releases from waste sites could be considered further in any future revision of this risk assessment report.

Result

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

Although not a formal conclusion of this risk assessment report, the properties of the substance and evidence of long-range transport indicate that it may need to be considered further by other regulatory bodies dealing with persistent organic pollutants (POPs) which may be transported long distances in the atmosphere.

3.3.4 Non-compartment specific effects relevant for the food chain (secondary poisoning)

A $PNEC_{oral}$ for secondary poisoning of 1 mg/kg food has been determined. The resulting PEC/PNEC ratios are shown in **Table 3.46**.

Table 3.46 PEC/PNEC ratios for secondary poisoning

Scenario	PEC (mg/kg wet weight)	PEC/PNEC
Fish-based food chain	2.2 [a] or 4.2 [b] (estimated)	2.2 [a] or 4.2 [b]
	1.38 (measured)	1.4
Earthworm-based food chain	18 (estimated)	18

[a] With a BCF of 14,350 l/kg
[b] With a BCF of 27,400 l/kg (see section 3.1.4.1)

The PEC/PNEC ratios indicate a concern for secondary poisoning of predators from eating fish and earthworms. The estimated PEC is calculated assuming half of the dose comes from local sources and half from regional sources (in accordance with the TGD). For the fish route, the PEC is consistent with measured levels found in the environment in industrialised areas. The predicted regional level in fish is 0.022-0.041 mg/kg wet weight and is similar to the levels found in fish in several parts of Europe. The PEC/PNEC ratio for this concentration is 0.022-0.041. This indicates that the concern for the fish-based food chain arises due to local exposure from polyurethane production sites.

For earthworms, the predicted regional concentration is around 1.7 mg/kg wet weight. The PEC/PNEC ratio for this concentration is 1.7. Atmospheric emissions of pentaBDPE from diffuse sources are predicted to make a major contribution to the levels in soil and hence earthworms at the regional level. Since the regional earthworm concentration also takes into account the possible build-up of the substance in soil over time, it can be concluded that widespread release of the substance from manufacture of foam and over the lifetime of the foam may lead to a risk of secondary poisoning. However it should also be noted that there is some uncertainty over the PEC for earthworms because the QSAR used in its determination may not be valid for substances with very high log K_{ow} values.

The above calculations do not include the regional contribution from "waste remaining in the environment". When this is taken into account the prediction regional concentration in earthworms is around 2.14 mg/kg wet weight and that of fish is 0.076-0.145 mg/kg wet weight. This leads to similar conclusions as above.

The PECs (sum of main components of the commercial formulation) estimated using the congener specific analysis given in Appendix E are 1.5-3.1 mg/kg for fish and 8.2 mg/kg for earthworm. This leads to similar results to those shown in **Table 3.46**. The measured data indicate that components of commercial pentaBDPE are widely distributed in the environment, and may be transported long distances from sources of release, possibly by atmospheric transport. It should be noted that the estimate of regional emissions to the environment does not include any contribution from the disposal phase of products containing the substance. Any emissions from this phase would lead to an increase in the concentrations estimated in biota at the regional level. These potential emissions are likely to be mainly to the air, but a significant proportion could be expected to reach soil or water (particularly the marine environment) by wet or dry deposition. It is not currently possible to quantify this increase, but these considerations do provide further support for a PEC/PNEC>1 at the regional level. It is also possible that in the long term levels may increase as a result of releases from waste sites. This could be considered further in any future revision of this risk assessment report.

The available laboratory studies and field measurements indicate that components of commercial pentaBDPE can accumulate through the food chain. For example, levels have recently been measured in marine predators such as dolphins, seals and birds that are higher than fish from the same area, indicating that accumulation through the food chain may be occurring. Bioaccumulation may lead to rises in tissue levels over a life-time of exposure. In addition, read-across from the existing mammalian data set is uncertain for these types of species, and may not be sufficient to take into account possible effects arising from continuous exposure to the substance over many years. Whilst the currently available information does not necessarily mean that these organisms are currently at risk of poisoning, the uncertainties mean that these findings are of concern. Future rises in tissue concentrations in terms of life-time exposure could be considered further in any future revision of this risk assessment report.

Result

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

This applies to use of the substance in polyurethane foams. High concentrations of pentaBDPE are predicted in and have been measured in fish and earthworms close to sources

of release. These result in a PEC/PNEC >1 and hence a risk of secondary poisoning of predators that is linked to local releases from foam production sites. A possible risk of secondary poisoning has also been identified at the regional level (linked to diffuse releases arising from use of the foam) for the earthworm-based food chain. In addition, the substance appears to be transported widely in the environment and accumulate through the food chain. Widespread diffuse source releases of the substance could therefore also lead to a build up in the environment and organisms over time. These additional factors, whilst not necessarily indicating a risk as such, lend support to the overall concern for this end-point.

3.3.5 Risks from breakdown/transformation products

Another area of potential environmental concern for both direct toxicity and secondary poisoning is the possible formation of brominated dibenzo-*p*-dioxins and dibenzofurans from articles containing the substance during combustion or other high temperature processes (e.g. incineration, landfill (where fires could occur) or accidental fires) (discussed in Appendix A). Recycling of polyurethane foam containing the substance is not thought to contribute to brominated dibenzo-*p*-dioxin or dibenzofuran formation due to the low temperatures involved.

Regulations on the design of municipal incinerators require a minimum incineration temperature of 850^{o}C for 2 seconds (EEC, 1989a and 1989b). Draft proposals for hazardous waste incinerators require a minimum temperature of 1,000^{o}C. From the information given in Appendix A, it can be seen that a combustion temperature of 850^{o}C is adequate to minimise the formation of brominated dibenzofurans and dibenzo-*p*-dioxins during incineration/pyrolysis of pentaBDPE in the laboratory. Proper incinerator design should therefore reduce the risk from any possible formation of brominated dibenzofurans and dibenzo-*p*-dioxins.

For example, in the United Kingdom, incineration processes are covered under the Environmental Protection Act (1990). Under Part 1 of the Act, two separate pollution control regimes were established under which specified industrial processes must apply for authorisation to operate: Integrated Pollution Control (IPC), regulated by the Environment Agency (formerly HMIP), and Local Authority Air Pollution Control (LAAPC), regulated by the local authorities.

Under LAAPC, existing general waste incineration processes under 1 tonne/hour should be subjected to an emission standard for chlorinated dioxins of 1.0 ng TEQ/m^3 by June 2000. Until then, such incinerators should have secondary combustion zone temperatures and residence times of 850^{o}C and 2 seconds. New general waste incinerators should have met the 1.0 ng TEQ/m^3 limit from September 1995. Under IPC, municipal solid waste (MSW) incinerators and other specified scheduled processes will have to conform to an emission standard for chlorinated dioxins of 1.0 ng TEQ/m^3, with a guide value of 0.1 ng TEQ/m^3. All new plants will have to conform to this standard, with existing plants required to meet this standard over various time scales, extending to the year 2000. It is estimated that chlorinated dioxin emissions from these processes should be reduced by 90%. Given the similarities between chlorinated and brominated dioxins and furans, the abatement technologies employed for chlorinated dioxins and furans should also be effective in limiting the risk from brominated analogues. In the case of accidental fires, given the large amounts of toxic products known to be formed - notably chlorinated dibenzo-*p*-dioxins and dibenzofurans - the presence of pentaBDPE in fires is unlikely to significantly affect the total release of toxic products from fires.

In summary, it can be concluded that pentaBDPE, as a source of bromine, can contribute to the formation of halogenated dibenzo-*p*-dioxins and furans generated during combustion

processes. Formation of these compounds in some of these processes is well known and emission control technology is available for incinerators that can reduce emissions to acceptable levels. Although incineration could take place at installations without suitable emission reduction equipment, it should be noted that in most situations pentaBDPE is unlikely to be the only source of halogenated dioxins/furans, and it is also not possible to quantify the amounts formed or assess their environmental significance. Emission control technology cannot be applied to accidental landfill or other fires.

3.3.6 Areas of uncertainty in the environmental risk assessment

There are uncertainties in the release estimates used in this assessment. This is because there is a general lack of information on the actual releases of the substance from its various lifecycle stages. As a result the assessment is based on "realistic worst case" estimates, using the best available information and estimation methods. These estimates are conservative but are in general supported by the available monitoring data. The main areas of uncertainty in these estimates arise from:

- the emission factors based on default values or extrapolated from other substances rather than from direct measurements;
- unknown amounts of substance imported into the EU in finished polyurethane articles;
- unknown long term trend in usage; and
- the applicability of some of the models used (for example, the earthworm uptake model and the root crop uptake model).

The main use of pentaBDPE in the EU is in polyurethane foams. There is some evidence (see Section 2.2.2.3) that it may be present in other polymeric materials, and there may have been other historical uses. Such articles may also be imported into the EU, and the actual amount of substance involved is unknown. A quantitative risk assessment for these potential uses is therefore not possible, but any emissions of the substance from these products could contribute to the regional diffuse emissions, and hence regional concentrations (see Section 3.1.0.2.5).

Regional emissions to the environment from the disposal phase of products containing the substance, for example from landfills and incinerators, are difficult to quantify and are not currently included in the PEC estimates (their contribution has been considered in a qualitative way). It is possible that in the long term levels may increase as a result of releases from waste sites. The implications of the presence of the substance in the tissues of higher organisms are also uncertain, especially in the context of future rises in tissue concentrations in terms of life-time exposure.

Finally, the risk to sewage treatment plant is unknown. The proposed risk reduction strategy recommends a restriction on the marketing and use of pentaBDPE under Directive 76/769/EEC. If this strategy is adopted, then the testing needed to address this issue will be adjourned unless expert advice is provided which indicates that a test may be relevant to the controls which emerge from negotiations under Directive 76/769/EEC.

4 HUMAN HEALTH

4.1 HUMAN HEALTH (TOXICITY)

4.1.1 Exposure assessment

4.1.1.1 Occupational Exposure

4.1.1.1.1 General discussion

Definitions and limitations

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

The sections entitled occupational exposure (inhalation) and occupational exposure (dermal) present exposure data predicted from the EASE (Estimation and Assessment of Substance Exposure) model. EASE is a general purpose predictive model for workplace exposure assessments. It is an electronic, knowledge based, expert system which is used where measured exposure data is limited or not available. The model is in widespread use across the European Union for the occupational exposure assessment of new and existing substances.

All models are based upon assumptions. Their outputs are at best approximate and may be wrong. EASE is only intended to give generalised exposure data and works best in an exposure assessment when the relevance of the modelled data can be compared with and evaluated against measured data. Dermal exposure is assessed by EASE as potential exposure rate predominantly to the hands and forearms (approximately 2000 cm^2).

Overview of exposure

PentaBDPE is a viscous liquid with a very low vapour pressure ($7.5 \cdot 10^{-5}$ Pa at 25°C), and a calculated saturated vapour concentration (SVC) of $7 \cdot 10^{-4}$ ppm at 25 °C. Therefore exposure to the vapour will not exceed $7 \cdot 10^{-4}$ ppm at ambient temperature. Since there is only exposure to the vapour this prediction will be applicable to all scenarios (i.e. the SVC is the maximum concentration achievable whatever the scenario). Where pentaBDPE is heated the vapour pressure will rise with a concomitant increase in the SVC. Increases in temperature may lead to some increase in volatilisation of pentaBDPE, however, this vapour will quickly condense to form a mist. The only scenario where this is likely is the exothermic generation of polyurethane foam, where the mist forms as the hot vapour cools. This hot fume/mist may also include other contaminants, such as isocyanates. It is reasonable to assume that companies will seek to reduce these releases irrespective of the presence of pentaBDPE vapour and mist. Therefore exhaust ventilation, which will in most cases be a ventilated enclosure, is assumed to be the minimum standard of control for this industry.

The number of workers exposed was not established through industry contacts. As the use of flame retardant polyurethane foams is extensive, the number of workers exposed to pentaBDPE could potentially be equally extensive. However, as there are many other flame retardants available only a proportion will be exposed to those containing pentaBDPE. It is estimated that the number of workers exposed to materials containing pentaBDPE could be several thousand.

Occupational exposure limits

There are no occupational exposure limits for pentaBDPE.

4.1.1.1.2 Occupational exposure to pentaBDPE

Occupational exposure to pentaBDPE may occur during the production of polyurethane foams and subsequent equipment manufacture.

Brief descriptions of the processes and sources of occupational exposure are discussed below for each industry followed by a general discussion of typical exposure levels.

During the manufacture of polyurethane foam

The manufacture of polyurethane foam involves the delivery of components to the mixer head, where they are mixed and charged to a mould or conveyor. The subsequent exothermic reaction may result in the release of "free" isocyanates and other components (including pentaBDPE) to the workplace air. The release of contaminants to the workplace air is generally mitigated by the use of local exhaust ventilation (LEV) and enclosures. The manufacture of slabstock polyurethane foam, for the upholstery industry, is carried out using a ventilated tunnel. The polyurethane foam expands to the confines of this tunnel during the reaction. During subsequent handling of the polyurethane foam workers may again be exposed as the warm foam cools, and thus continues to release contaminants to the workplace.

The manufacture of articles from polyurethane foam containing pentaBDPE

The fire retardant agent is physically bound within the polymer matrix and not chemically bound. Therefore, pentaBDPE could theoretically migrate from the polyurethane foam. Clearly the polyurethane foam will only be effective as long as the fire retardant agent is present and thus migration during the handling of polyurethane foam is considered to be unlikely. Where companies carry out hot wire cutting of polyurethane foam there is the potential for the release of pentaBDPE, however, emissions are likely to be controlled using LEV. This is again to primarily control releases of "free" isocyanate.

Occupational exposure (inhalation)

The number of workers exposed was not established through industry contacts. As the use of flame retardant polyurethane foams is extensive, the number of workers exposed to pentaBDPE could potentially be equally extensive. However, as there are many other flame retardants available only a proportion will be exposed to those containing pentaBDPE. It is estimated that the number of workers exposed to materials containing pentaBDPE could be several thousand.

During pentaBDPE's use in the polyurethane foam industry operators may be exposed to pentaBDPE during activities such as:

(a) charging vessels;
(b) blending;
(c) releases during the production of polyurethane foam;
(d) cleaning; and
(e) maintenance.

HSE has no occupational exposure data for pentaBDPE on its National Exposure Database (NEDB), and no data were received from industry. Although no exposure data were received, there are a number of points that can be considered to gain an understanding of the degree of occupational exposure to pentaBDPE.

(a) For pentaBDPE, an exposure range of 0 to 0.1 ppm was predicted using EASE. This exposure range is valid for any scenario at ambient temperature where no mist is generated. This is the lowest range available in EASE. However, pentaBDPE has a vapour pressure of $7.5 \cdot 10^{-5}$ Pa at 25 °C and a calculated SVC of $7 \cdot 10^{-4}$ ppm at 25°C. Occupational exposure to vapour from pentaBDPE will therefore not exceed $7 \cdot 10^{-4}$ ppm at 25°C, and in reality will be far below this value.

(b) The polyurethane foam industry use other chemicals that require a greater standard of control, for example aluminium trioxide and isocyanates.

(c) Where pentaBDPE is heated the vapour pressure will rise with a concomitant increase in the SVC. This may occur during the exothermic formation of polyurethane foam. Although increases in temperature may lead to increases in volatilisation of pentaBDPE, this will quickly condense and form a mist. Exposure to this mist is therefore only likely to occur in any situation where pentaBDPE or materials containing pentaBDPE are heated and the resulting mist is not controlled. The only scenario where mist generation is likely is the exothermic generation of polyurethane foam, where the mist forms as the hot vapour cools. Emissions released during the formation of polyurethane foam are controlled to minimise the release of other materials into the workplace, for example, isocyanates. This control will generally comprise of a ventilated hood or tunnel. It seems reasonable to assume that companies will seek to reduce these releases irrespective of the presence of pentaBDPE vapour and mist. Therefore exhaust ventilation, which will in most cases be a ventilated enclosure, is assumed to be the minimum standard of control for this industry. It is considered extremely unlikely that workers will enter enclosures when mist is present (i.e. when the process is running or just stopped). The atmosphere would be extremely noxious with poor visibility, and the area would probably be so confined as to warrant further considerations to prevent immediate danger to life. There is also very little maintainable plant inside tunnels/ enclosures that would require such work. This exposure scenario can therefore be discounted.

In conclusion, exposure to pentaBDPE vapour at ambient temperatures is unlikely to exceed the SVC of $7 \cdot 10^{-4}$ ppm at 25°C, and where it is heated controls are likely to be in place to reduce any possibility of exposure. During the manufacture of articles from polyurethane foam containing pentaBDPE exposure will be significantly lower than industries using pentaBDPE itself. Since exposure to the mist is not thought to be significant and therefore there is only exposure to vapour the exposure assessment addressed the issues as one, since

the exposure predictions hold for all scenarios. These predictions also hold irrespective of the duration and frequency of exposure which may range from minutes to full shift.

Dermal exposure

Dermal exposure may occur during the handling of receptacles containing pentaBDPE, and when coming in to contact with vessels and surfaces that have become contaminated from spillages. As a result of the low volatility of pentaBDPE, surfaces are unlikely to be contaminated from condensed vapour.

The EASE scenario which best matches industrial practice is non-dispersive use with intermittent contact (two to ten contacts a shift). This results in an exposure range of 0.1 to 1 mg/cm^2/day. However, for most tasks operators will be handling formulations with relatively low concentrations of pentaBDPE and exposure will be at the bottom of the above exposure range.

Dermal exposure may also occur when operators handle polyurethane foam containing pentaBDPE. This contact will be constant and thus predicted using EASE to be 1 to 5 mg/cm^2/day. However exposure is likely to be very low and in any case below this range as there will only be very low levels of pentaBDPE at the surface of the polyurethane foam.

4.1.1.2 Consumer Exposure

The current use pattern provided by Industry is that pentaBDPE is only used in polyurethane foam and that consumers do not come into direct contact with these foams. The foam is only used in ways in which it is enclosed and therefore it is concluded that exposure to consumers is negligible.

Use of pentaBDPE for textile applications no longer occurs in the EU.

4.1.1.3 Indirect exposure via the environment

The exposure of man to pentaBDPE via environmental routes has been estimated using EUSES (see Appendix B). The results are reported in Section 3.1.4 and are reproduced again in **Table 4.1**.

Table 4.1 Estimated daily human intake for exposure of man via environmental routes

Scenario	Route	Predicted concentration	Estimated daily dose (mg/kg bw/day)
Local – polyurethane foam production	Wet fish	4.38 mg/kg wet wt[a] or 8.36 mg/kg wet wt[b]	$7.2 \cdot 10^{-3}$ [a] or 0.014[b]
	Root tissue of plants	6.78 mg/kg	0.037
	Leaves of plants	0.0305 mg/kg	$5.2 \cdot 10^{-4}$
	Drinking water	$2.72 \cdot 10^{-4}$ mg/kg	$7.8 \cdot 10^{-6}$
	Meat	0.208 mg/kg	$9.0 \cdot 10^{-4}$
	Milk	0.066 mg/kg	$5.3 \cdot 10^{-4}$
	Air	28.3 ng/m^3	$6.1 \cdot 10^{-6}$
	Total local daily dose		0.046[a] - 0.053[b]
Regional sources	Wet fish	0.022 mg/kg wet wt[a] or 0.041 mg/kg wet wt[b]	$3.6 \cdot 10^{-5}$ [a] or $6.8 \cdot 10^{-5}$ [b]
	Root crops	0.335 mg/kg	$1.8 \cdot 10^{-3}$
	Leaf crops	$2.9 \cdot 10^{-4}$ mg/kg	$5.0 \cdot 10^{-6}$
	Drinking water	$1.35 \cdot 10^{-5}$ mg/kg	$3.9 \cdot 10^{-7}$
	Meat	$6.9 \cdot 10^{-3}$ mg/kg	$2.8 \cdot 10^{-5}$
	Milk	$2.06 \cdot 10^{-3}$ mg/kg	$1.7 \cdot 10^{-5}$
	Air	0.27 ng/m^3	$5.8 \cdot 10^{-8}$
	Total regional dose		$1.9 \cdot 10^{-3}$ [a] $2.0 \cdot 10^{-3}$ [b]

[a]Fish BCF = 14.350 l/kg
[b]Fish BCF = 27 400 l/kg

The daily human intake of pentaBDPE through environmental routes is estimated as:

Local (polyurethane foam production)	0.046-0.053 mg/kg bw/day
Regional sources	$1.9 \cdot 10^{-3}$ - $2.0 \cdot 10^{-3}$ mg/kg bw/day

Since commercial pentaBDPE is a mixture of components, it would be expected that the environmental behaviour and uptake for each component will be slightly different. In order to take this into account, the environmental modelling using EUSES was carried out individually for each component of the commercial formulation and the results summed to give an estimate for the commercial formulation. This is reported in Appendix E. Using this approach, the following total daily human intake figures from food were estimated:

Local (polyurethane foam production)	0.043-0.048 mg/kg bw/day
Regional sources	$7.3 \cdot 10^{-4}$ - $7.9 \cdot 10^{-4}$ mg/kg bw/day

These combined values derived from the individual components are very similar to the values obtained above, based on the commercial formulation.

In all cases, the majority of the total daily intake arises from the predicted concentrations in root crops. No measured data are available on the concentrations of pentaBDPE in root crops or indeed soil from which uptake could occur, and so it is not possible to comment on the

validity of these figures. Further information on the amounts of pentaBDPE that reach agricultural land (via sewage sludge or atmospheric deposition) would be useful in this respect.

There are extensive measurements of pentaBDPE in fish (see Section 3.1.4.3) and the concentrations estimated in the various scenarios appear to be reasonably consistent with the levels found in industrial areas.

In human samples, the levels of the various components of commercial pentaBDPE have been measured in many samples of adipose tissue and milk. The levels found, when expressed on a lipid weight basis show a remarkably consistent picture between the various surveys and samples (the levels in milk and adipose tissue are similar), with the levels generally being about 2-4 µg/kg lipid in both milk and adipose tissue with up to about 100 µg/kg lipid in adipose tissue and 11 µg/kg lipid in human milk being measured in some samples. The dominant congener found in the surveys is 2,2,4,4'-tetrabromobiphenyl ether (typically about 60-70% of the total), which is consistent with the pattern of bioaccumulation found in laboratory experiments and the environmental monitoring data. The time trend data indicate that the levels in human tissue have increased markedly over the period 1972-1997 and may still be increasing (see Section 3.1.4.3).

These measured data show that commercial pentaBDPE is entering the human food chain. Given that the elimination half-life from adipose tissue in experimental animals is around 25-47 days (see Section 4.1.2.1.2), then the daily intake from environmental routes that gives the above body burdens can be estimated as:

Measured concentration in adipose tissue	= 100 µg/kg lipid
Typical lipid concentration in humans	= 20% by weight (to convert to a body weight basis)
Measured concentration in humans	= 20 µg/kg bodyweight
Elimination half-life	= 25-47 days
Rate constant for elimination	= 0.0147-0.0277 day^{-1}
At equilibrium, rate of intake	= rate of elimination
X µg/kg body weight/day	= $20 \cdot 0.0147$ or $20 \cdot 0.0277$

Therefore the daily intake from food to give an approximated concentration in human adipose tissue of 100 µg/kg lipid is about 0.3-0.6 µg/kg bw/day. This is slightly lower than, but in reasonable agreement with, the figures estimated above for the regional daily intake from food.

4.1.1.4 Combined exposure

Exposure from occupational and environmental sources can be combined to give the daily body burden as shown in **Table 4.2**. Values have been calculated for based on the local scenario for exposure via the environment since this is much greater than that for regional sources. Body burdens following occupational exposure are estimated in section 4.1.3.1 (summarised in **Table 4.3**). For combined exposure it is the occupational exposure that is predominant. Consumer exposure is negligible and therefore does not contribute to the combined exposure. These estimates do not take account of bioaccumulation.

Table 4.2 Combined exposure to pentaBDPE

	Exposure (mg/kg/day)
Workers	2.02
Consumers	negligible
Man via Environment	0.048
Total (based on local environmental exposure)	2.068

The total combined exposure will be taken forward to the risk characterisation (section 4.1.3.4).

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

As stated in section 1.1 the typical manufactured material referred to as pentaBDPE contains a mixture of tetra, penta and hexabrominated diphenyl ethers, of which approximately 50-62% consists of pentabrominated isomers. In most cases the available toxicity studies have been conducted with this commercial mixture, and there are few studies in which a "purified" sample of pentaBDPE has been tested. These are indicated by the specific congener number. Within this section, the trade name of the commercial pentaBDPE preparation tested is given if known, otherwise the material tested is referred to as pentaBDPE.

There are no data on the toxicological effects of pentaBDPE in humans. In reviewing pentaBDPE, the Technical Meeting (TM) noted similarities between this substance and other substances found in the environment which have been cause for concern, such as PCBs, dioxins and PBBs. The structural and physico-chemical similarities were noted between these substances and pentaBDPE. From the available toxicological information, the TM also noted the similarity in aspects of the toxicity expressed, for example effects on the thyroid, the “chloracne-like” response and, in the view of some Member States’ national experts, effects on neurobehavioural development. Although the TM noted these similarities, they also acknowledged that the current risk assessment review related specifically to pentaBDPE and that it was not appropriate to include a detailed comparison of the toxicology of these other substances, although the similarities are taken into account in the risk characterisation.

4.1.2.1 Toxicokinetics

4.1.2.1.1 Studies *In Vitro*

In a study primarily designed to investigate the binding of polyBDE-OH metabolites to human transthyretin (T_4-TTr) groups of Wistar rats were pre-treated with stimulants of hepatic xenobiotic metabolism (Meerts 1998). One day post pre-treatment animals were sacrificed, the livers excised and hepatic microsomes prepared. The microsomes were subsequently incubated *in vitro* with 1 of 2 pure congeners of pentaBDPE (BDE-47 or BDE-99) (concentration not reported) in the presence of NADPH for 30 minutes. The microsomes suspension was then used in T_4-TTr competion binding studies. The limited results presented (qualitative tabulated information only) indicate that both BDE-47 and BDE-99 inhibit T_4-TTr binding in penobarbitol induced microsomes by ~60 and 20%, respectively suggesting that the parent molecule may be metabolised to hydroxylated metabolites.

4.1.2.1.2 Studies in animals

There are no quantitative data concerning the rate or extent of absorption of pentaBDPE by any route of exposure. However, data for other structurally similar polyhalogenated diaromatics which have similar physico-chemical characteristics, such as the penta and hexa brominated biphenyls (PBBs) and the penta and hexa chlorinated biphenyls (PCBs), demonstrate that 70 - 90 % absorption occurs following oral dosing (Fries, 1987; IARC 1986).

In relation to the potential for absorption following inhalation exposure, few data were available on structurally similar substances on which to draw conclusions. However, toxicity results in animals following inhalation exposure to PCBs suggest they are well absorbed via this route (Agency for Toxic Substance and Disease Registry (ATSDR), 1989; US EPA, 1988b). Furthermore, a study in guinea pigs showed that PCBs are well absorbed across the skin, with up to 56% of a dermally applied dose being absorbed (Wester et al, 1983).

Overall, although there are no actual quantitative data for pentaBDPE, it is concluded that it is likely to be well absorbed by all routes of exposure.

Inhalation

No data are available.

Oral

Male and female rats were given a single oral dose of 300 mg/kg Bromkal 70 in peanut oil (von-Meyerinck *et al* 1990). Control groups were given vehicle only. Groups of 4 rats of either sex were sacrificed at weekly intervals up to 10 weeks post-dosing for HPLC and GC/MS analysis of the brominated diphenyl ether content of perirenal fat. The results showed the presence of two isomers of pentaBPDE in the perirenal fat, pentaBDPE$_1$ and pentaBDPE$_2$, in addition to tetra- and hexabromodiphenyl ethers. The half-lives of elimination of the pentaBDPE isomers ranged from 25 - 47 days in males and females respectively. These results provide evidence that pentaBDPE is absorbed across the GI tract with subsequent distribution to adipose tissue from where it is slowly eliminated. It was not possible from the results in the report to determine the percentage absorption of pentaBDPE across the GI tract. Preferential distribution to fatty tissue would be predicted from the very high Log $P_{o/w}$ values for pentaBDPE.

Groups of 5 male and 5 female CD rats were given 0, 100 or 1000 ppm of pentaBDPE in the diet (approximately equivalent to 0, 8 or 80 mg/kg/day), for 28 days (Great Lakes Chemical Corporation, 1976a). Neutron activation analysis of the bromine content of the livers indicated 6 and 30-fold increases, for the low and top dose groups of both sexes, respectively, compared with the controls. The detection of bromine represents a marker for the presence of pentaBDPE and/or its metabolites. This study provides evidence for the absorption of pentaBDPE via the GI tract.

Groups of 5 male and 5 female Sprague-Dawley rats were administered daily dietary doses of pentaBDPE ranging from 0 to 100 mg/kg/day in corn oil, for 30 or 90 days (Great Lakes Chemical Corporation, 1985 and 1984). Bromine levels were measured in the liver and

thyroid gland, in both studies and also in the thymus, lungs and kidney in the 90-day study. Levels were increased in all tissues examined in both sexes at week 4 of treatment.

In the 30-day study, bromine levels in both liver and thyroid gland had returned to control values at the end of the 6 week recovery period. In the 90-day study bromine levels in all tissues examined showed a decreasing trend over the recovery period but were still slightly elevated at the end of a 24 week recovery period. The slow decline of bromine (indicative of the presence of parent pentaBDPE and/or its metabolites) in the tissues suggests a capacity for bioaccumulation with repeated exposure. In these studies the nature of the bromine detected was not characterised. However, as free bromine is water soluble, it can be assumed that the tissue detection of bromine represents the presence of a larger molecule, but it is unknown if this is the parent molecule or a metabolite.

Groups of 6 conventional and 6 bile-cannulated Sprague-Dawley rats were administered a single oral dose of 2.2 mg/rat 2,2',4,4',5-[^{14}C]pentaBDPE (BDE-99) in peanut oil (Hakk *et al* 1999). Urine, faeces and bile (from cannulated animals) were collected at 24 hour intervals over a 72 hour period post-dosing. At 72 hours post-dosing animals were sacrificed and liver, kidneys, GI tract, heart, testes, epididymal adipose tissue, adrenals, lungs thymus and blood excised for analysis. The level and nature of radioactivity recovered in the urine, bile, blood, air-dried faeces and lyophilised tissues was determined by chromatographic analysis.

The total recovery of radioactivity was 95.5 % in conventional rats and 96.2% in cannulated rats. Low levels of radioactivity (not quantified) were measured in all of the daily urine and bile samples. The cumulative urinary excretion of radioactivity over 72 hours in conventional rats was ~1% and in cannulated rats was ~0.3%. The cumulative biliary excretion of radioactivity over 72 hours in cannulated rats was ~4%. Chromatographic analysis of the bile indicated the presence of 4 metabolites; two monohydroxy pentabromodiphenyl ethers and two dihydroxy pentabromodiphenyl ethers and possibly of thio substituted pentabromodiphenyl ethers. No glucuronide or sulphate conjugates were identified.

Disposition data revealed that radioactivity preferentially deposited in the epididymal adipose tissue (3.8 and 0.8 % of the administered dose in conventional and cannulated rats respectively), the blood (1.4 and 0.9 % of the administered dose in conventional and cannulated rats respectively), the carcass (39 and 2.0 % of the administered dose in conventional and cannulated rats respectively), and the GI tract (6.1 and 1.5 % of the administered dose in conventional and cannulated rats respectively). When further fractionated it was demonstrated that of the radioactivity deposited in the carcass the majority was in the skin. All other tissues contained ,1% radioactivity at 72 hours.

The major route of elimination of BDE-99 was via the faeces with 43% of the administered dose of radioactive BDE-99 being recovered in the faeces of conventional rats and 86% for cannulated rats. This suggests that bile salts are required for the uptake of BDE-99 from the gastrointestinal tract. Of the radioactivity measured in the faeces of conventional rats only 72% could be extracted for chromatographic analysis of its nature. Analysis indicated that >90% of the recovered radioactivity was present as parent BDE-99. The remaining recovered radioactivity was determined as being 1 of 4 metabolites, these being; two monomethoxy pentabromodiphenyl ethers or two debrominated monomethoxy tetrabromodiphenyl ethers.

In a related study, groups of 6 conventional and 10 bile-cannulated Sprague-Dawley rats were administered a single oral dose of 2.2 mg/rat 2,2',4,4',5-[^{14}C]pentaBDPE (BDE-99) in peanut

oil (Larsen *et al* 1999). Urine and bile (from cannulated animals only) were collected at 24 hour intervals over a 72 hour period post-dosing. The excreta was analysed using chromatographic techniques and the presence and nature of any radioactivity determined.

Daily excretion of radioactivity in the urine and the bile was minimal (not quantified). The cumulative urinary excretion of radioactivity over 72 hours in conventional and cannulated rats was <1% of the administered dose. Of the recovered radioactivity in the urine of conventional rats 6.3% was protein bound to α2μ-globulin. None of the recovered radioactivity in the urine of cannulated rats was bound to α2μ-globulin, however a significant proportion was bound to a 79KDa protein, the amount of binding increasing with time (28 to 47%). The cumulative biliary excretion of radioactivity over 72 hours in cannulated rats was 3.7% of the administered dose (not determined for conventional rats).

Dermal

No studies are available.

4.1.2.1.3 Human studies

Polybrominated diphenyl ethers (polyBDPE), including pentaBDPE, were detected in pooled blood samples taken from 40 men (Klasson Wehler et al, 1997). Levels were of the order of ng/g of lipid. Similarly, as part of a feasibility study, polyBDPE, including pentaBDPE, were detected in the adipose tissue of a small group of elderly hospitalised patients (Lindström *et al*, 1997). Levels were of a similar order (ng/g adipose tissue). PentaBDPE has also been measured in the adipose tissue of a younger individual (de Boer *et al*, 1998 - see section 4.1.2.6.2 for further details).

In a briefly summarised paper which concentrates principally on analytical techniques, samples of human milk were analysed for polyBDPE content (Meironyté *et al*, 1998). The milk samples were collected and pooled from differing numbers (ranging from 20 to 116) of women aged between 20 and 31 years, over a 25 year period from 1972 to 1997. A graphical presentation of the data (expressed as total substance in the pooled sample) demonstrated an increase in total polyBDPE over the 25 year period, with tetrabromodiphenyl ether (TBDPE) accounting for by far the greatest fraction of polyBDPEs detected (60 to 70 %). Two isomers of pentaBDPE were also detected at pg/g lipid concentrations and also showed an increase in concentration with time. Maximal lipid level of approximately 4010 pg polyBDPE/g lipid, and 1100 pg pentaBDPE/g lipid were measured.

In a briefly summarised paper pg/g fat concentrations of pentaBDPE have been detected in individual breast milk samples from 39 women (Darnerud *et al*, 1998). The breast milk was obtained from primiparious mothers aged 22 to 36 years at week 3 post-partum (the year of collection was not reported, however the study is part of a current and ongoing investigation).The women had answered a questionnaire focusing on the present pregnancy “symptoms”, diet and other habits. PolyBDPE’s were extracted from the breast milk using a n-hexane/acetone mixture and separated via gas chromatography with electron capture detection.

PentaBDPE-85 (2,2’,3,4,4’-pentaBDPE) was used as an internal standard. Five major congeners were identified of which 60-70% was tetraBDPE. The levels of polyBDPE detected in the individual breast milk samples were generally within the range 1000 to

10 000 pg/g fat, with one individual presenting a level of 28 170 pg/g fat. Within this small group of samples there was no link between the concentration of polyBDPE and age, alcohol or fish consumption, place of residence or birth weight, although an increase in concentration with increasing cigarette smoking was apparently suggested. From the data presented it was possible to calculate the 97.5 percentile of polyBDPE in the breast milk as being approximately 10 000 pg/g fat. Assuming that 30% of this is pentaBDPE (e.g. based on the pooled milk data from Merinoyte *et al*, 1998) is can be estimated that the 97.5 percentile level of pentaBDPE in human breast milk from this study is 3300 pg/g fat.

These 5 studies demonstrate absorption of pentaBDPE in humans, that pentaBDPE is distributed to the adipose tissues and lipid and that it is excreted as a component of breast milk. It is noted that in the rat the half-life of elimination for pentaBDPE isomers was 25-47 days. Comparison of this with substances with similar half-lives in the rat suggests possibly a much longer half-life in the human, perhaps of the order of many months to years (Sarver et al, 1997).

4.1.2.1.4 Summary of toxicokinetics

Only limited data are available. Toxicokinetic evidence in humans indicates that pentaBDPE can be absorbed into the body and is distributed to the adipose tissue and lipids. Given the very high lipophilicity of pentaBDPE it can be assumed that pentaBDPE will bioaccumulate in these tissues. Following pregnancy pentaBDPE is excreted as a component of breast milk. There are no data available regarding the rate of elimination of pentaBDPE from human adipose tissue or breast milk. Animal data also indicate that pentaBDPE is absorbed following oral administration, although the extent of absorption cannot be assessed from the data available. There are no data on inhalation or dermal absorption. However, comparison with structurally similar substances such as PBBs and PCBs, suggests that pentaBDPE may be well absorbed by all routes of exposure, although a precise value for the extent of absorption cannot be determined. Only limited information on the metabolism of pentaBDPE is available from 2 studies in rats. Data from these studies indicate that the majority of an orally administered single dose of pentaBDPE is excreted unmetabolised in the faeces over a 72 hour period. There is negligible excretion of pentaBDPE in the urine (<1% of the administered dose). In the faeces minor amounts of metabolites identified as two monomethoxy pentabromodiphenyl ethers and two debrominated monomethoxy tetrabromodiphenyl ethers were found. Mono and dihydroxy metabolites have been identified in bile, together with possible thio-substituted pentabromodiphenyl ethers. The data also demonstrate that pentaBDPE is preferentially deposited to the skin and epididymal adipose tissue (~42%) over a 72 hour period. Evidence for a slow rate of elimination from rat adipose tissue ($t_{1/2}$ of 25-47 days) suggests that pentaBDPE is slowly (or not at all) metabolised within the body, and implies the potential for bioaccumulation. It is likely that the half-life in human adipose tissue would be significantly longer. The low water solubility and high molecular weight of parent pentaBDPE suggests that excretion would probably be via the biliary and faecal routes, as well as in breast milk. This view is supported partly by the limited data available from single dose studies in rats where excretion was seen largely via the faecal route.

4.1.2.2 Acute toxicity

4.1.2.2.1 Studies in animals

Inhalation

Groups of 5 male and 5 female CD rats were given whole body exposures to an aerosol mist of 2 or 200 mg/l pentaBDPE in corn oil, for 1 hour (Great Lakes Chemical Corporation, 1975). Aerosol droplet size was not given. No treatment-related mortalities occurred at either concentration. Animals in the high concentration group showed general signs of toxicity such as lacrimation, salivation and tachypnoea. Animals in both groups displayed increased, followed by decreased motor activity, eye squint and erythema (site not stated) during exposure. Nasal and respiratory "congestion" were noted in 3 rats at 200 mg/l up to day 3. Animals appeared normal by 24 hours after the lower dose and by day 4 after the higher dose.

Groups of 2 Wistar rats were exposed for a single period of 2.5, 4 or 6 hours to an aerosol emission of Tardex 50 (I.S.C Chemicals 1977a). The aerosol was generated by heating the test substance to 200 °C. Details of the atmospheric concentrations and aerosol droplet size were not given. No treatment-related deaths occurred and no significant signs of toxicity were observed. At post-mortem analysis, on day 7, 'slight' congestion in the lungs was observed in both animals exposed for 6 hours. All other organs and tissues appeared normal on gross examination.

Oral

In a series of studies groups of male and female rats were administered single doses of up to 10 000 mg/kg of different commercial preparations of pentaBDPE by gavage (Lunevale Products Ltd., 1977; Great Lakes Chemical Corporation, 1975; Ethyl Corporation, 1984; I.S.C. Chemicals Ltd., 1977 b and 1977c). LD_{50} values for these preparations of between 2640 and 6200 mg/kg were identified. All treatment-related deaths occurred between days 2 and 9 post-dosing. Signs of toxicity observed included diarrhoea, piloerection, abnormal gait, reduced activity, tremors and red staining around the nose and eyes. Animals which died showed pale, enlarged, necrotic livers and multiple small ulcerations of the gastric mucosa.

In a study by von-Meyerinck *et al* (1990) groups of 3 male Wistar rats were administered a single oral gavage dose of 0 or 300 mg/kg Bromkal 70 in peanut oil. Animals were sacrificed 4 days post-dosing. Treatment with Bromkal 70 resulted in a 1.5 -fold increase in relative liver weight, and in a 3-fold increase in the content and activity of cytochrome P450 levels, as well as marked increases in the activities of other liver microsomal enzymes. Western blot analysis of pentaBDPE treated microsomes showed the induction of a similar pattern of cytochrome P450 as for a PCB (Aroclor 1254).

In a study designed to assess the immunological and endocrine effects of DE-71 (Fowles *et al*, 1994). Groups of 6 female C57BL/6J mice were dosed once by gavage with 0, 0.8, 4, 20, 100 or 500 mg/kg DE-71 in peanut oil. Two days post-dosing all animals were given an intraperitoneal injection of sheep erythrocytes (SRBC). The potential immunotoxicity of DE-71 was assessed by measuring the plaque-forming cell (PFC) response to SRBC and also natural killer cell (NKC) activity *in vitro*. All animals were sacrificed 8 days post-treatment. No clinical signs of toxicity were reported. Relative liver weight and hepatic cytochrome P450 activity were increased at 500 mg/kg, compared with controls, with no effects being

observed at any other doses. The serum concentrations of total thyroxine (T4) were decreased at all dose-levels, but no dose-response relationship was apparent. Furthermore, data were presented only graphically, and no quantitative assessment was presented. No treatment-related changes in either the PFC response to SRBC or in NKC activity were seen, compared with controls. No conclusions regarding the immunotoxic potential of pentaBDPE can be drawn from this study.

Dermal

Groups of 5 male and 5 female Wistar rats were administered single doses of 1250 or 2500 mg/kg of Tardex 50 as a dispersion in cotton seed oil, or 5500 or 11000 mg/kg of Tardex 50L, under an occlusive dressing for 24 hours (I. S.C. Chemicals Ltd., 1977 b and 1977c). No treatment-related deaths occurred. Signs of toxicity observed from day 3 were weight loss, piloerection, lethargy, tremors, chromodacryorrhea, and diuresis. No gross changes were observed at necropsy.

In a limited study, 200 or 2000 mg/kg pentaBDPE was applied to the shaven backs of groups of 2 male and 2 female New Zealand white rabbits, under an occlusive dressing for 24 hours (Great Lakes Chemical Corporation, 1975). No deaths occurred and no significant changes in body weight were reported during the 14 day observation period. No other observations were made.

4.1.2.2.2 Other studies

In a brief report of a novel *in vitro* study in H4IIE rat hepatoma cells (CALUX assay), three isomers of pentaBDPE (PBDPE-85, -99 and - 119) were reported to exhibit varying degrees of partial Ah-receptor agonist and antagonist activities following single 24 hour exposures (Meerts et al, 1998). No signs of cytotoxicity were reported to be observed. No conclusions with regards to the significance of these findings can be drawn from the limited information reported.

4.1.2.2.3 Summary of acute toxicity

The effects of single inhalation exposures to pentaBDPE have not been adequately investigated in animals, although no deaths occurred following a one-hour exposure to an aerosol of 200 mg/l, suggesting pentaBDPE is of low acute toxicity following inhalation exposure. Studies in rats with commercial preparations containing pentaBDPE indicate that these preparations are of low acute toxicity via the oral and dermal routes of exposure, with LD_{50} values > 2000 mg/kg for these preparations, in both cases.

4.1.2.3 Irritation

4.1.2.3.1 Skin

Studies in animals

0.5 g pentaBDPE in semi-solid form, was impregnated on to a gauze patch following softening by heat, and applied under a semi-occlusive dressing to the skin of 6 albino rabbits for 4 hours (Dead Sea Bromide Works, 1983a). Erythema (grade 1) was observed in two

animals at 1 hour post-patch removal and in one animal 24 hours after patch removal. Oedema (grade 1) was observed in one animal 1 hour after patch removal.

In a briefly reported study, 0.5 ml of pentaBDPE, in the form of a viscous liquid, was applied under an occlusive dressing for 24 hours, to the shaved backs of 3 New Zealand white rabbits (Great Lakes Chemical Corporation, 1975). One animal showed signs of erythema (grade 1) at 24 and 72 hours. No other signs of irritation were observed. This study included 3 animals with abraded skin. Two animals with abraded skin at 24 hours and one at 72 hours showed signs of erythema (grade 2).

A dose of 0.5 ml Tardex 50L was applied under an occlusive dressing to the intact skin of 6 New Zealand White rabbits for 24 hours (I.S.C. Chemicals Ltd., 1977b). Erythema (grade 2) was observed in one animal at 24 hours post-patch removal, but had disappeared by 72 hours. Erythema (grade 1) was observed in two animals 72 hours post-patch removal. Oedema (grade 1) was observed in one animal 24 hour after patch removal, but had disappeared by 72 hours. This study was also conducted using 6 animals with abraded skin. Four animals with abraded skin showed erythema (grade 1 to 2) at 24 or 72 hours and one animal showed oedema (grade 1) at 72 hours, post-patch removal.

In a non-standard skin irritation study, 0.25 ml of 1.25, 2.5, 5.0 and 10.0 % v/v suspensions of Tardex 50 in maize oil were applied to the skin of 4 New Zealand White rabbits, for 6 hours daily for 5 days, and signs of irritation were recorded at 24 hours after each exposure (I.S.C. Chemicals, 1977d). The 10% test concentration was reported to cause slight irritation (grade 1 erythema) following the initial application, which became more pronounced (grade 2 erythema and oedema) with subsequent exposures. The 5 % test concentration was reported to elicit no response following the initial application, but reactions (grade 2 erythema and oedema) became visible after the second and subsequent applications. Concentrations of 2.5% and less showed no evidence of irritation following initial application, but well-defined reactions (grade 2 erythema and oedema) became apparent on days 3 or 4 of the treatment.

4.1.2.3.2 Eye

Studies in animals

In a briefly reported study, 0.1 ml pentaBDPE in the form of a viscous liquid, was instilled into the conjunctival sac of one eye of 6 rabbits, with observations being made at 24, 48 and 72 hours and again at day 7 post-instillation (Great Lakes Chemical Corporation, 1975). All treated eyes showed conjunctival redness (grade 2) at 24 hours which gradually cleared by day 7 post-treatment. All treated eyes displayed very slight to slight chemosis (grade 1 or 2) between 24 and 72 hours which was reversible in 3/6 animals by day 7. Signs of discharge were observed from all eyes at 24 hours, but were seen in only 2/6 eyes by day 7. One treated eye showed signs of corneal injury at the 72 hour examination. Slight alopecia was noted around the lower eye lid of 2/6 treated eyes at day 7.

PentaBDPE in semi-solid form (200 mg), was instilled into the conjunctival sac of one eye of 6 rabbits, with irrigation of the eyes after 24 hours (Dead Sea Bromide Works, 1983b). Observations were made at 1, 24, 48 and 72 hours and at 4 and 7 days post-dosing. All treated eyes showed conjunctival redness (4 animals with grade 1 and 2 animals with grade 2) at 1 and 24 hours post-treatment, all of which were cleared by 48 hours. No other signs of ocular irritation were observed throughout the duration of the study.

In two studies, 0.1 ml of Tardex 50L, as an undiluted viscous liquid or as a 25% v/v dispersion in liquid paraffin, was instilled into the conjunctival sac of one eye of 6 rabbits (I.S.C. Chemicals Ltd., 1977b). The eyes of 3 animals were left unwashed, whereas the remaining 3 were washed immediately post instillation. Each of the unwashed eyes treated with the undiluted sample displayed signs of conjunctival redness and chemosis (grade 1 or 2) between days 1 and 4 post treatment, with effects being completely reversible, in most animals by day 7. One animal still presented conjunctival redness (grade 1) at day 7, but the profile of response indicated that the effect was clearing. Similar effects, but of decreased severity and duration were observed in the irrigated eyes and those treated with the 25% dispersion, with effects being completely reversible in all animals by day 3 post-treatment.

4.1.2.3.3 Respiratory Tract

Evidence of tachypnoea and nasal and respiratory congestion are reported in rats following single inhalation exposures to very high concentrations 200 mg/l (8333 ppm) pentaBDPE aerosol mist for 1 hour or a heat generated aerosol emission of pentaBDPE (concentration not given) for 6 hours (see section 4.1.2.2.1). No effects were observed at 83 ppm.

4.1.2.3.4 Summary of irritation

The available data indicate that pentaBDPE produces only minimal to mild signs of dermal and eye irritation in animals following single exposure. Signs of respiratory tract irritation were seen in animals only following exposure to very high concentrations of pentaBDPE (>8000 ppm). However, no effects were observed at lower concentrations (80 ppm) and the lack of any substantial skin or eye irritancy suggest that it would be unlikely to produce significant respiratory tract irritation.

4.1.2.4 Corrosivity

Results from animal skin and eye irritation studies indicate that pentaBDPE is not corrosive.

4.1.2.5 Sensitisation

4.1.2.5.1 Skin

Studies in animals

No evidence of skin sensitisation was found in a guinea pig maximisation test, conducted to modern standards (CMA, 1996a). A group of 20 test animals received an intradermal injection of 5% pentaBDPE in corn oil, and a topical application of 100% pentaBDPE liquid, preceded by a topical application of 10% sodium lauryl sulphate [SLS] in corn oil. Control animals received vehicle only. Subsequent dermal challenge with 100% pentaBDPE resulted in no signs of erythema or oedema in any of the test or control animals.

In a poor maximisation study, a group of 15 test animals were given an intradermal injection of a 1.25% solution of Tardex 50L in liquid paraffin, followed by a topical administration of 12.5% Tardex 50L in petrolatum (preceded by a topical application of 10% SLS in petrolatum) (I.S.C. Chemicals Ltd., 1977b). No details of control animals were given. Following dermal challenge with 100% Tardex 50L, 3 animals showed signs of very slight erythema at 48 hours post treatment, which persisted in one animal for 72 hours.

In a poorly conducted study, 10 albino guinea pigs were intradermally induced with a 5% solution of Tardex 50L in liquid paraffin, followed by topical induction with 25% Tardex 50 L in petrolatum (preceded by 10% SLS in petrolatum) (I.S.C. Chemicals Ltd., 1977e). No control animals were used in this study. Six of the test animals died between the induction and challenge phases of the study. The cause of death was unclear; post-mortem examination of these animals revealed enlarged, inflamed gall bladder. The surviving 4 animals were challenged with a 100% solution of Tardex 50L and showed no evidence of skin sensitisation. No conclusions can be drawn from this study.

4.1.2.5.2 Respiratory tract

No data are available.

4.1.2.5.3 Summary of sensitisation

Evidence from studies in guinea pigs indicates that pentaBDPE does not possess significant skin sensitisation potential. No animal studies have investigated the respiratory sensitisation potential of pentaBDPE, although the absence of significant skin sensitisation potential and the generally unreactive nature of pentaBDPE suggest that it would not be a respiratory sensitiser.

4.1.2.6 Effects of repeated exposure

4.1.2.6.1 Studies in animals

Inhalation

No data are available.

Oral

Rats

Groups of 10 male and 10 female CD rats were fed diets containing 0, 100 or 1000 ppm (approximately equivalent to 0, 8 or 80 mg/kg/day) of pentaBDPE daily for 28 days (Great Lakes Chemical Corporation, 1976a). The study was limited in design, and did not incorporate any haematological or clinical chemistry investigations. No treatment-related mortalities, changes in appearance, behaviour, body weight gain or food consumption were observed. Increases in absolute liver weight of 9% in females at 100 ppm, and of 33% and 55% in males and females respectively at 1000 ppm occurred. Histopathological assessment of the liver showed enlargement of centrolobular and midzonal parenchymal cells in 3/5 males at 100 ppm, and in all animals at 1000 ppm. The cytoplasm of the enlarged parenchymal cells showed histological changes described as being of a finely granular "ground glass" appearance, and in addition, eosinophilic bodies were seen in affected cells at 1000 ppm.

1/5 and 3/5 male rats at 100 and 1000 ppm respectively, showed slight to moderate hyperplasia of the thyroid, the follicles of which were small, devoid of colloid and lined with basophilic columnar epithelium. No thyroid hyperplasia was evident in control animals. It is

unlikely that the thyroid effects are relevant to human health (see below). No other treatment-related gross or microscopic abnormalities were found.

Groups of 30 male and 30 female Sprague-Dawley rats were administered 0, 2, 10 or 100 mg/kg/day DE-71 in corn oil, in the diet for up to 90 days (Great Lakes Chemical Corporation, 1984). Ten animals per sex from each group were sacrificed on day 28 of dosing and a further 10 per sex at the end of the 90-day dosing period. Of the remaining animals, 5 per sex per group were sacrificed after recovery periods of 6 and 24 weeks. Extensive haematological and clinical chemistry analyses were conducted at days 28 and 90. At each sacrifice time, gross pathological examinations were conducted on all tissues from all animals, as were microscopic examinations of liver, lung, thyroid, thymus, kidney and all gross lesions. In addition, at the 13-week sacrifice all tissues from all animals were examined microscopically. Chemical analyses were also conducted of liver porphyrins and 12-hour urinary porphyrins at 4 and at 13 weeks.

There were no treatment-related mortalities or clinical signs throughout the study. Decreased mean body weights of less than 10% in top-dose animals were noted from week 6 of dosing through to week 4 of the recovery period. Absolute liver weights were increased by 11% in mid-dose animals and by up to 70 and 50 % in top-dose males and females respectively at both day 28 and at the end of the dosing period, with values returning to control levels over the 24 week recovery period. Absolute thyroid weights in top-dose males and females were increased by 30% at day 28 and at the end of the dosing period, and were still elevated in top-dose males only at the end of the 24 week recovery period.

Serum cholesterol levels were increased in a dose-related fashion with the increases being more marked in females than males. At 90-days serum cholesterol levels were increased by 60% in males and by 4-fold in females at the top dose. No other serum clinical chemistry changes were found. However, serum thyroxine (T4) levels were reduced by > 20% in both sexes of the mid and high-dose groups at day 28, but were reduced in mid-dose males only at the end of the dosing period. No treatment-related effect on serum triiodothyronine (T3) levels were observed. Levels of T4 or T3 were not assessed during the recovery period. Porphyrin levels in urine and liver were increased in both sexes at 100 mg/kg/day at week 4 and 13. By week 13, urinary porphyrins were increased by 2-fold and 13-fold in males and females respectively, and liver porphyrins were correspondingly increased by 8- and 400-fold. There were no effects on porphyrin levels in the low dose animals. At 10 mg/kg/day liver and urinary porphyrins were increased by approximately 2-fold in both sexes at 13 weeks.

Histopathological investigation showed evidence of hepatocytomegaly at 4 and 13 weeks, with the affected cells showing a finely granulated cytoplasm with a "ground glass" appearance. These effects were seen at all dose levels with a dose-related increase in incidence and severity, except were not seen in females at 2 mg/kg/day. In terms of reversibility, at 24 weeks post-dosing slight hepatocytomegaly was still evident in both sexes at 100 mg/kg/day, and in females at 2 and 100 mg/kg/day, there was an increased incidence of degeneration and necrosis of individual liver cells. One female at 2 mg/kg/day sacrificed at 24 weeks post-dosing had numerous multinucleated hepatocytes. The study report indicated that although binucleated liver cells are common in normal rat livers, cells with 3 or more nuclei are rarely found in normal livers, and the condition was therefore considered to be related to treatment. In the thyroid gland there was evidence of very slight to slight hyperplasia at 4 and 13 weeks in approximately half of the high dose males and females. The

incidence of the thyroid hyperplasia was reduced at week 6 of the recovery period and was not seen at 24 weeks post-dosing.

The effects on serum T4 levels and on the thyroid gland are considered to be a consequence of the induction of hepatic enzymes, which enhance T4 metabolism and excretion, leading to a compensatory increase in thyroid stimulating hormone (TSH) output from the pituitary, thus stimulating thyroid growth and metabolism. This conclusion is supported by evidence from a study by Carlson (1980 a), which specifically demonstrated the induction of hepatic UDP-glucuronyl transferase in rats administered pentaBDPE. This enzyme catalyses the conjugation of thyroid hormones and enhances their excretion in the bile. Human plasma contains thyroxine binding globulin (TBG), which is not found in rats or mice (Tanabe *et al* 1969, Capen, 1992 and 1994). TBG maintains a stable reservoir of T4 in the bloodstream and reduces the potential for fluctuations in plasma T4 levels in humans. Hence it is unlikely that the treatment related effects on thyroid status in the rat would occur in humans.

Overall, the results of this study indicate that the liver is the key organ affected by pentaBDPE; the effects observed include marked increases in liver weight associated with microscopic cytoplasmic changes, together with disturbances in porphyrin and cholesterol synthesis. Slight thyroid hyperplasia and reductions in plasma T4 levels are also observed, but these effects are considered to be indirect consequences of the induction of liver enzymes and, due to species differences in thyroid metabolism, are not likely to be of relevance to human health. In view of the effects on the liver, a clear NOAEL cannot be identified from this study.

In a subsequent study with a detailed range of clinical, haematological and pathological investigations, groups of 20 male and 20 female Sprague-Dawley rats were administered 0, 0.01, 0.05, 0.1, 0.5 or 1.0 mg/kg/day of DE-71, in the diet daily for 30 days (Great Lakes Chemical Corporation, 1985). Groups of 5 rats per sex at each dose level were sacrificed at 30 days, and at 6, 12 and 24 weeks post-dosing. No treatment-related changes in survival, body weight, food consumption, behavioural or clinical signs, haematology, clinical chemistry, macroscopic or histopathological changes were observed. There were no treatment-related changes in liver and urinary porphyrins. A NOAEL for the test substance of 1 mg/kg/day can be identified.

In studies by Carlson (1980a and 1980b) and von-Meyerinck *et al* (1990), designed largely to investigate hepatic enzyme induction, groups of rats were administered oral doses of between 0.44 and 100 mg/kg/day of commercial mixtures of pentaBDPE under various dosing regimes for up to 90 days. Control animals were given vehicle only.

The activities of a range of liver enzymes including cytochrome P450, cytochrome *c* reductase, UDP-glucuronyltransferase etc. were increased in a dose-responsive manner in these studies. In one study (Carlson 1980b), evidence for increased activities of some enzymes of about 30% above control values was observed at the lowest dose tested (0.44 mg/kg/day for 90-days). However, in this study it was briefly reported that light microscopic examination of livers from rats dosed with up to 1.8 mg/kg/day for 90 days revealed no substance-related changes. No pathological investigations were carried out at higher doses. Overall, the toxicological significance of the slight hepatic enzyme induction observed in the absence of any associated pathological changes is uncertain, and given the limited range of investigations in these studies no firm conclusions can be drawn.

Mice

In a study specifically designed to assess the immunological and endocrine effects of pentaBDPE, groups of 6-8 female C57BL/6J mice were dosed orally with 0, 18, 36 or 72 mg/kg/day DE-71 in peanut oil for 14 days (Fowles et al, 1994). The reporting of this study was lacking in clarity. The potential immunotoxicity of DE-71 was assessed by measuring the plaque-forming cell (PFC) response to sheep erythrocytes (SRBC) and also natural killer cell (NKC) activity. Six animals were used in the assessment of each of these endpoints. For determination of the PFC response animals were given an intraperitoneal injection of SRBC on day 9 of dosing. Other DE-71-treated animals (5 - 8 per endpoint) were used to assess NKC, endocrine and cytochrome P450 IA1 and IIB1 activity. These animals did not receive injections of SRBC. All animals were sacrificed on day 15 of the study and spleen, thymus, liver and body weights were measured.

A dose-related increase in relative liver weight was observed, with increases of 11, 20 and 28% respectively, compared with controls. Relative thymus weight was reduced at the top dose only, by 16% compared with controls, whilst relative spleen weight and total body weights were unaffected. Changes in plasma total and free T4 levels were presented graphically (actual data were not presented), and showed a dose-dependent decrease such that at the top dose, levels of total T4 were reported to be 60% of the control values. There was no concomitant suppression of NKC activity, and no treatment-related changes in NKC activity were seen. However, there were changes in the PFC response to SRBC, which was statistically significantly decreased in the top dose group, to 67% of control values. Elevations in corticosterone levels, also presented graphically (actual data were not presented) were correlated with the order of kill, suggesting a stress-related effect, which prevented identification of any clear independent treatment-related effect. Induction of the cytochrome P450s IA1 and IIB1 were observed at all dose levels.

Overall, this study provides evidence of increased cytochrome P450 activity and reduced serum T4 levels, as seen in studies in rats. The effects on serum T4 are judged to be of no significance to human health for the reasons given earlier. This study presented some evidence that pentaBDPE did not affect NKC activity, but that PFC activity was reduced at doses which also caused a reduction in the thymus weight. However, the reduction in thymus weight was not observed in other repeat dose studies, which used higher doses of DE-71 over longer periods, and so this isolated finding is thought to be of doubtful significance. Overall, no firm conclusions can be drawn from this limited study concerning the potential effects of pentaBDPE on the immune system.

In a study specifically designed to assess the effect of polybrominated diphenyl ethers on immunological parameters, groups of 6-8 female Sprague-Dawley rats and C57BL mice were dosed orally with 18 or 36 mg/kg/day Bromkal 70 in corn oil for 14 days (Darneurd and Thuvander, 1998). Other groups of animals were also treated with Aroclor, tetrabrominated diphenyl ether and a PCB. The reporting of this study was very brief and lacked detailed discussion. All animals were sacrificed on day 15 of the study and spleen, thymus, liver and body weights were measured. Potential immunotoxicity was assessed by lymphoid cell and lymphocyte sub-population counts, and *in vitro* immunoglobulin production measured in the supernatant from cultures of splenocytes stimulated with Pokeweed.
No clinical signs of toxicity were observed. An increase in liver weight was ‘apparently’ observed in both species (top dose rats and mice at both dose levels), but data were not presented. The only immunotoxic effects reported as a consequence of Bromkal 70 treatment

were a decrease in the *in vitro* production of IgG by Pokeweed stimulated splenocytes, and a decrease in the absolute numbers of double negative (immature $CD4^-$, $CD8^-$) thymocytes, in top dose mice but not in rats.

The toxicological significance and relevance to human health of these findings is uncertain. However no effects on immune system parameters were observed at 18 mg/kg/day and as this is at least an order of magnitude greater than the NOAEL for liver effects (1 mg/kg/day), it can be concluded that liver toxicity is the key critical endpoint for pentaBDPE.

Dermal

No conventional repeated dermal exposure studies are available. A repeated dermal exposure study is available which was designed to investigate the potential for "bromacne" (analogous to chloracne) development in the skin (I.S.C. Chemicals, 1977d). This type of dermal response is not detectable in conventional repeated exposure studies in laboratory rodents, but can be detected using the rabbit ear or the nude mouse models (Klien-Szanto et al, 1991).

In this study, 0.25 ml of Tardex 50 as a 2.5 % v/v suspension in maize oil was applied to the inner left pinna of 6 New Zealand White rabbits, daily for 28 days (I.S.C. Chemicals, 1977d). A 1% mix of coal tar in maize oil was applied to the inner right pinna to act as a positive control. The ears were examined prior to each exposure. No discernible skin reactions occurred during the first 3 days of treatment, with either the Tardex 50 or the coal tar. However signs of slight epithelial hyperplasia induced by both substances were just evident on day 4 and increased in severity for the remainder of the study. At the end of the study, moderate hyperaemia, considerable thickening of the ear, enlargement of the hair follicles, extensive exfoliation and hair loss and slight hyperkeratinization were observed with a similar degree of severity for both substances. The nature of this dermal reaction was judged to be indicative of a 'chloracne-like' response by the authors of the study. No observations of systemic toxicity were made.

In a non-standard dermal irritation study (see section 4.1.2.3.1) evidence of ‘slight’ irritation (grade 1 erythema) initially, becoming more pronounced over time (grade 2 erythema and oedema) were observed following 5 day application of 10 % Tardex 50 in maize oil.

Concentrations of 2.5 and 5 % gave no response initially, but defined reactions (grade 2) became apparent over time with subsequent exposures. No assessment of systemic toxicity was made in this study.

4.1.2.6.2 Human data

A brief single case report, is available, of an individual who developed acneforms on his face and back, claimed to be as a consequence of watching television (TV) and playing computer games (de Boer *et al* 1998). The individual was a 13 year old male who watched TV and played computer games for several hours a day over a period of 8 consecutive months, in a small (27 m^3), non-ventilated and insulated room.

After 1 month under these conditions the individual complained to a physician of headache, dizziness, painful lesions on the soles of his feet, chronic craniofacial pains and other symptoms (not reported). It was also noted that his scalp and facial hair were darker and had developed a metallic texture.

Two and a half years later the individual presented with 'chloracne-like' lesions on his head and back. These lesions were diagnosed as acne vulgaris and severe papulocystic acne with hyperpigmentic scarring. Enlarged parathyroid glands were also observed.

The following year (3.5 years later) the individual was diagnosed as having 'marfanoid features' (abnormality of the skeletal proportions). At eight years after the time spent in the room a fine postural tremor of the hands was diagnosed by a neurologist. At this time a blood sample was taken and examined for chromosomal abnormalities as an indicator of chemical exposure. This analysis revealed "4 chromosomal fragments" per 200 chromosomes, which were claimed to be consistent with chemical exposure. No further details are reported. Without further information the significance of this finding is not known.

It is reported that the individual had an enlarged liver and a shrunken gall bladder and had fasted for considerable periods. However it is not clear at which time point these effects were first observed, or their degree of severity (no further details reported).

The following year (9 years after spending time in the room) acting on a supposition that the health effects could be related to exposure to chemical vapours from the TV set, blood and adipose tissue samples were taken from the individual and analysed by GC/MS for polyBDPE content (Bromokal-70 DE was used as an internal control standard for the analysis). Adipose tissue and blood samples from local cows and poultry were also collected (number of specimens not reported) and analysed for polyBDPE content, in order to determine the possible presence of polyBDPE in the local environment.

At this time the TV set was also analysed for the presence of flame retardant substances. In the TV set several forms of polyBDPEs were detected (tetra, penta, hexa, hepta, nona and deca) in various parts of the set. Three isomers of pentaBDPE were detected, principally in the air inside the set. The levels detected were in the range of 10 to 51 ng/m^3 for each of the 3 isomers (87 ng/m^3 in total for pentaBDPE). Negligible levels of two pentaBDPE isomers were detected in the circuit boards (< 0.4 μg/kg). No pentaBDPE was detected in wipes of the back or side walls of the set or on wipes of the circuit boards.

In the adipose tissue sample taken from the individual at the age of 21 years, 2 isomeric forms of pentaBDPE were detected at levels of 4 μg 2,4,5,2',4'pentaBDPE/kg wet weight and 1 μg x,y'pentaBDPE/kg wet weight, respectively. The levels determined in the adipose tissue of cows and poultry were <0.01 and 0.02 μg 2,4,5,2',4'pentaBDPE/kg wet weight, respectively. Levels of 2 μg of 2,3,2',4'-tetraBDPE/kg wet weight were also detected in the adipose tissue of the individual compared with levels of <0.02 μg/kg in cows and < 0.8 μg/kg in poultry. Blood levels of the polyBDPE from the individual (penta and tetra) were negligible (<0.01 μg/kg) and comparable with levels in cows milk and less that those in poultry adipose tissue (<0.1 μg/kg). Levels of other polyBDPE were not reported.

It is important to note that no adipose tissue or blood samples from other humans were analysed, therefore it is unknown how the levels of pentaBDPE in this individual relate to background levels found within the population as a whole, or even if they represent an increase, decrease or no change with time since the individual spent time in the room. Although levels of pentaBDPE were detected within the TV set 9-years later it is not possible to establish a clear causal-relationship with the effects observed in the individual and the low concentrations of pentaBDPE measured. Also it is not known if the observed effects in the individual were in a response to pentaBDPE 'exposure' via the TV set (9-years prior) or to

another substance(s) from other possible sources. There are no details reported of any investigation regarding other possible sources of polyBDPE exposure (e.g. polyurethane foams, diet) or confounders (further TV watching, computer usage) encountered by the individual during the intervening period between the proposed exposure in 1982 and the sampling and analysis of the adipose tissue and blood in 1991.

4.1.2.6.3 Summary of repeated exposure

The only human data available regarding the potential effects of repeated exposures to pentaBDPE is a case study of an individual possibly exposed whilst watching television and playing computer games. It is not possible based on the information reported and the confounders of exposure to directly establish a causal link between pentaBDPE exposure and the effects reported in the individual.

The only information concerning the effects of repeated oral exposure to pentaBDPE comes from studies in rats and one in mice involving administration of commercial mixtures of pentaBDPE. These studies consistently indicate that the liver is the key target organ affected by pentaBDPE. The effects observed include increases in liver weight and hepatocytomegaly, cellular microscopic changes, induction of a range of liver enzymes, and disturbances in cholesterol and porphyrin synthesis. As a consequence of the induction of liver enzymes, T4 levels are reduced in rats and mice leading to increases in thyroid gland weight. However, due to species differences in thyroid metabolism the effects on thyroid status are not likely to be of relevance to human health. The liver and thyroid changes produced by a commercial preparation of pentaBDPE are apparent within 4 weeks of repeated oral dosing, with effects on the liver at 2 mg/kg/day and above, and changes in thyroid status at 10 mg/kg/day and above. From a well conducted 30-day study in rats administered a commercial preparation of pentaBDPE, a NOAEL of 1 mg/kg/day was identified. As this NOAEL is derived for a commercial product of pentaBDPE (DE-71), which contains 50-62% pentaBDPE, and given a maximum oral absorption of 90%, a NOAEL for pentaBDPE of 0.45 mg/kg bw/day, is determined. The human health significance of these rodent liver effects is unclear. At this dose, detailed investigations revealed no effects on liver function or histopathological appearance, or on thyroid status.

A decrease in the *in vitro* production of IgG by Pokeweed stimulated splenocytes, and a decrease in the absolute numbers of double negative (immature $CD4^-$, $CD8^-$) thymocytes, in mice but not in rats was reported as a consequence of Bromkal 80 treatment. No effects were observed at doses or up to and including 18 mg/kg/day inn either species. The toxicological significance and relevance to human health of these findings is uncertain.

Repeated dermal exposure of pentaBDPE to the rabbit ear, induces a proliferative reaction, characterised by moderate epithelial hyperplasia, similar to a 'chloracne-like' response. A NOAEL for this response with pentaBDPE cannot be determined from the available data.

4.1.2.7 Mutagenicity

4.1.2.7.1 Studies *in vitro*

Studies in bacteria

In a well-conducted plate incorporation mutagenicity test, pentaBDPE did not produce any increase in the number of revertants (Great Lakes Chemical Corporation, 1976b). *Salmonella typhimurium* strains, TA98, TA100, TA1535, TA1537 and TA1538, were tested with concentrations of 0.005 - 1 µl/plate pentaBDPE, both in the presence and absence of Aroclor-induced rat liver S9. Cytotoxicity, in the form of decreased revertant counts was observed at the top concentration tested.

In another well-conducted plate incorporation mutagenicity test, using the same *Salmonella* strains as above and a concentration range of 1.6 - 1000 µg/plate pentaBDPE, no increase in the number of revertants was observed either in the presence or absence of metabolic activation (Dead Sea Bromide Works, 1984). Cytotoxicity, as evidenced by a thinning of the bacterial lawn was observed in all strains except TA100, at the top concentration tested.

Negative results were also obtained for pentaBDPE when tested at concentrations of 100 – 10 000 µg/plate, in *Salmonella typhimurium* strains TA98, TA100, TA1535 and TA1537, both with and without Aroclor 1254-induced rat and hamster liver S9 (Zeiger et al, 1987). Cytotoxicity was apparently observed at the higher concentrations tested (no specific details were given). Negative results were also obtained for Bromkal 70-5 DE (Chemische Fabrik Kalk GmbH, 1978). In this briefly reported assay, the same *Salmonella* strains as above were tested using concentrations of 10 – 10 000 µg/plate Bromkal 70-5 DE both in the presence and absence of Aroclor induced-rat liver S9.

In contrast to the negative studies above, Tardex 50, when tested at concentrations of 10-10 000 µg/plate, in *Salmonella typhimurium* strains TA100, TA1535, TA1536, TA1537, and TA1538, produced a single point increase of more than 3-fold in the number of revertant colonies observed in strains TA1535 and 1538, only at the highest concentration tested and in the absence metabolic activation (I.S.C. Chemicals Ltd., 1977f). No increases in the number of revertants were seen in any other strain or in the presence of metabolic activation. No details of the reproducibility of these results were given. In light of the profile of responses seen, it is likely that this is a chance finding. Therefore no significance can be placed on the result obtained from this study.

Saytex 115, when assessed in a plate incorporation assay in *Salmonella typhimurium* strains TA98, TA100, TA1535 and TA1537 did not demonstrate any cytotoxicity nor any increase in the numbers of revertant colonies (Ethyl Corporation, 1985a).

Testing was carried out both in the presence and absence of metabolic activation, using a concentration range of 0.3 - 30 µg/plate. In view of the very low top-concentration tested, this study is considered to be inadequate and no conclusions can be drawn.

Studies in Fungi

In a well-conducted plate incorporation mutagenicity test with *Sacchromyces cerevisiae* strain D4, concentrations of 0.005 - 1 µl/plate of pentaBDPE did not produce any increase in

the number of revertants, either in the presence or absence of Aroclor-induced rat liver metabolic activation (Great Lakes Chemical Corporation, 1976b).

Studies in mammalian cells

Negative results were obtained in a well conducted cytogenetics assay using human peripheral blood lymphocytes, exposed *in vitro* to concentrations of 0.25 to 500 μg/ml of pentaBDPE without metabolic activation, and 32 to 3750 μg/ml of pentaBDPE with metabolic activation (CMA, 1996b). The exposure period was for 4 hours with fixation after a further 16 or 40 hours. Cytotoxicity, as evidenced by a 50% reduction in the mitotic index, was observed at 500 mg/ml in the absence of metabolic activation, and at 1250 μg/ml and above in the presence of metabolic activation. The test material was found to be insoluble in the solvent at concentrations of 3750 μg/ml and above. Positive, untreated and solvent controls gave results in the expected ranges.

4.1.2.7.2 Studies *in vivo*

No data are available.

4.1.2.7.3 Summary of mutagenicity

The mutagenic potential of pentaBDPE has been adequately explored *in vitro*. Evidence from several well conducted bacterial mutagenicity studies clearly shows that pentaBDPE is not a bacterial cell mutagen. Evidence in mammalian cells stems from a single well conducted cytogenetics assay, which provided negative results, indicating that pentaBDPE is not mutagenic. No studies have been carried out in vivo. However, given the negative results obtained *in vitro* and the apparent limited metabolism of pentaBDPE, it would be expected that pentaBDPE would not be genotoxic *in vivo*.

4.1.2.8 Carcinogenicity

No data are available.

4.1.2.9 Toxicity to reproduction

4.1.2.9.1 Studies in animals

Fertility studies

No standard fertility studies are available. A 90-day repeated-dose general toxicity study is available in which rats were administered 0, 2, 10 or 100 mg/kg/day DE-71 in the diet for up to 90 days (Great Lakes Chemical Corporation, 1984). In this study, no treatment-related changes in testes or ovary weights were observed at any time point. Gross and microscopic examinations showed no treatment-related changes in the gonads or accessory sex organs.

Developmental studies

In a pilot test, groups of 8 pregnant Sprague-Dawley rats were administered doses of 0, 100, 500, 2500, or 5000 mg/kg/day Saytex 115 in corn oil, by gavage on days 5 to 15 of gestation (Ethyl Corporation, 1985b). Severe signs of toxicity, including deaths were noted at doses of

500 mg/kg/day and above. All animals showed initial reductions in body weight gain, with those of the low-dose group returning to control levels by day 9 of gestation.

Post-mortem gross examination showed 3/8 and 4/8 of the decedents at 2500 and 5000 mg/kg/day respectively had resorbed all implantations. There was severe maternal toxicity at these dose levels. The remaining decedents had no resorptions and all conceptuses were developing normally. No changes in the average number of resorptions (early or late), number of live foetuses or litter sizes were observed, in the remaining animals following caesarean sectioning. No changes in fetal body weights, the percentage of male foetuses per litter or fetal gross external variations or malformations were observed.

In the full study groups of 25 pregnant Sprague-Dawley rats were administered doses of 0, 10, 100 or 200 mg/kg/day of Saytex 115 in corn oil, on days 6 to 15 of gestation (Hoberman et al 1988 [abstract only]; Ethyl Corporation, 1985c). Caesarean sections were conducted on day 20 of gestation and the foetuses examined for external, visceral and skeletal alterations.

No deaths occurred in the dams and the only sign of maternal toxicity observed was a reduced body weight gain of 20 and 30% compared to controls, at 100 and 200 mg/kg/day respectively, which showed 'some' recovery in the post-dosing period. No treatment-related effects were observed on the number of resorptions, litter sizes or fetal mortality. No changes in fetal body weight nor in the incidence of fetal gross external, soft tissue or skeletal variations were observed. Hence in these studies, there were no indications of adverse effects on the foetus at doses of up to at least 200 mg/kg/day, which induced significant reductions in maternal body weight gain. Developmental effects at higher doses were accompanied by severe maternal toxicity.

In a study (Eriksson *et al* 1998, Eriksson *et al* 1999) designed to investigate spontaneous behaviour (SB) and learning ability groups of 10 day old neonatal NMRI mice were administered by gavage a single dose of 0.8 or 12 mg/kg bw pentaBDPE (reported to be > 98% purity) sonicated in a 20 % (w:w) fat emulsion of lecithin/peanut oil and water (in order to reflect the 14% fat content of mouse milk). Control animals were administered the fat emulsion only. Animals were weaned and at 4 weeks the males were removed and raised in groups of 4-7 animals.

At 2 and 4 months post-dosing groups of 8 male animals per dose group were randomly selected from 3-4 different litters; runts were removed from the litters prior to selection. Over a 4 hour period (8 am to 12 noon) all animals were individually placed in an automated infrared light balance cage and were examined over a 60 minute period (the time was divided into 3 x 20 minute scoring periods) with respect to their spontaneous behaviour (locomotion, rearing and total activity). Although animal selection was randomised, it is not clear if the same animals were tested at 2 and 4 months or if two different test groups of animals were selected.
At 5 months post-dosing, groups of 16-18 males, administered 12 mg/kg only, were randomly selected from the same 3-4 litters as used previously (runts having been removed from the litters). Over 5 hours (9 am to 2 pm) on 4 consecutive days all animals were timed with respect to their ability to locate a platform submerged 1 cm below the water surface in a Morris swim maze (water depth 26 cm at 23 °C) on 5 occasions each day. The decrease in the time taken to locate the platform over the 20 trials was used to demonstrate the animals ‘spatial learning ability’.

On day 5 the platform was relocated and over 5 trials the animals were timed with respect to their ability to locate the new positioned platform. The decrease in the time taken to locate the 'new' platform over the 5 trials was used to demonstrate the animals 'relearning ability'. The order of animals tested in each of the trials was randomised and an equal number of animals per groups were tested each day. The testing procedures were all conducted by a single individual, without knowledge of the animals' treatment (i.e. exposed or control). A second individual was responsible for all routine maintenance and care of the animals. The animals tested were from the same test groups as those tested in the SB study but it is unclear if the same animals or others from the test groups were selected for this test.

Data from both the SB study and the swim maze (SM) study were assessed statistically with respect to the number of animals tested (n= 8-10 or 16-18, respectively).

During the studies no clinical signs of 'dysfunction' or of body weight changes were observed in treated animals compared with concurrent controls.

The group mean values, from the SB study, (presented in graphical form only) indicate that at both 2 and 4 months, during the first 20 minute scoring period the pentaBDPE treated animals were apparently less active compared to controls, and that the difference in activity (decrease) between treated and control animals was dose-related. During the second 20 minute scoring period the activities in all groups were comparable. Over the third scoring period the pentaBDPE treated animals appeared to be more active than controls, with the difference in activity (increase) between treated and control animals being dose-related. The standard deviations, as indicated on the plots, are in some instances quite large and span the mean differentials between test and control animals. It is reported that the changes in the activity of pentaBDPE treated animals are statistically significant. As indicated above, the statistical analyses were conducted with regards to the number of animals tested (n = 8-10) and not the alternative statistical unit the numbers of litters tested (n = 3-4) which it may be appropriate to use (Scialli, 1992; Haseman & Hogan, 1975). The authors of the study argue that as this is not a "classical" developmental toxicity study and as individual pups were administered the substance directly that the statistical analysis can be based on the number of animals tested rather than on a litter basis. However, it may be that on a litter basis the findings would not be statistically significant. Support for each approach was expressed by the TM, although no agreement was reached on which approach was more appropriate.

The data presented indicate a possible causal link between an observed delay in the onset of activity in male mice and pentaBDPE treatment. The authors report that historical positive and negative control data are available but none were presented in the study report for comparative purposes.

The mean times to reach the platform for each group (treated and controls), from the SM study were presented graphically only and no information on variation (e.g. standard deviation) was presented. The data indicate that during the 4 day "spatial learning" stage of the study that both treated (top-dose animals only) and control animals performed to an equivalent standard. In the "relearning" stage of the study it appears, from the data, that the pentaBDPE treated animals performed markedly better than controls on the first trial, and were comparable at the second trail. The performance of the pentaBDPE treated animals appeared to improve between trials 1 and 3 and then plateau at an 11 second latency period, between trials 4 and 5. The performance of the control animals continually improved between trials 1 and 4 and then plateau at a 5 second latency period As no standard deviation data are

presented it is difficult to judge the degree of variability that might be expected within this study. As with the SB study it is reported that the changes in the activity of pentaBDPE treated animals are statistically significant. However, as for the SB study there are questions over the most appropriate form of statistical analysis. Again no details regarding historical negative or positive control data for this study are reported.

The toxicological significance of these findings is unclear. The authors indicate that similar results have been obtained for substances such as PCBs, which in their view are suspected to be neurotoxic to humans and affect the behaviour of monkeys and rodents. However, a clear interpretation of the significance for human health of the behavioural differences seen in mice has not been established and thus uncertainty as to their significance remains.

4.1.2.9.2 Summary of reproductive toxicity

No fertility studies have been conducted in animals. However, no gross or histopathological evidence of damage to male or female gonads was seen in a 90-day study with oral doses of a commercial preparation of pentaBDPE of up to 100 mg/kg/day. A developmental study in rats has been conducted using a commercial preparation of pentaBDPE; in this study there were no indications of adverse effects on the foetus at doses up to at least 200 mg/kg/day. Developmental effects at higher doses were accompanied by severe maternal toxicity. From the limited data available there is no evidence for developmental toxicity with pentaBDPE.

A study investigating possible neurobehavioural effects in neonatal mice following single exposure to pentaBDPE is available, the results of which suggest differences in behavioural patterns between treated and control animals. However, there remains uncertainties with respect to the significance of the differences observed and their relevance to human health.

4.1.3 Risk Characterisation

4.1.3.0 General aspects

No quantitative data regarding the absorption, metabolism or excretion of pentaBDPE in humans are available, although there is qualitative evidence indicating the potential for absorption. Evidence from humans indicates that pentaBDPE is absorbed probably from environmental sources of exposure (route unknown) and is distributed to the adipose tissue and can be excreted via breast milk. Animal data indicate that pentaBDPE is absorbed following oral administration, although quantitation of the extent of absorption cannot be assessed from the data available. There are no data available regarding the potential absorption of pentaBDPE via the inhalation or dermal routes. However, comparison with structurally similar substances, such as PBBs, and PCBs, suggests that pentaBDPE may be well absorbed by all routes of exposure, although a precise quantified estimate of the extent of absorption cannot be determined. There is only limited information from 2 studies in rats regarding the metabolism of pentaBDPE. Data from these studies indicate that the majority of an orally administered single dose of pentaBDPE is excreted unmetabolised in the faeces over a 72 hour period. There is negligible excretion of pentaBDPE in the urine (<1% of the administered dose). In the faeces minor amounts of metabolites identified as two monomethoxy pentabromodiphenyl ethers and two debrominated monomethoxy tetrabromodiphenyl ethers were found. Mono and dihydroxy metabolites have been identified in bile, together with possible thio-substituted pentabromodiphenyl ethers. The data also demonstrate that pentaBDPE is preferentially deposited to the skin and epididymal adipose tissue (~42%) over

a 72 hour period. Additional animal data indicate that following single oral dosing pentaBDPE is retained in the fatty tissue, with a half-life of elimination in the rat of 25 to 47 days, suggesting that pentaBDPE has a potential to bioaccumulate. It is likely that the half-life for elimination in humans could be much longer. It is unclear whether or not the absorbed and distributed material is the parent compound and/or metabolites. The low water solubility and high molecular weight of parent pentaBDPE suggests that excretion would probably be via the biliary and faecal routes, as well as in breast milk. This view is supported partly by the limited data available from single dose studies in rats where excretion was seen largely via the faecal route.

Animal evidence indicates that pentaBDPE is of low acute toxicity via the inhalation, oral and dermal routes of exposure. PentaBDPE produces only minimal signs of dermal and eye irritation, following single exposure. Signs of respiratory tract irritation have only been observed following single exposures to very high concentrations of pentaBDPE. PentaBDPE does not demonstrate skin sensitisation potential, and is considered unlikely to lead to respiratory sensitisation.

Information concerning the systemic effects in animals following repeated oral exposures to pentaBDPE comes from studies in rats and one in mice involving the administration of commercial mixtures of pentaBDPE. These studies consistently indicate that the liver is the key target organ affected by pentaBDPE. The effects observed include increases in liver weight and hepatocytomegaly with histopathological changes, induction of a range of liver enzymes, and disturbances in cholesterol and porphyrin synthesis. As a consequence of the induction of liver enzymes, T4 levels are reduced in rats and mice leading to increases in thyroid gland weight. However, due to species differences in thyroid hormone balance the effects on thyroid status are not likely to be of relevance to human health. The liver and thyroid changes produced by a commercial preparation of pentaBDPE are apparent within 4 weeks of repeated oral dosing, with effects on the liver at 2 mg/kg/day and above, and changes in thyroid status at 10 mg/kg/day and above. From a well conducted 30-day study in rats administered a commercial preparation of pentaBDPE, a NOAEL of 1 mg/kg/day was identified. At this dose, detailed investigations revealed no effects on liver function, histopathological appearance, or on thyroid status. As this NOAEL is derived for a commercial product of pentaBDPE (DE-71), which contains 50-62% pentaBDPE, and given a maximum oral absorption of 90% we can therefore assume a NOAEL for pentaBDPE of 0.45 mg/kg bw/day, is determined.

A decrease in the *in vitro* production of IgG by Pokeweed stimulated splenocytes, and a decrease in the absolute numbers of double negative (immature $CD4^-$, $CD8^-$) thymocytes, in mice but not in rats was reported as a consequence of Bromkal 70 treatment. No effects were observed at doses or up to and including 18 mg/kg/day in either species. The toxicological significance and relevance to human health of these findings is uncertain.

In the only repeated dermal exposure studies available, pentaBDPE at concentrations ≥ 2.5% were shown to induce dermal irritation (Grade 2 erythema and oedema) or a 'chloracne-like' response in the rabbit ear, following repeated exposures.

Evidence from several well conducted bacterial studies shows that pentaBDPE is not a bacterial cell mutagen. Evidence in mammalian cells stems from a single well conducted cytogenetics assay, which provided negative results, indicating that pentaBDPE is not mutagenic. No studies have been carried out *in vivo*. However, given the negative results

obtained *in vitro* and the apparently limited metabolism of pentaBDPE, it would be expected that negative results would be obtained *in vivo*. No carcinogenicity data are available. No fertility studies have been conducted with pentaBDPE. However, no evidence of gross or histopathological evidence of damage to the gonads or accessory sex organs was seen in a 90-day study with oral doses of DE 71 of up to 100 mg/kg/day. In a developmental study in rats conducted using Saytex 115, there were no indications of adverse effects on the foetus at doses up to at least 200 mg/kg/day. Developmental effects at higher doses were accompanied by severe maternal toxicity. From the limited data available there is no evidence for developmental toxicity with pentaBDPE.

A study investigating possible neurobehavioural effects in mice dosed as neonates is available, the results of which suggest differences in behavioural patterns between treated and control animals. However, there remain uncertainties with respect to the significance of the differences observed and any relevance to human health.

Overall, the toxicological database for pentaBDPE is rather limited particularly in light of the potential for bioaccumulation. However, the minimum data requirements according to Article 9(2) of Regulation 793/93 have been met. From the information available it is apparent that the liver is the principal target organ affected by exposure to pentaBDPE. A NOAEL for effects on the liver can be identified from a detailed 30-day dietary study in rats at 0.45 mg/kg/day. Changes in immune system parameters have been observed in mice, but the significance of the changes seen to human health is unclear. However, no effects were observed at doses or up to and including 18 mg/kg/day, a level more than an order of magnitude greater than that for liver effects. Therefore this endpoint has not been considered further for risk assessment purposes. In addition, repeated dermal administration of pentaBDPE to the rabbit ear produced signs of a chloracne-type of response.

Differences in behaviour between control and mice treated as neonates have been suggested following single oral dosing. Even though the toxicological significance is unclear and the appropriate statistical analyses uncertain, as the lowest dose at which differences were reported (0.8 mg/kg/day) is around the NOAEL for liver effects and because of the uncertainties, this endpoint has been considered for risk assessment purposes.

4.1.3.1 Workers

Introduction

Occupational exposure may occur during the production of flame retardant polyurethane foams. Polyurethane foam are then supplied to end product manufacturers, for example, the automotive and aerospace industries.

The number of workers exposed is not known. As the use of flame retardant polyurethane foams is extensive, the number of workers exposed to pentaBDPE could potentially be equally extensive. However, as there are many other flame retardants available only a proportion will be exposed to those containing pentaBDPE.

PentaBDPE is a viscous liquid with a very low vapour pressure ($7.5 \cdot 10^{-5}$ Pa at 25°C), and a calculated saturated vapour concentration (SVC) of $7 \cdot 10^{-4}$ ppm at 25°C. Therefore exposure to the vapour will not exceed $7 \cdot 10^{-4}$ ppm at ambient temperature. Where pentaBDPE is heated the vapour pressure will rise with a concomitant increase in the SVC. Increases in

temperature may lead to some increase in volatilisation of pentaBDPE, however, this vapour will quickly condense to form a mist. Situations where exposure to mist is possible are likely to be controlled as a result of the nature of the work or the presence of substances of greater concern, for example, isocyanates. During the manufacture of articles from polyurethane foam containing pentaBDPE, exposure will be significantly lower than industries using pentaBDPE itself.

Dermal exposure may occur during the handling of receptacles containing PentaBDPE, and when coming in to contact with vessels and surfaces that have become contaminated from spillages. Dermal exposure may also occur when operators handle polyurethane foam containing pentaBDPE or coated fabrics. The highest exposure is likely to be during the formulation and use of coatings, and the use of pentaBDPE in the manufacture of polyurethane foams. Dermal exposure was predicted to be up to 0.1 mg/cm^2/day using EASE modelling refined for the duration of exposure or concentration of pentaBDPE in the formulation.

Comparison of exposure and effects

The maximum potential airborne concentration of the vapour of pentaBDPE to which workers could be exposed is not likely to exceed $7 \cdot 10^{-4}$ ppm (~0.16 mg m^{-3}), which is the saturated vapour pressure concentration at 25°C. Assuming such exposure occurred over an 8-hour period, that a worker inhales 10 m^3 over an 8-hour shift, weighs 70 kg, and absorbs 100% of the inhaled amount, this could lead to a theoretical body burden of 0.02 mg/kg/day. However, this is likely to be a considerable over-estimate, as it is constructed from a "worst-case" set of assumptions. This worst-case estimate of body burden arising from inhalation exposure (0.02 mg/kg/day) is 22-fold lower than the NOAEL for liver effects of 0.45 mg/kg/day identified from a 30-day repeat dose study in rats (as shown in **Table 4.2**).

In relation to dermal exposure, no data are available on the extent of exposure in workers. However, EASE modelling predicts highest potential exposures of 0.1 mg/cm^2/day. There are no quantitative data regarding the extent of pentaBDPE absorption following dermal exposure. However comparison with structurally similar substances suggests that pentaBDPE may be well absorbed across the skin.

Assuming a maximum dermal exposure area of 2000 cm^2, that a worker weighs 70 kg, and that 60 % dermal absorption (using analogy with structurally-related substances such as PCBs) occurs, a theoretical body burden of ~2 mg/kg/day is estimated. However, this is likely to be a considerable over-estimate, as it is constructed from a "worst-case" set of exposure assumptions. This worst-case estimate of body burden arising from dermal exposure is ~4-fold greater than the NOAEL for liver effects of 0.45 mg/kg/day identified from a 30-day repeated dose study in rats (as shown in **Table 4.2**).

As dermal uptake is the critical route of exposure for workers and as inhalation exposure contributes so little to the total body burden, it is not considered necessary to conduct a risk assessment for combined exposures following simultaneous inhalation and dermal exposures. The MOS calculated from a combined body burden (as shown in **Table 4.2**) will be approximately equivalent to that following dermal exposure only.

Table 4.3 Margin of Safety (MOS) values for risk of liver effects in workers exposed via inhalation and dermally

Route of exposure	Body Burden (mg/kg/day)	MOS for Liver effects (NOAEL 0.45 mg/kg/day)
Inhalation	0.02	22.5
Dermal	~ 2	0.225
Combined	2.02	~ 0.223

The above estimates suggest that the dermal route may be the most significant route of exposure to pentaBDPE occupationally. However, there are considerable uncertainties in this analysis; there are no measured data available, either for the amount of dermal exposure in workers, or for actual extent of dermal absorption. There are also uncertainties regarding the human health significance of the rodent liver effects. Further considerable uncertainties relate to the methods used to calculate the MOS. A comparison has been made between the estimated body burden, albeit using worst-case assumptions, and the NOAEL determined from the 30 day study in rats using a commercial preparation of pentaBDPE (DE-71), which contains 50-62% pentaBDPE. However, pentaBDPE is highly lipophilic and evidence from animal studies suggests that it would bioaccumulate in fatty tissue. Thus the calculation and use as a comparator of a daily body burden is likely to be inappropriate for this substance, where the body burden may increase with time until steady state levels are reached. There is uncertainty about whether or not such accumulated material would remain inert in fatty tissue and thus not contribute to systemic toxicity and consequently whether or not release would be required for expression of toxicity. With respect to the toxicity information, the NOAEL used is from a relatively short-term 30 day study. Given the bioaccumulative nature of the material, it is uncertain whether or not such a NOAEL would be appropriate for much longer term exposures, though information from the 90 day study suggests a similar dose-response relationship at least for that study duration. Thus information from a chronic repeat-dose study may be required.

Overall, these uncertainties indicate that the method used to calculate the above MOS has significant limitations and that further information, including the development of a suitable methodology for the risk assessment of bioaccumulative substances is required.

It would appear that pentaBDPE may have a potential to produce a 'chloracne-like' response in the rabbit ear. The human experience with dioxins and PCBs indicates that this effect is not just associated with skin contact, but can be systemically mediated. However, a NOAEL cannot be identified for this effect, and the risk to workers is uncertain.

Overall, considerable uncertainties exist regarding: the extent of occupational inhalation and dermal exposure, the extent to which dermal absorption may contribute to the overall body burden, the mechanism of the 'chloracne-like' response observed in the rabbit ear study and the approach to risk assessment for this substance. Hence, at this stage, it is not possible to fully characterise the risk to human health for occupational settings.

Conclusion i) There is a need for further information

Recommended action:

Information is needed on the extent of dermal exposure in workers.

The extent of dermal absorption (quantitative data) should be clarified by the conduct of an appropriate dermal absorption study using pentaBDPE (e.g. an *in vitro* study using human or pig skin); depending upon the outcome of this study (i.e. an indication of significant skin absorption) then it may be necessary to undertake an oral toxicokinetic study in order to provide adequate comparative information for interpretation of the oral dosing toxicity studies available.

Health surveillance data are required to investigate signs of chloracne in workers.

Further information should be obtained on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. A methodology should be developed to address this situation. This may involve the conduct of a lifetime study in rodents depending upon the way in which the methodology for assessing lifetime exposure is developed and any data requirements that may be indicated for such a methodology.

4.1.3.2 Consumers

The current use pattern provided by Industry is that pentaBDPE is only used in polyurethane foam and that consumers do not come into direct contact with these foams. The foam is only used in enclosed uses and therefore it is concluded that consumer exposure is negligible.

Since it is concluded that exposure to consumers from pentaBDPE-containing foams is negligible, then it follows that the risk to consumers is also negligible.

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

4.1.3.3 Indirect exposure via the environment

In section 4.1.1.1, the maximum total daily adult human intake (TDHI) of commercial pentaBDPE via the environment is estimated by the EUSES model to be 0.048 mg/kg/day via local sources and $7.9 \cdot 10^{-4}$ mg/kg/day via regional sources.

Margin of Safety (MOS) values (as shown in **Table 4.4**) have been calculated by comparing the TDHI from both regional and local sources with the NOAEL for liver effects derived from the 30-day oral rat study.

Table 4.4 Margin of safety (MOS) values for risk of liver effects in adults following environmental exposure to pentaBDPE

Exposure Scenario	Daily Uptake (mg/kg/day)	MOS based on liver effects (NOAEL 0.45 mg/kg/day)	Conclusion
Regional Sources	$7.9 \cdot 10^{-4}$	570	**i**)
Local Sources	0.048	9.37	**i**)

The low exposure and thus body burden via regional sources and the resultant relatively high MOS (570) would suggest a low concern for the risks of effects on the liver. Conversely the relatively high estimates of exposure and thus body burden via local sources and the MOS of 9.4 would indicate a cause for concern. However, the methodology used to calculate the MOS's is the same as that used above for the worker risk assessment. There are considerable

uncertainties associated both with the toxicity data available and this approach to calculating the MOS. Thus, the uncertainties outlined above under the worker risk assessment also apply to the regional and local exposure scenarios and consequently further information is required, as indicated for the worker risk assessment (i.e. a suitable methodology for risk assessing lifetime exposure of a substance with a potential to bioaccumulate). Furthermore the estimates of local exposure and thus body burden are based on models, thus introducing an additional degree of uncertainty into the calculation of the MOS but suggesting concern for local exposures. In order to confirm that the modelled exposures present realistic estimates, further information is required, specifically measurement of exposure from local sources.

The risks to infants from exposure to human breast milk and cows' milk are characterised later in section 4.1.3.5. The risk to the general population from the consumption of cows' milk is integral to the risk for total exposure via the environment presented above. However, it should be noted that infants may not be the only susceptible part of the population for the cows' milk scenario since this is usually consumed throughout life and, as mentioned above, the methodology does not yet exist to accurately characterise the risk from substances with the potential to bioaccumulate. Further work to refine the above risk characterisation should take this into account.

Thus for risk of liver effects via both regional and local sources of exposure:

Conclusion i) There is a need for further information

Recommended action:

Further information should be obtained on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. A methodology should be developed to address this situation. This may involve the conduct of a lifetime study in rodents depending upon the way in which the methodology for assessing lifetime exposure is developed and any data requirements that may be indicated for such a methodology.

Information is required relating to actual measured exposure data from local sources.

A NOAEL for the potential development of a 'chloracne-like' response cannot be identified from the available data, therefore a risk assessment for this effect cannot be conducted. Furthermore, it is unclear if the effect observed in the rabbit ear is systemically mediated or a local response to repeated application of substance. Further information regarding dermal absorption, as proposed in the occupational exposure risk assessment, would help clarify the mechanism of this effect and any potential risks for this endpoint. However as levels of exposure via local and regional sources are very low it is predicted that any risk to human health are likely to be minimal.

Risk of 'chloracne-like' responses following exposure via regional and local sources:

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

4.1.3.4 Combined exposure

Combined exposures are based on the local environmental exposure and the risk characterisations are presented in **Table 4.5**.

Table 4.5 Risk characterisation for combined exposure

Exposure (mg/kg/day)	MOS based on liver effects NOAEL 0.45 mg/kg/day	MOS based on behavioural differences LOEL 0.8 mg/kg/day	Conclusion for both endpoints
2.068	~0.22	<0.4	i)

The MOS values from the risk characterisation for both liver effects and behavioural effects are unacceptably low. The combined exposure is dominated by the occupational exposure. The estimates of both occupational exposure and exposure via the environment are derived from models. The estimates require revising either by refinement of the models or the provision of measured data in order to determine whether risk reduction measures should be considered.

In addition, as described for workers in section 4.1.3.1, there is a need to obtain information on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. Hence **conclusion i**) is reached.

Conclusion i) There is a need for further information

The further information is that described in section 4.1.3.1 and section 4.1.3.3.

4.1.3.5 Exposure to infants via milk

4.1.3.5.1 Exposure to infants via human breast milk

PentaBDPE has been shown to be present in human breast milk. It is, therefore, appropriate to assess whether or not this presents a risk to breast-feeding babies. Although the environmental exposure estimates, provided in section 4.1.1.3, are for both local and regional sources, given the nature of the actual available data it is not possible to interpret the origin of the exposures giving rise to the levels of pentaBDPE in human breast milk. Therefore, for the purposes of risk assessment, exposure of infants via the breast milk is considered in a generic manner applying to local and/or regional sources of exposure.

Data regarding levels of polyBDPE in individual human breast milk samples are available (Darnearud *et al* 1999). From these data the 97.5 percentile level of polyBDPE present in human breast milk has been determined as being 10 000 pg polyBDPE per gram of fat. Data are also available (Meironyté *et al* 1999 and Darnearud *et al* 1999) which indicate that, of the polyBDPEs measured in human breast milk samples, tetraBDPE is the major constituent accounting for 60 - 70% of the total polyBDPEs measured. Other polyBDPE congeners detected were tri-, penta-, and hexa-BDPE. Based on this information an estimate of the levels of pentaBDPE present in the breast milk of 30% of the total polyBDPE can be assumed. Therefore, using the Darnearud *et al*, 1999 data for total polyBDPEs in breast milk, it is possible to calculate a 97.5 percentile level of pentaBDPE in the human breast milk of 3000 pg pentaBDPE per gram of fat (i.e. 30% of 10 000 pg/g).

In evaluating the body burden of polyBDPE and of pentaBDPE in an infant as a result of breast-feeding a cautious approach is adopted. It is assumed that an infant breast feeds for 1 year, and that this year of life is subdivided into two periods (0 to 3 months and 3 to 12 months), reflecting the changing feeding demands of the infant. It is assumed that over the first 3 months the infant has an average weight of 6 kg (data taken from the UK growth charts, published by the Child Growth Foundation, London 1995; Freeman *et al* in press and Cole 1994), that the infant ingests 0.8 kg of milk per day, that 100 % of the ingested pentaBDPE is absorbed and that the breast milk has a fat content of 3.5% (WHO 1998). From 3 to 12 months it is assumed that the infant has an average weight of 10 kg (data taken from same source as above), that the infant ingests 0.5 kg of milk per day, that 100 % of the ingested pentaBDPE is absorbed and that the breast milk has a fat content of 3.5% (WHO 1998). It is also assumed that the content of polyBDPE and pentaBDPE remains constant during the breast-feeding period.

Using the following equation and the assumptions, as detailed above, the average daily uptake (ADU_{infant}) of the breast-feeding infant is estimated for both the 0-3 month and 3-12 month periods of infant life. The resultant uptakes are then summed to generate an average uptake for the infant in mg/kg/day.

$$ADU_{infant} = \frac{C_{milk\text{-}fat} \cdot f3 \cdot f4 \cdot IR_{milk}}{BW_{infant}}$$

where:

$C_{milk\ fat}$	represents the concentration of the polyBDPE or pentaBDPE in mg per kg of fat in the breast milk (derivation of polyBDPE/pentaBDPE milk levels to mg/kg given below) (0.01)
f_3	represents the fraction of fat in the breast milk (3.5/100=0.035)
f_4	represents the fraction of the ingested pentaBDPE absorbed (100/100=1)
IR_{milk}	represents the ingestion rate of milk by the infant (kg/day)
BW_{infant}	represents the average infant body weight over the exposure period (kg)

Derivation of polyBDPE and pentaBDPE milk levels to mg/kg fat

PolyBDPE

10 000 pg	PolyBDPE measured per g of breast milk fat
$10\,000 \cdot 10^{-12}$ g	PolyBDPE per g of fat
$1 \cdot 10^{-8}$ g	PolyBDPE per g of fat
$1 \cdot 10^{-5}$ mg	PolyBDPE per g of fat
$1 \cdot 10^{-5}$ mg	PolyBDPE per $1 \cdot 10^{-3}$ kg of fat
$1 \cdot 10^{-2}$ mg	PolyBDPE per 1 kg of fat
0.01 mg	PolyBDPE per kg of fat

PentaBDPE

3000 pg	PentaBDPE measured per g of breast milk fat
$3000 \cdot 10^{-12}$ g	PentaBDPE per g of fat
$3.0 \cdot 10^{-9}$ g	PentaBDPE per g of fat
$3.0 \cdot 10^{-6}$ mg	PentaBDPE per g of fat

$3.0 \cdot 10^{-6}$ mg	PentaBDPE per $1 \cdot 10^{-3}$ kg of fat
$3.0 \cdot 10^{-3}$ mg	PentaBDPE per 1 kg of fat
0.0030 mg	PentaBDPE per kg of fat

The calculations of uptake have been conducted with respect to both polyBDPE and pentaBDPE in order to provide a complete and comparative assessment of uptake. Full details of each calculation are presented below in **Table 4.1.3.5.a**.

PolyBDPE

0-3 months:

$$ADU_{infant} = \frac{0.01 \cdot 0.035 \cdot 1 \cdot 08}{6} = 0.00005 \text{ mg/kg/day}$$

3-12 months:

$$ADU_{infant} = \frac{0.01 \cdot 0.035 \cdot 1 \cdot 05}{10} = 0.00002 \text{ mg/kg/day}$$

Average for first 12 months:

ADU_{infant} = 0.00007 mg/kg/day

= $7 \cdot 10^{-5}$ mg/kg/day /2

ADU_{infant} = $3.5 \cdot 10^{-5}$ mg/kg/day

PentaBDPE

0-3 months:

$$ADU_{infant} = \frac{0.0030 \cdot 0.035 \cdot 1 \cdot 08}{6} = 0.00014 \text{ mg/kg/day}$$

3-12 months:

$$ADU_{infant} = \frac{0.0030 \cdot 0.035 \cdot 1 \cdot 05}{10} = 0.00053 \text{ mg/kg/day}$$

Average for first 12 months:

ADU_{infant} = 0.000019 mg/kg/day

= $1.9 \cdot 10^{-5}$ mg/kg/day /2

ADU_{infant} = $0.95 \cdot 10^{-5}$ mg/kg/day

MOS Generation

MOS values (as shown in **Table 4.6**) have been estimated by comparing the ADU of the breast-fed infant for both polyBDPE and pentaBDPE with the NOAEL for liver effects (as derived from a 30-day oral rodent study using a commercial preparation of pentaBDPE). For risk assessment purposes the ADUs have also been compared with the lowest dose of

0.8 mg/kg/day used in Eriksson et al (1998, 1999), even though there are uncertainties over the statistical analysis and interpretation of the significance to human health of the observed differences in behaviour in mice dosed as neonates.

Table 4.6 MOS values for liver effects and behavioural differences in infants exposure to pentaBDPE via breast milk

Exposure scenario	Daily Uptake (mg/kg/day)	MOS Liver effects (NOAEL 0.45 mg/kg/day)	MOS Behavioural Differences (LOEL 0.8 mg/kg/day)
Breast Milk (PolyBDPE)	$3.5 \cdot 10^{-5}$	12 857	22 857
Breast Milk (PentaBDPE)	$0.95 \cdot 10^{-5}$	47 368	84 111

The MOS values calculated using the ADU_{infant}, NOAEL for liver effects and "LOEL" for differences in behaviour are clearly large being ~12 850- 22 850 for polyBDPE and 47 360 – 84 111 for pentaBDPE. Normally such large MOS values would be indicative of a reassuring difference between the estimated body burden and the levels at which toxicity is observed, even allowing for extrapolation between and within species (traditionally a factor of 10 for each), the short term duration of the toxicity studies (again conventionally using a factor of 10 to allow for extrapolation from short to long term) and that the population of interest, the breast feeding infant, may be unusually sensitive (again allowing a factor of 10). This would lead to little cause for concern and thus a **conclusion** (**ii**) under ESR. However, it is important to consider the interpretation of the MOS values in light of the state of scientific knowledge and uncertainties in the analysis.

The estimates of ADU_{infant} are based on measurements of polyBDPE in human breast milk and assumptions regarding the pentaBDPE content, the feeding infant, its daily consumption and uptake of the substance. Some of the assumptions would seem reasonable (average body weight, milk intake, fat content) as they are based on available information. The proportion of pentaBDPE assumed to be present in the milk is also based on available data. The absorption of pentaBDPE is unknown and therefore as a worst case it is assumed that all is absorbed; this might represent an overestimate. It is also assumed that the concentration of pentaBDPE in milk is constant with time, both over the one-year duration of feeding for an infant and for the population of breast feeding mothers throughout the years of their child bearing potential. In relation to the one-year feeding duration, it is likely that levels of polyBDPE/pentaBDPE would be higher during early breast feeding as the substance stored in fatty tissue becomes mobilised but as these stores deplete then the levels may fall during the later stages in breast feeding. Unfortunately, from the available data it is not possible to determine the time course of excretion via breast milk. The consequence is that it is unclear whether or not the calculated 97.5 percentile is a reasonable value to use in a calculation. In order to clarify this, further information on the time course of the excretion of pentaBDPE in breast milk is required.

With respect to the variation in time of levels of pentaBDPE in breast milk in the population, the available data indicate that they have been increasing, albeit at low concentrations and at a low rate, with time over the 25 year period 1972 - 1997. It is unclear whether or not this trend will continue into the future. It may be that levels in the population could increase further or may increase only a little further (or not at all) once steady state with environmental levels is reached. Knowledge of such trends is important in terms of risk assessment as any further increases in the levels in breast milk would serve to reduce the

value of MOS as exposure (and thus body burden) would increase. Thus in order to determine the trends further information is required through the continued monitoring of levels in breast milk in future years.

Turning to a consideration of the toxicity information there are a number of important uncertainties that need to be considered. The NOAEL for liver effects is obtained from a 30 day study. As argued above under the risk assessment for workers, this relatively short-term study is considered insufficient in assessing the risk from a bioaccumulative substance and data from a longer term study may be required. Furthermore, it is unclear whether or not the liver of the young animal is more or less susceptible to the effects of pentaBDPE than the adult animal; further information is required to assess any differences in response with age. Because of concerns relating to development, the risk assessment has also been conducted comparing the estimated body burdens via uptake from milk with the lowest dose used in the study in which differences in behaviour between mice dosed as neonates with pentaBDPE or vehicle were possibly observed. There are a number of uncertainties regarding this study including the significance of the observations made to human health and development. Although, in the view of the rapporteur, no firm conclusions can be drawn from this study, further work is required in order to determine whether or not these apparent differences are reproducible, to determine the effects of repeated oral dosing (the available study only used a single dose) and to investigate further the relationship, if any, between differences in behaviour and human development. Over and above the uncertainties relating to liver effects and differences in behaviour, given that pentaBDPE has been measured in human breast milk, the scientific database is lacking significant information on whether or not other effects may be produced in breast feeding offspring as no standard study on reproduction including the lactation period is available.

Since pentaBDPE can bioaccumulate there would be a need to consider lactation following exposure of more than one generation. Thus in order to investigate whether or not other effects might be observed through exposure to breast milk a multi-generation reproduction study is required. Designed correctly, such a study could also help to address the issue of whether or not the young animal is more sensitive to liver effects and whether or not differences in behaviour are produced.

It is clear, therefore, that a considerable amount of uncertainty remains with respect to this risk assessment. Thus although large MOS values were calculated the uncertainties are such that it is currently not possible to say whether or not these MOSs provide reassurance of little or no risk to the breast feeding infant either at the present time or in the future. However, much of the uncertainty could be reduced by the gathering of further information as indicated above and thus for exposure of infants via breast milk a **conclusion** (**i**) there is a need for further information and/or testing is reached.

The following information is required:

- information on the toxicokinetics of pentaBDPE with respect to breast milk including uptake from breast milk into the infant, the time course of the excretion via breast milk during lactation in humans and the future trends in levels in human breast milk;

- information on the relative toxicity to the liver of pentaBDPE in young (neonatal) and adult animals;

- further studies on potential effects on behaviour following neonatal dosing in order to determine the reproducibility of effects, the effects of repeated dosing and the significance of the effects to human development;

- a multi-generation reproduction study in order to investigate whether or not other effects might be observed through exposure to breast milk. Designed correctly, such a study could address the issue of whether or not the young animal is more sensitive to liver effects and whether or not differences in behaviour are produced.

Need for immediate consideration of risk reduction measures?

It is noted, however, that much of the information required above (and for other areas of the risk assessment such as the need for a long term toxicity study) will take some considerable time to be generated or gathered. There is evidence that pentaBDPE is highly persistent and bioaccumulative. Also, of particular note, it has been detected, albeit at relatively low levels, in human breast milk, the levels increasing with time. These properties and data are of concern in themselves, although, as indicated in the analysis above, with the available information it is not possible to say whether or not on a scientific basis there is a current or future risk to human health. However, given these properties, it would be of concern if by the time the further information has been gathered the analysis indicated a risk to breast feeding infants.

Thus, although it is concluded that further information should be gathered in order to refine the risk assessment, in light of the properties of pentaBDPE and the time it would take to gather the information, consideration should be given at a policy level of the need to take risk reduction measures now in the absence of adequate scientific knowledge and thus the need for consideration of risk reduction options at this time.

4.1.3.5.2 Exposure to infants via cows' milk

Estimates for the concentration of pentaBDPE in cows' milk using the EUSES model are presented in section 4.1.1.3. The concentration estimated for local sources is 66 µg/kg which is higher than the measured levels found in human breast milk (generally 2-4 µg/kg lipid). The concentration estimated for regional sources is about 2 µg/kg which is similar to that found in human breast milk. Given that intake of cows' milk can be similar to, or greater than, that of human breast milk during the first year of life, on the basis of the risk characterisation in section 4.1.3.5.1, it is likely that similar or slightly higher MOS values would be calculated. These calculations would also be subject to some of the uncertainties outlined in section 4.1.3.5.1. However, the risk characterisation for human breast milk was based on measured concentration data whereas the exposure values for cow's milk are modelled estimates. It is considered that in addition to some of the information required in the conclusion i for exposure to human breast milk (section 4.1.3.5.1), the exposure estimates for cows' milk should be investigated further in order to improve the accuracy of the risk characterisation.

Hence **conclusion (i)** is reached.

Conclusion i) There is a need for further information

The following information is required:

- information on the toxicokinetics of pentaBDPE with respect to cows' milk including uptake from milk into the infant;

- information on the relative toxicity to the liver of pentaBDPE in young (neonatal) and adult animals;

- further studies on potential effects on behaviour following neonatal dosing in order to determine the reproducibility of effects, the effects of repeated dosing and the significance of the effects to human development;

There is a need for exposure information from local and regional sources on the concentration of pentaBDPE in cows' milk.

4.2 HUMAN HEALTH (PHYSICO CHEMICAL PROPERTIES)

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

PentaBDPE has a very low vapour pressure, no explosive or oxidising properties and retards combustion. It does have a high viscosity and is likely to cling to human tissue but this can be easily avoided by gloves. Therefore, it can be concluded that there is no cause for concern for human health arising out of the physico-chemical properties.

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

5 RESULTS

5.1 INTRODUCTION

Pentabromodiphenyl ether is used as an additive flame retardant mainly in the polyurethane foam industry. The commercially supplied product is a mixture of brominated diphenyl ethers. Generally, the commercially supplied product consists of 50-62% w/w pentabromodiphenyl ether, 24-38% w/w tetrabromodiphenyl ether, 4-12% w/w hexabromodiphenyl ether, with traces of tri- and heptabromodiphenyl ether. The product is a viscous liquid or semi-solid with low vapour pressure and water solubility.

PentaBDPE is not currently manufactured in the EU. The amount imported into the EU has declined in recent years, and is currently < 150 tonnes/year (as of 1999).

5.2 ENVIRONMENT

Local releases of pentaBDPE to the environment may occur from the manufacture and processing of polyurethane foam. In addition, losses of the flame retardant from finished articles may occur during the lifetime of the article (e.g. due to volatilisation or loss of particlulates). These releases have been quantified in the assessment and used to calculate PECs for various environmental compartments. Releases to the environment could also occur from the disposal (e.g. to landfill) of finished articles. It has not proved possible to quantify fully the releases from disposal and so these have been considered qualitatively in the assessment.

For the aquatic compartment the PEC/PNEC ratio is <1 for surface water but >1 for sediment from local sources. Concern at the regional level for water and sediment is low.

For the terrestrial compartment, the PEC/PNEC is >1 for local sources. Concern at the regional level is low.

No adverse effects are expected on the atmosphere from the use of pentaBDPE.

The available information indicates a risk from secondary poisoning from both local and diffuse sources of release. High concentrations of pentaBDPE are predicted in and have been measured in fish from close to sources of release. These result in a PEC/PNEC >1. The regional concentrations in earthworms also result in a PEC/PNEC >1. In addition, the substance appears to be transported widely in the environment and accumulates through the food chain.

Result

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

There is a data gap for toxicity to sewage microorganisms. A test on sewage treatment plant microorganisms would be required if this data gap were to be filled.

It is possible that in the long term levels in all compartments may increase as a result of releases from waste sites. No agreed methods for assessing this release currently exist in the Technical Guidance Document, but preliminary estimates have been incorporated into the

assessment. These estimates are highly uncertain. This, and life-time exposure, may need to be considered further in any revision of this risk assessment report.

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

This applies to the aquatic (surface water and sediment) compartment and the terrestrial compartment at the region level, the aquatic (surface water) compartment at the local level, and to the assessment of atmospheric effects.

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

This applies to the assessment of secondary poisoning arising from use in polyurethane foams, due to both local releases from foam production sites and diffuse releases arising from use of the foam. Once released to the environment from both point and diffuse sources, the substance appears to be transported widely and accumulates through the food chain.

It also applies to the local assessment for sediment and the terrestrial compartment.

It should also be noted that although not a formal conclusion of the risk assessment, the properties of the substance and evidence of long-range transport indicate that it may need to be considered further by other regulatory bodies dealing with persistent organic pollutants (POPs) which may be transported long distances in the atmosphere.

5.3 HUMAN HEALTH (TOXICOLOGICAL PROPERTIES)

The toxicity database for pentaBDPE is limited, but the minimum data requirements according to Article 9(2) of Regulation 793/93 have been met. PentaBDPE is of low acute toxicity by inhalation, oral and dermal routes of exposure. It lacks significant irritant properties to the skin and eye, with respiratory tract irritation only occurring at very high exposure concentrations (> 8000 ppm). PentaBDPE also lacks sensitisation potential. Repeated dose oral studies in rodents indicate that the liver is the principal target organ affected by pentaBDPE. From a well conducted 30-day study in rats administered a commercial preparation of pentaBDPE, a NOAEL of 1 mg/kg/day was identified.

As this NOAEL is derived for a commercial product of pentaBDPE (DE-71), which contains 50-62% pentaBDPE, and given a maximum oral absorption of 90% we can therefore assume a NOAEL for pentaBDPE of 0.45 mg/kg bw/day, is determined. A decrease in the *in vitro* production of IgG by Pokeweed stimulated splenocytes, and a decrease in the absolute numbers of double negative (immature $CD4^-$, CD8) thymocytes in mice, but not in rats, was reported as a consequence of Bromkal 70 treatment. No effects were observed at doses or up to and including 18 mg/kg/day in either species. The toxicological significance and relevance to human health of these findings is uncertain. A repeated dose dermal study in the rabbit ear model indicates that pentaBDPE has the potential to induce a 'chloracne-like' response.

Negative results from bacterial and from one well conducted mammalian cell assay *in vitro* indicates that pentaBDPE would not be mutagenic *in vivo*. There are no carcinogenicity data for pentaBDPE. There are no fertility studies available for pentaBDPE, but in a well conducted 90-day study no histological changes were observed in the gonads or accessory

sex organs of either sex at doses up to 100 mg/kg/day of a commercial preparation of pentaBDPE. In a developmental study no evidence for specific developmental toxicity was seen with pentaBDPE when tested up to maternally toxic doses. A study investigating possible neurobehavioural effects in neonatal mice is available, the results of which suggest differences in behavioural patterns between treated and control animals. However, there remains uncertainties with respect to the significance of the differences observed and their relevance to human health.

5.3.1 Occupational Exposure

The potential for inhalation exposure to pentaBDPE in the occupational setting is considered to be very low, particularly in view of the very low saturated vapour pressure of this substance. There are no measured data on dermal exposure, but modelled data suggest that this may be the most significant route of exposure in workers. There are no human data on the health effects of pentaBDPE, but toxicity studies in animals provide evidence for marked disturbances of liver metabolism and possibly the development of a 'chloracne-like' response. The estimated body burden of pentaBDPE arising from occupational exposure, chiefly via dermal contact, is approximately 4-fold greater than the NOAEL of 0.45 mg/kg/day for rodent liver effects. However, the relevance of the rodent liver effects to human health is uncertain.

There are considerable number of uncertainties in this analysis; there are no measured data available, either for the amount of dermal exposure in workers, or for actual extent of dermal absorption. There are also uncertainties regarding the human health significance of the rodent liver effects. Further considerable uncertainties relate to the methods used to calculate the MOS. A comparison has been made between the estimated body burden, albeit using worst-case assumptions, and the NOAEL from the 30 day study in rats (for a commercial preparation of pentaBDPE). However, pentaBDPE is highly lipophilic and evidence from animal studies suggests that it would bioaccumulate in fatty tissue. Thus the calculation and use as a comparator of a daily body burden is likely to be inappropriate for this substance, where the body burden may increase with time until steady state levels are reached. There is uncertainty about whether or not such accumulated material would remain inert in fatty tissue and thus not contribute to systemic toxicity and consequently whether or not release would be required for expression of toxicity. With respect to the toxicity information, the NOAEL used is from a relatively short-term 30 day study. Given the bioaccumulative nature of the material, it is uncertain whether or not such a NOAEL would be appropriate for much longer term exposures, though information from the 90 day study suggests a similar dose-response relationship at least for that study duration. Thus information from a chronic repeat-dose study may be required.

Overall, these uncertainties indicate that the method used to calculate the above MOS has significant limitations and that further information, including the development of a suitable methodology for the risk assessment of bioaccumulative substances is required.

Overall risk assessment conclusions for occupational exposure:

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

Information is needed on the extent of dermal exposure in workers.

The extent of dermal absorption (quantitative data) should be clarified by the conduct of an appropriate dermal absorption study using pentaBDPE (e.g. an *in vitro* study using human or pig skin); depending upon the outcome of this study (i.e. an indication of significant skin absorption) then it may be necessary to undertake an oral toxicokinetic study in order to provide adequate comparative information for interpretation of the oral dosing toxicity studies available.

Health surveillance data are required to investigate signs of chloracne in workers.

Further information should be obtained on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. A methodology should be developed to address this situation. This may involve the conduct of a lifetime study in rodents depending upon the way in which the methodology for assessing lifetime exposure is developed and any data requirements that may be indicated for such a methodology.

5.3.2 Consumers

Consumer exposure to pentaBDPE is negligible since in the EU pentaBDPE is only used in polyurethane foam enclosed in products. It follows that risks to consumers are also negligible.

Hence **conclusion** (**ii**) is reached:

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

5.3.3 Indirect exposure via the environment

There are considerable uncertainties associated both with the toxicity data available and the approach to calculating the MOS for indirect exposure via the environment, and also with respect to the modelled exposure data used for local sources of exposure. Thus the uncertainties outlined for the worker risk assessment also apply to the exposure scenarios of regional and local sources of exposure and consequently further information is required, as indicated for the worker risk assessment (e.g. a suitable methodology for risk assessing lifetime exposure of a substance with a potential to bioaccumulate). Furthermore the estimates of local exposure are based entirely on modelled data, thus introducing an additional degree of uncertainty into the calculation of the MOS. In order to refine the calculation of the MOS and the risk assessment for local sources of exposure further information relating to actual measured exposure data is required.

Thus for risk of liver effects via both regional and local sources of exposure:

Conclusion i) There is a need for further information.

Further information should be obtained on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. A methodology should be developed to address this situation. This may involve the conduct of a lifetime study in rodents depending upon the way in which the methodology for assessing lifetime exposure is developed and any data requirements that may be indicated for such a methodology.

Information is required relating to actual measured exposure data from local sources.

Conclusion (**ii**) is reached for the potential development of a 'chloracne-like' response. Although an NOAEL cannot be identified from the available data, levels of exposure via local and regional sources are very low. It is, therefore, predicted that any risk to human health is likely to be minimal.

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

5.3.4 Combined exposure

The MOS values from the risk characterisation for both liver effects and behavioural effects are unacceptably low. The combined exposure is dominated by the occupational exposure. The estimates of both occupational exposure and exposure via the environment are derived from models. The estimates require revising either by refinement of the models or the provision of measured data in order to determine whether risk reduction measures should be considered.

In addition, as described for workers in section 4.1.3.1, there is a need to obtain information on the effects of prolonged (e.g. lifetime) exposure for a substance that has the potential to accumulate within the body. Hence **conclusion** (**i**) is reached.

Conclusion i) There is a need for further information**.**

The further information required is that described in section 4.1.3.1 and section 4.1.3.3.

5.3.5 Exposure to infants via milk

For infants fed human breast milk the MOS values calculated using the ADU_{infant}, NOAEL for liver effects and "LOEL" for differences in behaviour are clearly large being ~12 850-22850 for polyBDPE and 47 360 – 84 111 for pentaBDPE. Normally such large MOS values would lead to little cause for concern and thus a conclusion (ii) under ESR. However, it is important to consider the interpretation of the MOS values in light of the state of scientific knowledge and uncertainties in the analysis. The estimates of ADU_{infant} are based on measurements of polyBDPE in human breast milk and numerous assumptions regarding the pentaBDPE content, the feeding infant and regarding the significance of toxicological endpoints of concern to the neonate (detailed in section 4.1.3.5.1).

It is clear that a considerable amount of uncertainty remains with respect to this risk assessment. Thus although large MOS values were calculated the uncertainties are such that it is currently not possible to say whether or not these MOSs provide reassurance of little or no risk to the breast feeding infant either at the present time or in the future. However, much of the uncertainty could be reduced by the gathering of further information as indicated above (in section 4.1.3.5.1) and thus, for exposure of infants via breast milk, conclusion (**i**) is reached.

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

The following information is required:

- information on the toxicokinetics of pentaBDPE with respect to breast milk including uptake from breast milk into the infant, the time course of the excretion via breast milk during lactation in humans and the future trends in levels in human breast milk;

- information on the relative toxicity to the liver of pentaBDPE in young (neonatal) and adult animals;

- further studies on potential effects on behaviour following neonatal dosing in order to determine the reproducibility of effects, the effects of repeated dosing and the significance of the effects to human development;

- a multi-generation reproduction study in order to investigate whether or not other effects might be observed through exposure to breast milk. Designed correctly, such a study could address the issue of whether or not the young animal is more sensitive to liver effects and whether or not differences in behaviour are produced.

Need for immediate consideration of risk reduction measures?

It is noted, however, that much of the information required above (and for other areas of the risk assessment such as the need for a long term toxicity study) will take some considerable time to be generated or gathered. There is evidence that pentaBDPE is highly persistent, bioaccumulative and of particular note has been detected, albeit at relatively low levels, in human breast milk, the levels increasing with time. These properties and data are of concern in themselves, although, as indicated in the analysis above, with the available information it is not possible to say whether or not on a scientific basis there is a current or future risk to human health. However, given these properties, it would be of concern if once the further information has been gathered the analysis indicated a risk to breast feeding infants.

Thus, although it is concluded that further information should be gathered in order to refine the risk assessment, in light of the properties of pentaBDPE and the time it would take to gather the information, consideration should be given at a policy level of the need to take risk reduction measures now in the absence of adequate scientific knowledge and thus the need for consideration of risk reduction options at this time.

For infants fed cows' milk: estimates for the concentration of pentaBDPE in cows' milk using the EUSES model are higher than (local sources) or similar to (regional sources) the measured levels found in human breast milk. Given that intake of cows' milk can be similar to, or greater than, that of human breast milk during the first year of life, on the basis of the risk characterisation in section 4.1.3.5.1, it is likely that similar or slightly higher MOS values would be calculated. These calculations would also be subject to some of the uncertainties outlined in section 4.1.3.5.1. However, the risk characterisation for human breast milk was based on measured concentration data whereas the exposure values for cows' milk are modelled estimates. It is considered that in addition to some of the information required in the conclusion i reached for exposure to human breast milk (section 4.1.3.5.1), the exposure estimates for cows' milk should be refined in order to improve the accuracy of the risk characterisation.

Hence **conclusion** (**i**) is reached.

Conclusion i) There is a need for further information.

The following information is required:

- information on the toxicokinetics of pentaBDPE with respect to cows' milk including uptake from milk into the infant;
- information on the relative toxicity to the liver of pentaBDPE in young (neonatal) and adult animals;
- further studies on potential effects on behaviour following neonatal dosing in order to determine the reproducibility of effects, the effects of repeated dosing and the significance of the effects to human development;

There is a need for exposure information from local and regional sources on the concentration of pentaBDPE in cows' milk.

5.4 HUMAN HEALTH (PHYSICO-CHEMICAL PROPERTIES)

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

Hence **conclusion** (**ii**) is reached:

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

5.5 NOTE FOR ALL INFORMATION REQUIRED UNDER CONCLUSION (i)

A risk reduction strategy has been developed which proposes a restriction on the marketing and use of pentaBDPE under Directive 76/769/EEC. If this strategy is adopted, then all testing requirements should be adjourned unless expert advice is provided which indicates that a test may be relevant to the controls which emerge from negotiations under Directive 76/769/EEC.

Penta addendum 17th October 2001

The dermal absorption of tetrabromodiphenyl ether (TeBDPE) was evaluated in a well conducted study in which it was used as a surrogate for pentabromodipenyl ether (PeBDPE) (Inveresk Research, 2000). It was used as a surrogate on the basis that its absorption through the skin would be similar to, if not greater than that of PeBDPE; as compared to PeBDPE its water solubility is higher, its lipophilicity is probably higher and its molecular weight is lower. In addition, it is the second most abundant congener within the PeBDPE commercial product and unlike PeBDPE it can be synthesized as a pure compound.

^{14}C TeBDPE was applied to dermatomed skin membranes *in vitro* using a flow through diffusion cell system. Twelve samples of human skin (breast skin) from 8 donors and 10 samples of rat skin (dorsal skin) from 6 different animals were used. The surface area of exposed skin within the diffusion cells was $0.64cm^2$. A volume of 32µl TeBDPE was applied in acetone (20% w/v); the dermal area dose was $10mg.cm^{-2}$. The donor chamber of the diffusion cells was unoccluded, allowing the acetone vehicle to evaporate. The receptor fluid, ethanol (concentration not stated), was collected hourly for the first six hours post dosing and then every 2 hours up until 24 hours. The integrity of the barrier function was assessed for all skin samples prior to the main study using tritiated water. Any sample exhibiting a Kp greater than $2.5x10^{-3}cm.h^{-1}$ was excluded from the study.

At the end of the 24-hour study period the unabsorbed dose (i.e. the amount remaining on the skin surface and the amount in the stratum corneum), the absorbed dose (i.e. the amount in the receptor fluid) and the dermal delivery (i.e. the absorbed dose and the amount remaining in the dermis) of TeBDPE were determined by liquid scintillation counting.

The mean recovered dose using the human and rat skin samples was 100.69% and 100.21% respectively. The dermal delivery of TeBDPE applied to human skin was 3.13% ± 1.5% of the applied dose; of this 1.94% ± 0.98% was absorbed. Of the 97.56% of the unabsorbed dose 4.45% was in the stratum corneum. The dermal delivery of the substance to the rat skin was 17.94% ± 11.12% of the applied dose, of this 14.81% ± 11.50% was absorbed. Of the 82.27% of the unabsorbed dose 9.08% was in the stratum corneum.

Based on the results of this study it can be concluded that TeBDPE shows limited absorption through human skin, in the region of 3%. Furthermore, based on this result, it can also be concluded that PeBDPE will have limited absorption through human skin. However, overall the results of this study do not affect the conclusions of the Risk Assessment Report for PeBDPE.

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GLOSSARY

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

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

PNEC(s)	predicted no effect concentration(s)
$PNEC_{water}$	predicted no effect concentration in water
(Q)SAR	quantitative structure activity relation
STP	sewage treatment plant
TGD	Technical Guidance Document[6]
UV	ultraviolet region of spectrum
UVCB	Unknown or Variable composition, Complex reaction products or Biological material
v/v	volume per volume ratio
w/w	weight per weight ratio

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

Appendix A Decomposition products formed during use as flame retardants

Much concern has been expressed over the possible formation of brominated dibenzofurans, and to a lesser extent, brominated dibenzo-*p*-dioxins from brominated diphenyl ethers during production, processing, use, accidental fires and disposal (e.g. incineration). This Appendix reviews the known data on all polybrominated diphenyl ethers on this issue and attempts to draw some conclusions from the data with regards to the environmental exposure. Occupational exposure to breakdown products formed from octa- and decabromodiphenyl ether is considered in the risk assessment reports for these two substances.

Analytical methods

An important consideration when assessing the extent of formation of brominated dibenzofurans from brominated diphenyl ethers is the analytical method used. Due to the lack of analytical standards, both for the brominated dibenzofurans and for the brominated diphenyl ethers, there is a possibility of incorrectly assigning chromatographic peaks. This could be a severe problem when determining brominated dibenzofurans in the presence of brominated diphenyl ethers. This arises for several reasons as discussed below.

Most analyses of brominated dibenzofurans are carried out using a gas chromatographic (GC) system, using either electron capture detector (ECD), which is fairly specific for halogen atoms, or low- or high-resolution mass spectrometry (MS).

The GC-MS system can be used in two main modes. The most common mode, usually giving the greatest sensitivity, is selected ion monitoring (SIM). In this mode, the masses of a few characteristic ions of the compound of interest are used for detection. For brominated furans, the ions most commonly monitored are around the molecular weight of the compound of interest (since bromine exists as two main isotopes, ^{79}Br and ^{81}Br, in the approximate ratio 1:0.979, a cluster of ions around the molecular mass ion is obtained). Such an approach is usually reasonably specific for the detection of the compound of interest since it only detects ions of a specific mass. However, when determining brominated dibenzofurans in the presence of brominated diphenyl ethers, severe analytical interferences can occur. This is because in the mass spectrometer, both types of compound fragment mainly by losing Br_2. When this occurs in the brominated diphenyl ether, it is possible that a brominated dibenzofuran will be formed. This will then behave identically to any other brominated dibenzofuran present in the sample, leading to an overestimate of the concentration of dibenzofuran originally present in the sample or even to a false positive identification of the brominated dibenzofuran. This problem is magnified by the lack of analytical standards for the brominated dibenzofurans to allow positive identification and quantification of the chromatographic peaks in the analysis. It is interesting to note that in many analyses, the only analytical standard is 2,3,7,8-tetrabromodibenzofuran, and that the concentration of this is almost always much less than that of the other brominated dibenzofurans detected in the analysis.

Analyses achieved by GC-MS in the full scan mode or by GC-ECD again suffer from the lack of analytical standards to allow a positive identification of any suspected peak in the chromatogram.

With regard to the analysis of brominated-*p*-dioxins, the problem of possible interference from polybrominated diphenyl ethers is less when analysis is carried out by GC-MS in SIM

mode, however, again there is a lack of analytical standards to allow positive identification and quantification of the chromatographic peaks (again 2,3,7,8-tetrabromodibenzo-*p*-dioxin is often the only compound available).

The problems of analysis of brominated dibenzofurans in the presence of brominated diphenyl ethers has been discussed by Cramer et al (1990), Bonilla et al (1990), Hileman et al (1989), Ebert et al, 1999 and Donnelly et al (1987) and criteria for confirmation of gas chromatography - mass spectrometry analysis have been developed (Donnelly et al, 1987). All these methods stress that brominated diphenyl ethers cause significant interference in the analysis of brominated dibenzofurans by GC-MS and the sample clean-up method used should remove all traces of polybrominated diphenyl ethers before analysis of the brominated dibenzofurans.

An example of the possible extent of interference of polybrominated diphenyl ethers in the analysis of brominated dibenzofurans was given by Hardy (1993). A pyrolysed sample of decabromodiphenyl ether was analysed three times using an improved analytical methodology each time. In the first analysis, the level of tetrabromodibenzofuran was reported to be 1,200,000 ppb but by the third analysis, using an improved method, the level was found to be <1 ppb. Although no details of the methods used are given in this paper, it does indicate that severe interferences can occur.

In the following Sections, details of the analytical methods used have been given. Although in most analyses a sample clean-up step was employed prior to analysis, it is not always clear if this step was designed to remove the parent brominated diphenyl ether from the brominated dibenzofurans of interest. Thus, as can be seen from the discussion above, many of the results should be treated with caution due to possible analytical interferences from the parent polybrominated diphenyl ethers.

Pyrolysis studies

A possible cause for concern in the use of brominated diphenyl ethers is that they may form brominated dibenzofurans and brominated dibenzo-*p*-dioxins during accidental fires or incineration processes. As a result, several laboratory studies have been carried out to determine the extent of formation of these substances when brominated diphenyl ethers are heated or burned at high temperatures. As can be seen, many different experimental designs have been used, both with and without oxygen and with different pyrolysis times, making direct comparison from one experiment to another difficult.

In the following sections the general abbreviations used will be:

PBDF	-	Polybrominated dibenzofuran
PBDD	-	Polybrominated dibenzo-*p*-dioxin

In some of the tables, the following abbreviations will be used:

MBDF	-	Monobromodibenzofuran	MBDD	-	Monobromodibenz-*p*-dioxin
DBDF	-	Dibromodibenzofuran	DBDD	-	Dibromodibenzo-*p*-dioxin
T_3BDF	-	Tribromodibenzofuran	T_3BDD	-	Tribromodibenzo-*p*-dioxin
T_4BDF	-	Tetrabromodibenzofuran	T_4BDD	-	Tetrabromodibenzo-*p*-dioxin
PeBDF	-	Pentabromodibenzofuran	PeBDD	-	Pentabromodibenzo-*p*-dioxin
HxBDF	-	Hexabromodibenzofuran	HxBDD	-	Hexabromodibenzo-*p*-dioxin
H_7BDF	-	Heptabromodibenzofuran	H_7BDD	-	Heptabromodibenzo-*p*-dioxin
OBDF	-	Octabromodibenzofuran	OBDD	-	Octabromodibenzo-*p*-dioxin

Pyrolysis of commercial polybrominated diphenyl ethers

Buser (1986) studied the pyrolysis of three commercial flame retardants, a pentaBDPE (consisting mainly of tetra- and pentabromodiphenyl ether with smaller amounts of hexabromodiphenyl ether and traces of tri- and heptabromodiphenyl ether), an octabromodiphenyl ether (consisting of hexa-, hepta-, octa- and nonabromodiphenyl ether with traces of pentabromodiphenyl ether) and a decabromodiphenyl ether (consisting mainly of deca- with traces of nonabromodiphenyl ether). The pyrolysis experiments were carried out in quartz vials in the presence of air at temperatures of 510-630^{o}C for 60 seconds, of which 3-5 seconds were within 20^{o}C of the desired final temperature. The flame retardant was added as a solution in toluene (200 µl of a 1 mg flame retardant/ml toluene solution) and the vials were sealed after evaporation of the toluene. After pyrolysis, the residues were analyzed by GC/MS and the amounts of the various compounds present were determined semiquantitatively by a GC-MS (TIC) technique using reference to 2,3,7,8-tetrabromodibenzofuran standard. For the pentabromodiphenyl ether, at 510^{o}C around 10% of the compound was found to decompose and the amount of PBDFs/PBDDs formed were around 0.5-1% total yield. At 630^{o}C, the pentabromodiphenyl ether was found to be 97-98% decomposed and the total yield of PBDFs/PBDDs formed was around 10%. Mono- through to pentabrominated PBDFs/PBDDs were detected at both temperatures, with the major components being tetra- and penta-BDF and two isomeric tri-BDDs. The octabromodiphenyl ether was found to be around 96% decomposed on pyrolysis at 630^{o}C and the yield of PBDFs/PBDDs being around 5%. Tri- to hepta- PBDFs/PBDDs were detected, the major components being two penta-BDDs and a hexa-BDFs. The decabromodiphenyl ether was about 90% decomposed on pyrolysis with tetra- to octa- PBDFs/PBDDs being formed in 1-2% yield, with the main component being a hepta-BDF. In all cases where tetra-BDFs were formed, the 2,3,7,8- isomer was found to be only a minor component of the total tetrabrominated isomers. The technical products were also analysed for the presence of brominated dibenzofurans and dibenzo-*p*-dioxins but none could be detected.

Thoma et al (1987a) studied the pyrolysis of several commercial brominated diphenyl ether flame retardant formulations. In the experiments 1 g of the flame retardant was heated in a quartz tube for 10 minutes at either 700^{o}C, 800^{o}C or 900^{o}C. The residue was then analyzed for polybrominated dibenzo-*p*-dioxins and dibenzofurans by a GC/MS technique (SIM mode), using 1,2,3,4-tetrabromodibenzo-*p*-dioxin as a standard for quantifying both the PBDD and PBDF concentrations. The results of the experiment are shown in **Table A1**. The results at 800^{o}C are also reported in Zacharewski et al (1988 and 1989), although the values obtained for Bromkal 70-DE and Bromkal 70-5-DE have been swapped over.

As can be seen from the Table, the commercial pentaBDPE preparations all appear to produce large quantities of brominated furans, and to a lesser extent brominated dioxins (the lower formation of brominated dioxins was thought to be due to lack of oxygen during the pyrolysis). The maximum formation occurs at temperatures between 700-800°C. The amounts of brominated dioxins and furans formed from the pyrolysis of decabromodiphenyl ether is much lower than that observed with the pentabromo compounds.

Table A1 Formation of brominated dibenzo-*p*-dioxins and dibenzofurans from the pyrolysis of polybrominated diphenyl ethers (Thoma et al, 1987a)

PBDD/ PBDF	Bromkal 70 DE residues (mg/kg)			Bromkal 70-5-DE residues (mg/kg)			Bromkal G1 residues (mg/kg)			Fr 300 BA residues (mg/kg)		
	700°C	800°C	900°C	700°C	800°C	900°C	700°C	800°C	900°C	700°C	800°C	900°C
MBDF	2834	2122	3175	402	767	1631	2200	2100	1800	nd	nd	nd
MBDD	10136	6248	3108	1302	1638	1620	8400	4400	3400	nd	nd	nd
DBDF	50824	89090	45394	9189	14092	26984	44900	39500	31800	nd	nd	nd
DBDD	145219	75279	26005	30491	26208	16379	138600	64800	36300	nd	nd	nd
T_3BDF	243621	177124	131149	54744	71009	87808	199400	150000	120500	nd	nd	nd
T_3BDD	95825	54880	19967	28202	23557	14258	92300	42300	25700	nd	nd	nd
T_4BDF	211709	181624	98575	95131	109402	105013	330400	213600	176900	26	93	nd
T_4BDD	12949	10436	5670	7601	7455	4826	15400	9200	7400	nd	nd	nd
PeBDF	8167	13590	5760	11958	14319	12584	37900	21800	22000	24	nd	259
PeBDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
HxBDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	46	166	178
HxBDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
H_7BDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	482	1304	4357
H_7BDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	33	142	153
OBDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	1885	5600	10792
OBDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	805	3630	2621

Bromkal 70 DE - tetra- and pentabromodiphenyl ether
Bromkal 70-5-DE - pentabromodiphenyl ether
Bromkal G1 - pentabromodiphenyl ether
FR 300 BA - decabromodiphenyl ether
nd = not detected

Thoma and Hutzinger (1987) also studied the formation of pyrolysis products from Bromkal 70-5-DE (a commercial pentaBDPE) and Fr 300 BA (a commercial decabromodiphenyl ether). In this study, small amounts of the polybrominated diphenyl ethers were rapidly heated to either 600, 700, 800 or 900°C and the pyrolysis products/volatiles were swept directly into the injector of a GC/MS using a helium current (no details of the analytical reference compounds used was given). No oxygen was present in the system and as a result, no PBDD were detected. Also, due to the very brief residence time at the pyrolysis temperature, complete decomposition of the polybrominated diphenyl ethers was not seen. The pyrolysis products obtained from the two flame retardants were markedly different.

With Bromkal 70-5-DE (mainly penta- and tetrabromodiphenyl ether), small amounts of tribromophenol and tetrabromobenzene were formed at 600°C.
At 700°C, larger amounts of these two products were detected, along with small amounts of di- to tetrabromodibenzofurans. At higher temperatures, the amounts of PBDFs appeared to increase slightly. With Fr 300 BA (a decabromodiphenyl ether), around 60% of the parent compound was decomposed at 600°C and the main pyrolysis product formed was hexabromobenzene along with traces of pentabromobenzene. At 700°C, the amount of pentabromobenzene formed was found to increase and tetrabromobenzene was also found to form, along with hepta- and octabromodibenzofuran and hexabromonaphthalene. At higher temperatures, a further increase in the amounts of tetra- and pentabromobenzene formed was seen, but no PBDFs were detected.

Hutzinger et al (1989) studied the pyrolysis of Bromkal 70-5-DE (a commercial pentaBDPE) using 3 different oven designs (DIN apparatus, BIS apparatus and VCI apparatus). Pyrolysis was carried out for 10 minutes at 600^{o}C and any brominated dibenzofurans or dioxins formed were quantified by a GC-MS technique using 1,2,3,4-tetrabromodibenzo-*p*-dioxin reference. The estimated amounts formed are shown in **Table A2**.

Table A2 Formation of brominated dibenzofurans and dibenzo-*p*-dioxins from pyrolysis of a commercial pentabromodiphenyl ether at 600^{o}C

Brominated dioxin/furan produced	DIN oven (mg/kg)	BIS oven (mg/kg)	VCI oven (mg/kg)
DBDF	43,612	5,116	15,164
DBDD	31,344	48,921	119,977
T_3BDF	60,778	31,116	126,238
T_3BDD	61,353	115,747	140,945
T_4BDF	67,666	46,573	87,827
T_4BDD	3,880	9,955	12,374
PBDF	14,363	8,003	22,700

Dulmer et al (1989b and 1989c) studied the decomposition of decabromodiphenyl ether at temperatures between 300 and 800^{o}C in a VCI oven for 10 minutes. Brominated dibenzofurans and dibenzo-*p*-dioxins were analysed by GC-MS in SIM mode using one pure isomer for each congener group of the brominated dioxins/furans as reference. Polybrominated dibenzofurans were found to be formed during the pyrolysis of the samples with the maximum formation occurring at around 700^{o}C. The results of the experiments are shown in **Table A3**.

Table A3 Results of Dulmer et al (1989b) for pyrolysis of decabromodiphenyl ether

PBDF	Concentration of PBDFs (mg/kg flame retardant) at various temperatures					
	300°C	400°C	500°C	600°C	700°C	800°C
MBDF	-	-	-	-	-	2
DBDF	4	8	-	3	2	1
T_3BDF	4	13	-	4	25	3
T_4BDF	-	15	11	-	100	102
PBDF	-	16	218	380	591	218
HxBDF	-	42	109	61	1,965	988
H_7BDF	-	-	1,081	1,734	4,539	418
OBDF	-	-	-	-	-	-

Klusmeier et al (1988) also studied the pyrolysis of decabromodiphenyl ether (88.1% deca-, 11.0% nona-, 0.5% octa and 0.1% hexabromodiphenyl ether) in a VCI apparatus. In this case analysis of the pyrolysis products was carried out using GC with electron capture detector (ECD) and identification of peaks was by mass spectrometry. Only qualitative results were reported due to the lack of suitable reference compounds. In these experiments, only hepta- and octabrominated dibenzofurans and dibenzo-*p*-dioxins were formed. Two variables were found to be important in determining the amounts of degradation products formed, the oven temperature and the air flow-rate through the system. The air flow-rate effectively determines the residence time of the sample in the hot zone of the apparatus. For example, at 400^{o}C and an air flow rate of 100 cm^3/min, a large proportion of the decabromodiphenyl ether sample had decomposed into a variety of products including the hepta- and octabrominated dibenzofurans and dibenzo-*p*-dioxins but at the same temperature using an air flow-rate of 400 cm^3/min, only a small amount of decomposition of the decabromodiphenyl ether was seen. At higher temperatures (800-1,000^{o}C), using low air flow-rates, only trace amounts of decomposition products could be detected, indicating a possible complete degradation of the decabromodiphenyl ether to hydrogen bromide, carbon dioxide and carbon monoxide.

Striebich et al (1990) studied the pyrolysis of a 1:1 mixture of two commercial polybrominated diphenyl ether products (contained tri- to decabromodiphenyl ethers). The mixture, dissolved in toluene, was injected onto quartz wool in a flow reactor system. The solvent was evaporated and the mixture was vaporised by temperature programming (75-300^{o}C). The gas phase material was then fed into a quartz thermal reactor where it was pyrolysed for 2 seconds at a temperature between 300 and 800^{o}C in either air or nitrogen. The products were analysed by GC-MS in either SIM or TIC mode. At 800^{o}C in either air or nitrogen atmospheres, the polybrominated diphenyl ethers were essentially completely decomposed to HBr or other non-detectable products (no brominated dibenzofurans or dibenzo-*p*-dioxins were detected). At lower temperatures, detectable amounts of brominated dibenzofurans and dibenzo-*p*-dioxins were found (see **Table A4**) along with other products such as brominated benzenes, brominated alkanes and brominated alkenes.

Table A4 Results of Striebich et al (1990) for the pyrolysis of a mixture of polybrominated diphenyl ethers

PBDD/PBDF	Maximum yield	
	Nitrogen atmosphere 650°C	Air atmosphere 625°C
DBBF	0.03%	nd
DBDD	nd	0.04%
T_3BDF	0.03%	0.03%
T_3BDD	nd	0.04%
T_4BDF	0.03%	0.03%
T_4BDD	nd	0.01%

nd = not detected

Luijk et al (1991) investigated the pyrolysis of commercial penta-, octa- and decabromodiphenyl ethers using a similar micropyrolysis method to that used by Buser. Sealed vials of the flame retardant were placed in a heating furnace set a 100°C above the desired temperature. When the desired temperature was reached (after 60-70 seconds) the vials were heated for a further 10 seconds. The samples were then extracted and analysed for the presence of brominated dibenzofurans and brominated dibenzo-*p*-dioxins by GC-MS in SIM mode. The results are shown in **Table A5**.

Table A5 Results from micropyrolysis experiments of Luijk et al (1991)

PBDD/PBDF	Amount of PBDD/DF produced with various brominated diphenyl ether/temperatures			
	Penta at 500°C	Penta at 600°C	Octa at 600°C	Deca at 600°C
T_4BDD	5,300 mg/kg	41,000 mg/kg	4,100 mg/kg	110 mg/kg
T_4BDF	6,200 mg/kg	65,000 mg/kg	700 mg/kg	80 mg/kg
PBDD	220 mg/kg	13,000 mg/kg	2,000 mg/kg	360 mg/kg
PBDF	80 mg/kg	150,000 mg/kg	4,600 mg/kg	160 mg/kg
H_6BDD	-	1,000 mg/kg	23,000 mg/kg	380 mg/kg
H_6BDF	-	3.800 mg/kg	22,000 mg/kg	570 mg/kg

Pyrolysis of flame retarded polymers

Pyrolysis experiments were carried out using mixtures of the flame retardants with polyethylene or polystyrene (Thoma et al, 1987a). In these tests, 0.95 g of plastic and 0.05 g of flame retardant were mixed and then melted for 3 minutes at 200°C to produce an homogeneous phase. The resulting plastic was then pyrolysed for 10 minutes at either 700, 800 or 900°C. The residue was then analyzed for polybrominated dibenzo-*p*-dioxins and dibenzofurans by a GC/MS technique (SIM mode), using 1,2,3,4-tetrabromodibenzo-*p*-dioxin as a standard for quantifying both the PBDD and PBDF concentration.

In the plastic/pentabromodiphenyl ether mixtures, only brominated dibenzofurans were formed (possibly due to a low oxygen concentration in the system). The concentrations found were of the same order as those found in the pyrolysis experiments with flame retardant alone

(although it is not clear whether the concentrations are measured on a mass/mass of flame retardant added, mass/mass of total plastic added or mass/mass of residue formed). In the case of the decabromodiphenyl ether/plastic mixtures, both polystyrene and polyethylene appeared to enhance the brominated dibenzofuran formation, resulting in the formation of considerable amounts of mono- to tribrominated compounds as well as the higher brominated compounds previously seen in the pyrolysis of pure decabromodiphenyl ether.

Thoma et al (1987b) carried out identical experiments to those above using Bromkal 70-5-DE flame retardant (pentaBDPE) and PVC as the plastic at a pyrolysis temperature of 800^{o}C. In this case, no halogenated dioxins or furans were detected but instead chlorine exchange for the bromine atoms occurred resulting in a mixture of tetra- and pentahalogenated diphenyl ethers. This indicates that, under the conditions of the test, halogen exchange reactions were favoured over ring closure reactions.

In a further study by Dulmer et al (1989a), polymers containing one of several brominated flame retardants, including penta-, octa- and decabromodiphenyl ether were pyrolysed at either 600 or 800°C in three different oven designs (DIN-oven, BSI-oven and VCI-oven). The polymer samples were in granulate form and the sample size was 5-10 g in the DIN- and BSI-ovens and 20-50 mg in the VCI-oven. No information on the pyrolysis time was given. After pyrolysis, analysis (GC/MS) was carried out for PBDDs and PBDFs in both the pyrolysis gases and the solid residues and the yield of these products was estimated on a mass of flame retardant basis (e.g. mg PBDF/kg flame retardant). The analyses were carried out using GC-MS in SIM mode with external standards of one isomer of each brominated congener of dibenzofuran and dibenzo-*p*-dioxin.

The following combinations of polybrominated diphenyl ethers and polymers were tested:

Polystyrene/10% decabromodiphenyl ether/4% antimony(III) oxide
Polypropylene/12.5% decabromodiphenyl ether/7.5% antimony(III) oxide
ABS/14% octabromodiphenyl ether/6% antimony(III) oxide
Polyurethane/25.4% pentabromodiphenyl ether

High yields of PBDFs were formed during the pyrolysis of all the above combinations of flame retardants and polymers (PBDDs were also formed but in much smaller amounts). The yields were higher at 600°C than 800°C. For the octa- and decabromodiphenyl ethers, mono- through to octabromodibenzofurans were detected and with the pentabromodiphenyl ether, mono- to hexabromodibenzofurans and dibenzo-*p*-dioxins were found. Hutzinger et al (1989) reported the results of very similar pyrolysis studies (possibly even the same experiments) and these results are reproduced in **Table A6**. In these tests, samples of polymers containing polybrominated diphenyl ethers (High impact polystyrene (HIPS) containing decabromodiphenyl ether; ABS containing 18% octabromodiphenyl ether; polyurethane containing 25.4% pentabromodiphenyl ether) were pyrolysed for ten minutes at 800^{o}C in each of the three ovens. Analysis for brominated dibenzofurans and dibenzo-*p*-dioxins was carried out by GC-MS in SIM mode, quantification being made by comparison with dioxin and furan congeners of every bromination degree (except for pentabromodibenzofuran which used pentabromodibenzo-*p*-dioxin as standard and hexabromodibenzofuran and all other higher dioxins and furans which were quantified with hexabromodibenzo-*p*-dioxin).

Table A6 Results of polymer pyrolysis experiments at 800°C (concentrations expressed on a mg/kg polymer basis?) (Hutzinger et al, 1989)

PBDD/ PBDF	HIPS with decabromodiphenyl ether			ABS with octabromodiphenyl ether			Polyurethane with pentabromodiphenyl ether		
	DIN oven	BIS oven	VCI oven	DIN oven	BIS oven	VCI oven	DIN oven	BIS oven	VCI oven
MBDF	16	299	36	7.1	79	110	767	20	50
MBDD				1.3	18.5	9.1	13	36	7
DBDF	9	132	9	0.47	11.4	48.8	72	62	1
DBDD				0.084	2.8	5.0	6	28	0.1
T_3BDF	58	145	14	0.41	0.85	20.2	397	102	nd
T_3BDD				0.034	0.11	5.0	5	48	nd
T_4BDF	151	52	51	0.88	0.71	4.9	305	1547	nd
T_4BDD				0.023	0.013	0.81	10	43	nd
PeBDF	114	396	nd	0.013	nd	nd	87	98	nd
PeBDD							2	6	nd
HxBDF	175	652	nd				nd	5	nd
HxBDD									
H_7BDF	3	8	nd						
H_7BDD									
OBDF									
OBDD									

nd = not detected

Dulmer et al (1989b and 1989c) studied the decomposition of three commercial polybutylene terephthalate polymer samples containing varying amounts of decabromodiphenyl ether (9-11% by weight) and antimony (III) oxide (2.7-7% by weight) at temperatures between 300 and 800°C in a VCI oven for 10 minutes. A sample of commercial decabromodiphenyl ether alone was also pyrolysed under the same conditions (see Section 2.1). Brominated dibenzofurans and dibenzo-*p*-dioxins were analysed by GC-MS in SIM mode using one pure isomer for each congener group for the brominated dioxins/furans as reference. Polybrominated dibenzofurans were found to be formed during the pyrolysis of the polymer samples under certain conditions at yields of up to 16%, based on the concentration of flame retardant initially present. The maximum conversion to PBDFs occurred at temperatures between 400 and 500°C and it was thought that the antimony (III) oxide might play a catalytic role in the formation of PBDFs. The results of the experiments are shown in **Tables A7-9.**

Table A7 Results of Dulmer et al (1989b) for pyrolysis of polybutylene terephthalate with 11% decabromodiphenyl ether and 5.5% antimony (III) oxide

PBDF	Concentration of PBDFs (mg/kg flame retardant) at various temperatures					
	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
MBDF	-	754	3,012	5,551	3,513	3,076
DBDF	9	2,357	10,219	15,343	8,445	1,547
T_3BDF	9	10,747	37,911	32,751	28,592	1,274
T_4BDF	9	14,979	52,634	37,437	35,963	1,511
PBDF	55	2,293	18,391	20,666	13,504	555
H_6BDF	703	127	3,713	10,438	2,639	109
H_7BDF	1,320	-	246	946	491	-
OBDF	-	-	-	-	-	-

Table A8 Results of Dulmer et al (1989b) for pyrolysis of polybutylene terephthalate with 9% decabromodiphenyl ether and 7% antimony (III) oxide

PBDF	Concentration of PBDFs (mg/kg flame retardant) at various temperatures					
	300°C	400°C	500°C	600°C	700°C	800°C
MBDF	-	-	13,088	7,633	8,510	1,144
DBDF	-	-	15,754	10,643	9,721	244
T_3BDF	47	456	34,408	24,842	19,276	44
T_4BDF	1,472	4,544	48,762	35,230	23,353	367
PBDF	5,560	18,132	24,753	16,154	6,988	156
H_6BDF	2,886	24,446	18,587	8,832	1,633	22
H_7BDF	420	6,910	2,877	922	100	-
OBDF	-	-	-	-	-	-

Table A9 Results of Dulmer et al (1989b) for pyrolysis of polybutylene terephthalate with 11% decabromodiphenyl ether and 2.7% antimony (III) oxide

PBDF	Concentration of PBDFs (mg/kg flame retardant) at various temperatures					
	300°C	400°C	500°C	600°C	700°C	800°C
MBDF	-	2,202	3,413	2,129	610	18
DBDF	-	5,187	6,124	1,674	82	-
T_3BDF	-	15,033	15,952	1,738	36	15
T_4BDF	-	17,836	17,463	901	9	12
PBDF	-	9,127	3,349	391	-	-
H_6BDF	464	2,457	901	82	-	-
H_7BDF	2,375	1,329	246	36	-	-
OBDF	trace	trace	-	-	-	-

Lenoir et al (1994) studied the effects of water and various metals on the pyrolysis of polybutylene terephthalate containing 10% decabromodiphenyl ether and 6% antimony trioxide in a BIS apparatus under a nitrogen atmosphere. The presence of water in the atmosphere was shown to increase the concentrations of polybrominated dibenzofurans and dibenzo-*p*-dioxins formed at 600°C. Experiments using D_2O and $H_2{}^{18}O$ indicated that neither the hydrogen or oxygen from the water molecule is incorporated into the dibenzofuran or dibenzo-*p*-dioxin products formed. It was thought that the presence of water would shift the equilibrium ($Sb_2O_3 + 6HBr \Leftrightarrow 2SbBr_3 + 3H_2O$) to favour Sb_2O_3, which has been shown in other experiments to enhance the yields of brominated dibenzofurans and dibenzo-*p*-dioxins. The effect of various metals (e.g. Cu, Fe, Zn, Pb, Sn) on the pyrolysis products from the system was also investigated by adding the powdered metal to the polymer at a concentration of 2.5% by weight. The yields of polybrominated dibenzofurans were found to be reduced in the presence of metals when pyrolysis of the plastic containing decabromodiphenyl ether was carried out at 500°C, but the yields of polybrominated dibenzo-*p*-dioxins were found to be increased (e.g. Sn showed a factor of 8 increase and Cu showed a factor of 67 increase). This effect was explained by the redox potential of the metals, which are related to the ability of the metals to act as electron donors. Metal oxides were also shown to affect the yields of brominated dibenzofurans and dibenzo-*p*-dioxins, with oxides of Zn and Cu reducing the yields strongly (both show reactivity to debromination resulting in formation of lower brominated products such as mono- and dibrominated dibenzofurans and dibenzo-*p*-dioxins), were as Fe_2O_3 increased the overall yields.

Pinkerton et al (1989) studied the formation of brominated furans and dioxins during the pyrolysis of high impact polystyrene (HIPS) containing decabromodiphenyl ether and antimony (III) oxide using a mass burning apparatus at temperatures of 500-800°C. The soot and char residues were analysed for brominated dibenzofurans and dibenzo-*p*-dioxins by a GC-MS technique (no details were given of the reference compounds used). No PBDF or PBDD were detected (detection limit 100 μg/kg) in soot and char from pyrolysis of HIPS containing no decabromodiphenyl ether and no brominated dibenzo-*p*-dioxins were detected in soot or char in the experiments using HIPS with decabromodiphenyl ether. However, brominated dibenzofurans were detected in soot and char from the experiments with HIPS containing decabromodiphenyl ether and the results are shown in **Table A10**.
It was estimated that the maximum concentration of 2,3,7,8-tetrabromodibenzofuran formed was 1.8 mg/kg in the soot/char, but it was stated that this is very much a maximum level as the exact level could not be determined due to interference from co-eluting peaks during the GC-MS analysis.

Table A10 Levels of brominated furans formed during burning of HIPS containing decabromodiphenyl ether at 500-800°C (Pinkerton et al, 1989)

PBDF	Concentration in char (mg/kg)	Concentration in soot (mg/kg)
Mono-	0.64	556
Di-	0.54	641
Tri-	0.23	352
Tetra-	<0.1	73
Penta-	<0.1	3.5
Hexa- to octa-	<0.1	<0.1

Lahaniatis et al (1991) studied the formation of 2,3,7,8-tetrabromodibenzo-*p*-dioxin and 2,3,7,8-tetrabromodibenzofuran during the pyrolysis of several polymer/polybrominated diphenyl ether formulations. The experiments were carried out at 400-800°C using a BIS apparatus. Around 100 mg of the sample was pyrolysed for 10 minutes with an air flow of 500 ml/minute and the products formed were analysed by GC-ECD using external standards and by GC-MS (SIM mode) using ^{13}C-labelled 2,3,7,8-tetrabromodibenzofuran or dibenzo-*p*-dioxin as internal standard. The samples tested were polybutylene terephthalate (PBTP) containing 10% decabromodiphenyl ether and 6% antimony trioxide, PBTP containing 10% decabromodiphenyl ether alone, 5 samples of epoxide resin containing 3-6% decabromodiphenyl ether alone, and 2 samples of phenolic resin containing 3-6% pentabromodiphenyl ether and copper. The results are shown in **Table A11**. In similar experiments reported by Lahaniatis et al (1989), Bieniek et al (1989) and Clausen et al (1987), samples of polybutylene terephthalate containing 10% decabromodiphenyl ether and 6% antimony trioxide were pyrolysed at various temperatures and the total amounts of brominated dibenzo-*p*-dioxins and dibenzofurans were determined. These results are shown in **Table A12**. Considering the results as a whole, it is clear that the 2,3,7,8- isomers make up only a very small fraction of the total amount of brominated dibenzo-*p*-dioxins and dibenzofurans apparently formed in these experiments.

Table A11 Formation of 2,3,7,8-tetrabromodibenzofuran and dibenzo-*p*-dioxin from pyrolysis of various polymer/flame retardant formulations (Lahaniatis et al, 1991)

Polymer sample	2,3,7,8-TBDD (mg/kg polymer)			2,3,7,8-TBDF (mg/kg polymer)		
	400°C	600°C	800°C	400°C	600°C	800°C
PBTP/10% decabromodiphenyl ether/6%Sb_2O_3	0.02	0.01	nd	52	5.7	nd
PBTP/10% decabromodiphenyl ether	nd	nd	nd	2.5	4.2	0.08
Epoxide resin/3-6% decabromodiphenyl ether	min 0.05 max 0.3	min 0.3 max 0.8	min 0.01 max 0.03	min 0.4 max 1.0	min 0.6 max 2.5	min 0.01 max 0.04
Phenolic resin/3-6% pentabromodiphenyl ether/Cu	/	7	/	/	5.7	/

nd - not detected detection limit 0.01 mg/kg
/ - not determined

Table A12 Formation of brominated dibenzofurans during the pyrolysis of PBTP containing 10% decabromodiphenyl ether and 6% antimony trioxide (Lahaniatis et al, 1989; Clausen et al, 1987; Bieniek et al, 1989)

PBDF	Concentration determined (mg/kg polymer)				
	400°C	500°C	600°C	700°C	800°C
MBDF	100	300	100	50	nd
DBDF	500	400	200	10	nd
T_3BDF	3000	2000	400	nd	nd
T_4BDF	4000	3000	600	nd	nd
PBDF	4000	1000	200	nd	nd
H_6BDF	1000	200	nd	nd	nd
H_7BDF	500	nd	nd	nd	nd

nd - not detected - detection limit 20 mg/kg

Donnelly et al (1989) studied the pyrolysis of a polybutylene terephthalate resin at 400°C for 10 minutes in a quartz tube with an air passing over the sample. The resin contained 7% decabromodiphenyl ether, along with antimony trioxide (concentration between 2 and 9%). The analytical method used was a GC-MS method with extensive sample clean up to remove possible interferences. Further, checks were carried out to ensure that any polybrominated diphenyl ethers present did not interfere with the brominated dibenzofuran peaks. Thus, these results can be considered as being more reliable than many of those mentioned above although, again, there is a lack of analytical standards for quantification of the amounts present (in this case a 2,3,7,8-tetra- and 1,2,3,7,8-pentabromodibenzofuran and octabromodibenzo-*p*-dioxin were used and response factors for other brominated dibenzofurans and dibenzo-*p*-dioxins were estimated from these). The results from the analysis is given in **Table A13**.

As can be seen from the results the levels measured are much smaller than those reported in some other experiments. Polybrominated xanthenes were also thought to be formed (e.g. total tetra- = 4.1 mg/kg, total penta = 1.2 mg/kg, total hexa- = 0.21 mg/kg and total heptabrominated xanthene = 0.07 mg/kg; all estimated concentrations).

Table A13 Pyrolysis of polybutylene terephthalate at 400°C containing decabromodiphenyl ether (Donnelly et al, 1989)

PBDF/PBDD	Concentration in pyrolysate (mg/kg polymer)
Tetrabromodibenzofuran	1.4
Pentabromodibenzofuran	1.1
Hexabromodibenzofuran	0.25
Heptabromodibenzofuran	0.043
Octabromodibenzofuran	0.0028
Tetrabromodibenzo-*p*-dioxin	0.35
Pentabromodibenzo-*p*-dioxin	0.86
Hexabromodibenzo-*p*-dioxin	1.2
Heptabromodibenzo-*p*-dioxin	0.13

The pyrolysis of samples (1 g) of HIPS containing decabromodiphenyl ether (10.3-12.7%) and antimony trioxide (4.7-5.5%) has been studied at various temperatures using a quartz tube reactor (Luijk et al, 1991). Two experimental systems were used. In the first, the whole reactor (quartz tube) was heated in a furnace and in the second, only the sample in the reactor was heated. Nitrogen was passed through the system and the volatile pyrolysis products were collected in cold traps and a water scrubber. Analysis of the degradation products was carried out by GC-MS with octabromodibenzofuran used as internal standard (the relative response factor for other congeners were estimated from data for available standards). The analytical method used a series of criteria proposed by Donnelly et al (1987) for confirmation of the detection and quantification of polybrominated dibenzo-*p*-dioxins and dibenzofurans in the presence of polybrominated diphenyl ethers.

In the tests, little or no brominated dibenzo-*p*-dioxins were formed but detectable amounts of brominated dibenzofurans were found. In the experiments where the whole reactor system was heated (test system I), no significant difference in the yield of brominated dibenzofurans was seen over the temperature range 500-700°C. This was because once the temperature

inside the reactor reached the depolymerisation temperature of HIPS (>310°C) all the degradation products were swept through the system by the carrier gas and so little or no sample was exposed to the final furnace temperature. In the second series of experiments (test system II), a marked decrease in the amounts of brominated dibenzofurans was seen with increasing temperature. In this system, any volatile products formed were heated to the same temperature as the furnace. The results are shown in **Table A14**. The highest yield was seen at a sample temperature of 360°C. In the experiments it was found that highly brominated dibenzofurans were also formed when the HIPS was heated at 275°C for 20 minutes (see **Table A14**). Pyrolysis-mass spectrometry studies indicated that the following reactions were occurring during the thermal decomposition of the flame retarded HIPS: emission of decabromodiphenyl ether; debromination of the decabromodiphenyl ether by exchange of H and Br (to form lower brominated diphenyl ethers); formation of antimony oxybromides and antimony bromides; formation of brominated dibenzofurans; and the addition of polybromophenoxy groups to the polymer chain.

Table A14 Pyrolysis of HIPS/decabromodiphenyl ether/Sb_2O_3 (Luijk et al, 1991)

Atmosphere	Temp. (°C)	Concentration of PBDF (mg/kg polymer)						
		DBDF	T_3BDF	T_4BDF	PBDF	H_6BDF	H_7BDF	OBDF
Test system I								
nitrogen	500	40	190	370	260	130	na	na
nitrogen	625	40	240	510	340	170	na	na
nitrogen	695	90	200	260	170	40	na	na
nitrogen	780	50	240	620	400	130	na	na
nitrogen	860	60	130	200	90	3	na	na
air	500	10	20	70	60	20	na	na
air	700	30	130	310	190	50	na	na
Test system II								
nitrogen	275	0	0	0.3	10	260	710	3,300
nitrogen	360	60	130	130	560	250	60	50
nitrogen	450	50	30	50	90	130	40	10
nitrogen	560	50	20	20	20	20	4	3
nitrogen	640	2	0.7	0.3	0.2	0.3	0.03	0
nitrogen	720	0.1	0.04	0.03	0.02	0.02	0	0
nitrogen	825	0.03	0.03	0.03	0.02	0.01	0	0

na = not analysed

Other experiments

Bruckmann et al (1990) studied the presence of brominated dibenzofurans and dibenzo-*p*-dioxins several hours after a fire in a stock house. The stock house was known to contain around 2.5 tonnes of a mixture of decabromodiphenyl ether and antimony trioxide. After the fire, the bags of flame retardant were found to be mostly intact and only the surface of some bags had been melted by the heat of the fire. In total, 4 wipe samples and 6 samples of fire residues were taken from the site and analysed for the presence of brominated dibenzofurans and dibenzo-*p*-dioxins by GC-MS. Tetra- to octabromodibenzofurans were found in the samples.

Benbow and Cullis (1975) looked at the overall emissions from burning polymers containing decabromodiphenyl ether. The polymer samples tested had the following composition: a) 100 g

polystyrene, 15 g decabromodiphenyl ether, 4.3 g antimony trioxide; b) 100 g polystyrene, 15 g decabromodiphenyl ether; c) 100 g polypropylene and 10 g decabromodiphenyl ether. The fate of decabromodiphenyl ether during the combustion was found to depend on whether the polymer undergoes flameless degradation or is ignited and burns with a flame. During flameless combustion (temperature around 400^{o}C) decabromodiphenyl ether appeared to volatilise virtually unchanged from the polymer. However, when the polymer burned with a flame, decabromodiphenyl ether was converted almost quantitatively (86.5-93.0% for sample a, 96.6-98.7% for sample b and 95.2% for sample c) to HBr.

Fluthwedel and Pohle (1993) compared the levels of polybrominated dibenzofurans and dibenzo-*p*-dioxins in combustion residues of electronic equipment from both laboratory studies and real fires. The analysis looked at both the total levels formed and the sum of the levels for the congeners prescribed under the German Gefahrstoffverordnung (GefStoffV; which gives a limit of 2 µg/kg for the sum of 8 2,3,7,8-substituted congeners). The results of the analysis are shown in **Table A15**. In the test fire results, 2,3,7,8-substituted congeners accounted for around 3.1-8.7% of the total congeners found in the fire residues and 2.6-5.2% of the total congeners found in the soot deposits. In real fires, the proportion of 2,3,7,8-substituted congeners was around 5.4% of the total for the fire residues and 8.7-19.9% of the total for the soot deposits. The results show that the levels found in real fires are around 2-3 orders of magnitude lower than those seen in laboratory studies, although a direct comparison is not possible as few experimental details are reported in the paper.

Table A15 Comparison of polybrominated dibenzofuran and dibenzo-*p*-dioxins formed during combustion in laboratory tests and real fires (Fluthwedel and Pohle, 1993)

		Fire residues		Soot deposits on walls	
		Total PBDD/F (µg/kg)	PBDD/F as in GefStoffV (µg/kg)	Total PBDD/F (µg/m²)	PBDD/F as in GefStoffV (µg/m²)
Test fires	min	1,310	22	6,220	64
	max	8,700,000	116,540	1,610,000	26,310
Real fires	min	1	1	134	17
	max	107,000	1,148	13,100	149

Summary and conclusions from pyrolysis experiments

Although there is some uncertainty about the actual amounts of polybrominated dibenzofurans and dibenzo-*p*-dioxins formed in the pyrolysis experiments, it is clear that they are formed when polybrominated diphenyl ethers are heated, either alone or in a polymer matrix at high temperatures.

Quantitation of the actual amounts formed is currently very difficult due to the lack of analytical standards for both the brominated diphenyl ethers and the brominated dibenzofurans and dibenzo-*p*-dioxins. As a result, severe analytical interference may occur when determining brominated dibenzofurans and in some cases brominated dibenzo-*p*-dioxins, in the presence of brominated diphenyl ethers, leading to an overestimate of the concentrations formed. Even so, polybrominated dibenzo-*p*-dioxins and dibenzofurans have still been detected in experiments (although at much lower levels than in other studies) where precautions were taken to remove possible interferences from the analysis [e.g. see results of Donnelly et al (1989) and Luijk et al (1991)]. Since many different test systems have been used, it is difficult to compare directly the results from one test system to the other, however, the following conclusions can tentatively be drawn from the results.

- formation of brominated dibenzo-*p*-dioxins, especially the 2,3,7,8-tetrabromo dibenzo-*p*-dioxin is generally low.

- formation of brominated dibenzofurans appears to be greater from the lower brominated diphenyl ethers (e.g. pentabromodiphenyl ether) than the higher brominated (e.g. decabromodiphenyl ether) ones (although this could be due to increased analytical interference with pentabromodiphenyl ether).

- several factors appear to affect the formation of brominated dibenzofurans. These include the temperature, the residence time at the temperature, the presence of oxygen, the type of polymer matrix and the presence of other additives, particularly antimony trioxide.

- at temperatures of 800^{o}C and above for 2 seconds, complete destruction of the brominated flame retardants and brominated dibenzofurans appears to occur.

Decomposition under use

Polymer manufacturer

Most of the information reported in the Section refers to octa- and decabromodiphenyl ether use in plastics (see also the risk assessment reports for those two substances). For pentabromodiphenyl ether, the only current use in the EU is in polyurethane foams, which is produced and processed by different methods to the plastic materials considered for deca- and octabromodiphenyl ether. Of particular importance is that the processing temperatures used for polyurethane foam are much lower than those of the plastic materials containing octa- and decabromodiphenyl ether, and so the potential for formation of brominated dibenzofurans and dibenzo-*p*-dioxins from manufacture of polyurethane foams containing pentabromodiphenyl ether is lower than indicated in this Section for plastic materials containing octa- and decabromodiphenyl ether.

McAllister et al (1990) investigated the possibility of brominated dioxin and furan formation during the moulding of flame retarded plastic under various conditions, ranging from those recommended by the polymer manufacturer to highly abusive. They used commercially available polymer formulations and laboratory scale injection moulding machines typical of those used in industry. The polymers used were high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) and polybutylene terephthalate (PBTP). The polymers were known to contain either decabromodiphenyl ether (12% by weight in HIPS and 6.5% by weight in PBTP) or octabromodiphenyl ether (16.0% by weight in ABS), along with antimony trioxide as synergist. The concentration of brominated dioxins and furans in the moulded polymer were measured and compared with the concentrations present in the base resin before moulding.

The analytical method used was a GC-MS technique using ^{13}C-labelled tetra- and pentabromodibenzofurans as internal standards. The results are shown in **Table A16**. It was stated in the paper that, due to analytical interferences from the brominated diphenyl ethers, the values reported are likely to be maximum values. The study concluded that under normal conditions, the addition of polybrominated diphenyl ethers to the polymers resulted in no increase in the amounts of brominated dioxins/furans during moulding as compared to those already present in the base resin. Under abusive conditions, slightly higher levels of brominated furans were measured. The 2,3,7,8-tetrabrominated dioxin and furan were not detected in any sample except for low concentrations in the ABS polymer under abusive conditions.

Table A16 Formation of brominated dibenzo-*p*-dioxins and dibenzofurans from processing of plastics containing polybrominated diphenyl ethers (McAllister et al, 1990)

Formulation	Conditions	Brominated dioxin/furan concentration (mg/kg polymer)
HIPS with 12.0% weight decabromodiphenyl ether	Base resin, not moulded	Total T_4BDF=0.01 Total PeBDF=0.04 Total HxBDF=<5.3
	Normal conditions: 215-220°C, 30 second cycle	Total T_4BDF=0.01 Total PeBDF=0.05 Total HxBDF=<14.3
	Abusive conditions: 235-245°C, 5 minute cycle	Total T_4BDF=0.01 Total PeBDF=0.06 Total HxBDF=<5.5
	Extreme conditions: 265-270°C, 7 minute cycle	Total T_4BDF=0.02 Total PeBDF=0.2 Total HxBDF=<34.1
PBTP with 6.5% weight decabromodiphenyl ether	Base resin, not moulded	Total T_4BDD=<0.001 Total PeBDD=<0.001 Total T_4BDF=0.003 Total PeBDF=0.02 Total HxBDF=0.11
	Normal conditions: 255°C, 23 second cycle	Total T_4BDD=<0.0002 Total PeBDD=<0.0002 Total T_4BDF=0.003 Total PeBDF=0.002 Total HxBDF=0.013
	Abusive conditions: 255°C, 5 minute cycle	Total T_4BDD=<0.002 Total PeBDD=<0.013 Total T_4BDF=0.03 Total PeBDF=>7.8 Total HxBDF=>16.1
	Extreme conditions: 255°C, 7 minute cycle	Total T_4BDD=0.001 Total PeBDD=0.006 Total T_4BDF=1.0 Total PeBDF=>54 Total HxBDF=>7.0
ABS with 16% weight octabromodiphenyl ether	Normal conditions: 225°C, 1 minute cycle	1,2,3,7,8-PeBDD=<0.002 2,3,7,8-TBDF=<0.002 Total T_4BDD=<0.001 Total PeBDD=0.03 Total T_4BDF=0.003 Total PeBDF=1.1 Total HxBDF=<135.0
	Abusive conditions: 245°C, 10 minute cycle	1,2,3,7,8-PeBDD=0.02 2,3,7,8-TBDF=0.004 Total T_4BDD=0.01 Total PeBDD=<0.13 Total T_4BDF=0.17 Total PeBDF=<14.0 Total HxBDF=<118.0

Due to analytical interferences from the brominated diphenyl ethers the measured levels of brominated dioxins/furans represent the maximum possible level. It is possible that the actual levels are much lower than those reported

A very similar set of experiments has been reported by Donnelly et al (1989) [It is possible that this set of experiments is the same as those reported by McAllister et al (1990)]. The results are shown in **Table A17**. The analyses were carried out by a GC-MS technique involving SIM. The possibility of interference from polybrominated diphenyl ethers in the analyses was investigated and so these results can be considered as being reasonably reliable estimates, although, again, there is a lack of analytical standards for quantification of the amounts present (in this case a 2,3,7,8-tetra- and 1,2,3,7,8-pentabromodibenzofuran and octabromodibenzo-*p*-dioxin were used and response factors for other brominated dibenzofurans and dibenzo-*p*-dioxins were estimated from these).

Table A17 Formation of brominated dibenzo-*p*-dioxins and dibenzofurans from processing of plastics containing polybrominated diphenyl ethers (Donnelly et al, 1989)

Formulation	Conditions	Brominated dioxin/furan concentration (mg/kg polymer)
HIPS with 12.0% weight decabromodiphenyl ether	Base resin, not moulded	Total PeBDF=0.0045 Total HxBDF=0.95 Total HpBDF=0.72 Total OBDF=0.15
	Abusive extrusion conditions: 238-243°C, 5 minute cycle	Total T_4BDF=0.00226 Total PeBDF=0.0226 Total HxBDF=0.107 Total HpBDF=0.078 Total OBDF=0.00052
	Extreme extrusion conditions: 266-271°C, 7 minute cycle	Total T_4BDF=0.000012 Total PeBDF=0.0086 Total HxBDF=0.2 Total HpBDF=2.1 Total OBDF=3.2
PBTP with 6.5% weight decabromodiphenyl ether and antimony trioxide	Normal moulding conditions: 254°C	Total T_4BDF=0.001-0.0053 Total PeBDF=0.018-0.035 Total HxBDF=0.067-0.170 Total HpBDF=0.18-0.41 Total OBDF=0.52-1.5
	Normal extrusion conditions: 254°C, 23 second cycle	Total T_4BDF=0.0052-0.0097 Total PeBDF=0.061-0.130 Total HxBDF=0.62-1.6 Total HpBDF=2.3-3.8 Total OBDF=2.4-4.1
	Abusive extrusion conditions: 254°C, 5 minute cycle	Total T_4BDF=0.076-0.24 Total PeBDF=13-43 Total HxBDF=69-180 Total HpBDF=48-94 Total OBDF=1.2-11
	Extreme extrusion conditions: 254°C, 10 minute cycle	Total T_4BDF=1.02-2.59 Total PeBDF=68.2-82.8 Total HxBDF=272-708 Total HpBDF=72.5-108
PTBT with 5.2% weight decabromodiphenyl ether and antimony trioxide	Normal moulding conditions: 250°C	Total T_4BDF=0.0038-0.018 Total PeBDF=0.054-0.1 Total HxBDF=0.24-0.27 Total HpBDF=0.28-0.44 Total OBDF=0.71-2.3

Table A17 continued overleaf

Table A17 continued

Formulation	Conditions	Brominated dioxin/furan concentration (mg/kg polymer)
PTBT with 7.0% decabromodiphenyl ether and antimony trioxide	Normal conditions: 250°C	Total T_4BDF=0.014-0.026 Total PeBDF=0.065-0.109 Total HxBDF=0.23-0.25 Total HpBDF=0.5-0.98 Total OBDF=0.41-1.6
PTBT with 8% decabromodiphenyl ether and antimony trioxide	Normal conditions: 250°C	Total T_4BDF=0.00088-0.0041 Total PeBDF=0.027-0.060 Total HxBDF=0.081-0.31 Total HpBDF=0.23-0.56 Total OBDF=0.5-1.3
PTBT with 17.4% decabromodiphenyl ether and antimony trioxide	Normal moulding conditions: 250°C	Total HxBDF=0.025-0.15 Total HpBDF=0.77-2.1 Total OBDF=1.3-3.5
ABS with 16% weight octabromodiphenyl ether and antimony trioxide	Normal extrusion conditions: 227°C, 1 minute cycle	Total T_4BDF=0.0028-0.0036 Total PeBDF=0.87-1.8 Total HxBDF=2.1-2.38 Total HpBDF=0.5-0.78 Total OBDF=0.026-0.064
	Abusive extrusion conditions: 246°C, 10 minute cycle	Total T_4BDF=0.15-0.17 Total PeBDF=29-34 Total HxBDF=8.2-10 Total HpBDF=0.5-0.92 Total OBDF=19

Fluthwedel and Pohle (1993) reported results of analysis for the presence of polybrominated dibenzofurans and polybrominated dibenzo-*p*-dioxins in various electronic equipment casings and parts. Total levels of between 0.0067 and 4.24 mg/kg were found. Of the 16 samples analysed, 11 exceeded the proposed German limit value of 1 µg/kg for the sum of 4 tetra-/pentabrominated dibenzofurans/dibenzo-*p*-dioxins (maximum level measured 32.7 µg/kg) and the proposed limit value of 5 µg/kg for the sum of 8 tetra- to hexabrominated dibenzofurans/dibenzo-*p*-dioxins (maximum level measured 74.6 µg/kg). The proportion of 2,3,7,8-substituted congeners was around 5.8% of the total.

Use in television sets

Bruckmann et al (1990) studied the possible emissions of brominated dibenzofurans and dibenzo-*p*-dioxins from television sets under normal operating conditions. A new television set was placed in a closed room (volume 26.8 m^3) and was operated between 7 am and 12 pm for three days. The surface temperature of the television back was usually 38-40°C. Although not explicitly stated in the report, the television set back presumably contained decabromodiphenyl ether. Air samples were collected on polyurethane foam cartridges. After extraction, the residues were analysed by GC-MS, using ^{13}C-labelled 2,3,7,8 tetrabromodibenzofuran as internal standard. Identification of the brominated dibenzofurans and dibenzo-*p*-dioxins was by their masses and isotope ratios and quantification was by means of external standards. The levels of brominated dibenzofurans found in the air in the room are shown in **Table A18**.

Due to lack of suitable standards, an isomer specific analysis could not be undertaken. Brominated dibenzo-*p*-dioxins and hepta- and octabromodibenzofurans were not detected in this experiment (detection limit 0.1-0.2 pg/m^3). This experiment has, however, been criticised

due to the lack of background levels measured in the room before the experiment was undertaken (Ranken et al, 1990).

Table A18 Formation of brominated dibenzofurans from the operation of a flame retarded television (Bruckmann et al, 1990)

Brominated furans formed	0.15 m above TV	Centre of room (2.2 m from TV; height 1.5 m)	Ambient air
Tribromo	143 pg/m^3	25 pg/m^3	<0.05 pg/m^3
Tetrabromo	11 pg/m^3	2.7 pg/m^3	0.16 pg/m^3
Pentabromo	0.5 pg/m^3	0.5 pg/m^3	<0.05 pg/m^3
Hexabromo	<0.1 pg/m^3	<0.1 pg/m^3	<0.05 pg/m^3

Ranken et al (1990) carried out a similar experiment to measure possible emissions of polybrominated dibenzofurans and dibenzo-*p*-dioxins from televisions. In this series of experiments, three television sets were used, two bought locally and one supplied by a manufacturer. Analysis of the rear panels of the two purchased sets showed that they were made of polystyrene and had a bromine content of 11.5% which suggested that they contained decabromodiphenyl ether. The back of the third set was known to be high impact polystyrene/decabromodiphenyl ether/antimony trioxide. The tests were carried out in a 1.81 m^3 test chamber, through which air was drawn and any compounds emitted were trapped on a silica gel sampler. Any brominated dibenzofurans and dibenzo-*p*-dioxins extracted from the samplers were analysed for using GC-MS in SIM mode using ^{13}C-labelled brominated dibenzofuran standards (2,3,7,8- tetrabromo-, 2,3,4,7,8-pentabromo and 1,2,3,7,8,9-hexabromodibenzofuran). The first experiment involved drawing air through the empty test chamber for 8 hours/day for 3 days in order to obtain the background level (total volume of air 17.95 m^3). Then, the two purchased televisions were placed in the chamber and the air was again sampled for 3 days and this was then repeated with the televisions operating for 3 days. A final analogous series of experiments were run using the television set provided by the manufacturers (3 days when the set was not operating and 24 hours continuous operation). No brominated dibenzofurans or dibenzo-*p*-dioxins were detected in any of the experiments. The detection limits are shown in **Table A19**.

Table A19 Detection limits for the determination of polybrominated dibenzofurans and dibenzo-*p*-dioxins (Ranken et al, 1990)

Dioxin/furan	Detection limit (pg/m^3)
2,3,7,8-tetrabromodibenzo-*p*-dioxin	0.17-1.53
Total tetrabromodibenzo-*p*-dioxin	0.17-1.53
1,2,3,7,8-pentabromodibenzo-*p*-dioxin	0.35-0.39
Total pentabromodibenzo-*p*-dioxin	0.35-0.39
2,3,7,8-tetrabromodibenzofuran	0.09-0.33
Total tetrabromodibenzofuran	0.09-0.33
1,2,3,7,8-pentabromodibenzofuran	0.14-0.19
2,3,4,7,8-pentabromodibenzofuran	0.14-0.19
Total pentabromodibenzofuran	0.14-0.19

Fluthwedel and Pohle (1993) reported the results of a series of experiments looking at the emissions of polybrominated dibenzofurans from various electronic equipment including televisions, printers and monitors. After 3 days sampling, the sum of polybrominated dibenzofurans released was estimated at around 320-1,800 pg/device. Investigations of air levels in a room containing electronic equipment gave a total air concentration of 1.27 pg/m^3 of polybrominated dibenzofurans.

Disposal

It has been estimated that in England, Wales, Germany, France and Spain, approximately 63% of old personal computers are disposed of to landfills, 22% are incinerated and 15% are subject to recycling (WWF, 1998). In the United Kingdom, it is thought that currently the vast majority of electrical and electronic equipment is disposed of to landfill or is incinerated. Recycling is of equipment is in its infancy and is not currently carried out to a significant extent. A draft EC Directive on waste electrical and electronic equipment was issued in April 1998. This sets future targets for reuse and recycling this type of equipment. This means that the current disposal practices may change in the future.

When considering the disposal of articles containing polybrominated diphenyl ether, it should be born in mind that they will be mixed with other waste prior or during disposal. As a result, their contribution to formation of hazardous products (e.g. halogenated dibenzo-*p*-dioxins and furans) as to be considered along with the contribution from all other sources.

The final mode of disposal for polyurethane foam containing pentabromodiphenyl ether is likely to be ultimately to landfill or incineration. Scrap foam can be recycled but these recycled products will also eventually end up being disposed of in a similar manner.

Incineration

The chlorine and bromine load of municipal solid waste incinerator feeds have been estimated by various sources and were summarised by Hardy (1997). Chlorine is the most abundant halogen present in municipal solid waste and a typical concentration of 0.7% wt (i.e. 7 g/kg) has been given. A study of the chlorine content of municipal wastes in the United Kingdom found that the chlorine level was in the range 5-15 g/kg (Clayton et al). The refuse was broken down into various types and these are shown in **Table A20**.

Table A20 Chlorine content of municipal wastes (Clayton et al)

Refuse type	% of total refuse	Chlorine content (% by weight)
Paper	33%	0.37%
Plastic film	3%	2.69%
Dense plastic	3%	6.79%
Textiles	4%	0.70%
Miscellaneous combustibles	5%	2.44%
Putrescibles	20%	0.67%
<10 mm fraction	10%	0.32%
Ferrous metals	7%	nd
Non-ferrous metals	1%	nd
Miscellaneous non-combustibles	5%	nd
Glass	9%	nd

Bromine is present at much lower concentrations than chlorine in municipal waste, and typical bromine levels of around 15 mg/kg (Hardy, 1997) and 20-90 mg/kg of the total waste (Wilken et al, 1990) or 1-4% (Buser, 1987) and 1-15% of the total chlorine (Hardy, 1997) have been reported.

Several studies have looked at the effect of the total bromine load in waste on the formation of halogenated dibenzo-*p*-dioxins and furans and the results are summarised below. Ten Berge (1995) reported data on the halogen contents on dioxin emissions (as TCDD-equivalents) from municipal waste incinerators in the Netherlands. The results are shown in **Table A21**, and show no relationship between the dioxin emissions from the incinerators and the bromine level in the waste.

Table A21 Bromine and chlorine levels of waste at municipal incinerators in the Netherlands

Waste incinerator	Bromine content of waste (g Br/tonne)	Chlorine content of waste (g Cl/tonne)	Bromine content of waste (% of total Cl)	Dioxin emission from incinerator (µg TEQ/tonne)
A	8.4	2,982	0.28%	28
B	33	3,684	0.90%	262
C	15.6	3,700	0.42%	45
D	9.6	5.274	0.18%	507
E	5.4	1,920	0.28%	42
F	5.4	4,284	0.13%	277

Similarly, Öberg et al (1987) found very little difference in the amounts of chlorinated dibenzo-*p*-dioxins and furans formed at an industrial waste incinerator (afterburner temperature 1000-1030^{o}C) in Sweden when high loads of bromine were present. Low levels of monobromochloro dibenzo-*p*-dioxins and furans were found in the cleaned flue gas. Lahl et al (1991) found an increase in both the chlorinated and bromochlorinated dibenzo-*p*-dioxins and furans formed in the electrostatic precipitator ash after 2 kg of printed circuit board containing a polybrominated diphenyl ether was added to a municipal incinerator (oven capacity 14 tonnes/hour). The maximum increase (around 2-3 times) was seen around half an hour after the addition of the plates. Of the mixed halogenated compounds formed only species containing 1 bromine atom per molecule were formed. No increase in the halogenated dibenzo-*p*-dioxin and furan emissions was seen in the stack gas.

During incineration, it is well known that the halogenated dibenzo-*p*-dioxins and furans are formed in the cooler post combustion zone of the waste incinerator via *de novo* synthesis. The relative proportions of bromine to chlorine in the waste prior to incineration indicates that the major dibenzo-*p*-dioxins and furans formed will contain chlorine only, with mixed bromine/chlorine containing species (most likely containing 1 bromine) making only a very minor contribution. The amounts of bromine only containing dibenzo-*p*-dioxins and furans will be similarly small (Buser, 1987; Hardy, 1997). In addition to this, European Regulations exist on the design of municipal incinerators in order to minimise the formation of chlorinated dibenzo-*p*-dioxins and furans (EEC, 1989a and 1989b) during incineration. Proper incinerator design should also reduce the potential for release to the environment from the brominated dibenzo-*p*-dioxins and furans.

Landfill

A large proportion of waste containing the brominated diphenyl ether flame retardants may ultimately end up in landfill. The waste for landfill is likely to be of a similar composition as that considered above for incineration. Once in the landfill, the potential for formation of halogenated dibenzo-*p*-dioxins and dibenzofurans is likely to be small unless a landfill fire occurs. Although these fires are unintentional, they are known to occur and the temperature in a landfill fire can reach up to 800^{o}C (FRS, 1998).

As high temperatures are involved, there is the possibility for formation of halogenated dibenzo-*p*-dioxins and furans under these conditions. However, the residence time of the substance in a landfill fire is likely to be much longer than found in the laboratory pyrolysis studies that have been carried out and so it is not possible to say anything about the extent of formation under these conditions.

Recycling

Plastics

A recent study in Germany looked at the formation of polybrominated dibenzofurans and dibenzo-p-dioxins as a result of recycling of plastics containing polybrominated diphenyl ether flame retardants (Riess et al, 1998). In the study, polymer samples were obtained from a recycling company and were analysed for plastic type and flame retardants present. A total of 78 television housings and 34 personal computer housings were analysed and polybrominated diphenyl ethers were identified in 78% of the samples. A sample of impact modified polystyrene containing a polybrominated diphenyl ether (not identified but possibly octabromodiphenyl ether) was further analysed for the presence of polybrominated dibenzofurans and dibenzo-p-dioxins both before and after undergoing recycling. The analytical method used incorporated a suitable clean-up method to ensure that the polybrominated diphenyl ether present did not interfere with the analysis of the brominated dioxins and furans. The analysis was carried out for the isomers required under the German "Dioxinverordnung" and the results are shown in **Table A22**. The limits under the Dioxinverordnung are 1 µg/kg for the sum of isomers 1-4 and 5 µg/kg for the sum of isomers 1-7 (higher limits of 10 µg/kg for the sum of isomers 1-4 and 60 µg/kg for the sum of isomers 1-7 apply until 15 July 1999; van Riel, 1995). As can be seen from the results, although the limits of the Dioxinverordnung were exceeded, there was no increase in the levels of the brominated dibenzofurans and dibenzo-p-dioxins as a result of the recycling process. There was also some evidence that the distribution of congeners for the polybrominated diphenyl ethers themselves and the polybrominated dibenzofurans and dibenzo-p-dioxins changed slightly in the samples before and after recycling with a slight reduction in the concentration of the higher brominated congeners and a slight increase in the concentration of the lower brominated congeners (e.g. the concentration of the octabromodiphenyl ether component decreased and the concentration of the hexa- and heptabromodiphenyl ether components increased slightly during the recycling step). The paper concluded that recycling of the flame retarded material might be practicable if it is mixed with other material (not containing polybrominated diphenyl ethers) prior to recycling.

Table A22 Levels of brominated dibenzofurans and dibenzo-p-dioxins in impact modified polystyrene containing brominated diphenyl ether both before and after recycling (Riess et al, 1998)

No	Isomer	Level before recycling	Level after recycling
1	2,3,7,8-TBDD	<0.009 µg/kg	<0.016 µg/kg
2	1,2,3,7,8-PeBDD	<0.027 µg/kg	<0.032 µg/kg
3	2,3,7,8-TBDF	0.407 µg/kg	0.431 µg/kg
4	2,3,4,7,8-PeBDF	5.45 µg/kg	4.05 µg/kg
5	1,2,3,4,7,8-HxBDD + 1,2,3,6,7,8-HxBDD	<0.11 µg/kg	<0.023 µg/kg
6	1,2,3,7,8,9-HxBDD	<0.11 µg/kg	<0.023 µg/kg
7	1,2,3,7,8-PeBDF	<0.019 µg/kg	<0.021 µg/kg
Sum 1-4		5.90 µg/kg	4.53 µg/kg
Sum 1-7		6.14 µg/kg	4.59 µg/kg

Meyer et al (1993) studied the levels of polybrominated dibenzofurans and dibenzo-*p*-dioxins (as per the German Dioxin Regulations) in ABS containing a polybrominated diphenyl ether (not identified in the study) in newly moulded parts (first processing) and of old parts that were reground and subsequently reprocessed. The results are shown in **Table A23**. Although the results of the analysis indicate that the polybrominated dibenzofurans and dibenzo-*p*-dioxins were present at levels in excess of those given in the German Dioxin Regulations, there was no increase in these levels on subsequent recycling/reprocessing of the plastic. Similar results were obtained mixed electronic scrap that contained polybrominated diphenyl ethers. The service life for the types of electronic equipment considered in this study was thought to be around 3-15 years.

Table A23 Levels of polybrominated dibenzofurans and dibenzo-*p*-dioxins in ABS during processing and reprocessing (Meyer et al, 1993)

PBDD/PBDF	Concentration (µg/kg or ppb)			
	New moulding	Old moulding		
	First processing	First processing	After recompounding	After recompounding and injection
2,3,7,8-TBDD	nd (<0.2)	nd (<0.2)	nd (<0.2)	nd (<0.5)
1,2,3,7,8-PeBDD	6	1	2	3
2,3,7,8-TBDF	2	4	7	4
2,3,4,7,8-PeBDF	na	na	na	na
1,2,3,4,7,8-HxBDD + 1,2,3,6,7,8-HxBDD	25	6	20	50
1,2,3,7,8,9-HxBDD	<2	5	7	8
1,2,3,7,8-PeBDF	na	na	na	na

na = not analysed due to analytical interference
nd = not detected

A further detailed study of recycling of plastic containing decabromodiphenyl ether has been published (GfA, 1999). The decabromodiphenyl ether used in the study was a 1:1:1 mixture

of three different decabromodiphenyl ether products currently supplied. The plastic used in the study was HIPS and this was studied using a normal extrusion and injection moulding procedure and also after under a further going 5 cycles of grinding and injection moulding (to simulate recycling). The samples were analysed in duplicate for the present of lower brominated diphenyl ethers (tri- to heptabromodiphenyl ethers) as well as the polybrominated dibenzofurans and dibenzo-*p*-dioxins as prescribed in the German Dioxin Regulations. Details of the conditions used and the results of the analyses are shown in **Table A24**.

The results of the GfA (1999) study show that there is no formation of lower brominated diphenyl ethers in the plastic as a result of processing or repeated recycling. The trace levels found are related to the trace levels present in the commercial decabromodiphenyl ether products used. Further, the levels of polybrominated dibenzo-*p*-dioxins and furans are well below those prescribed in the German Dioxin Regulations in all samples, including the repeatedly recycled sample. The information available on the levels of polybrominated dibenzofurans and dibenzo-*p*-dioxins in plastics during recycling indicate that that levels present do not increase during recycling. In two earlier studies the total levels of polybrominated dibenzofurans and dibenzo-*p*-dioxins present exceeded those prescribed in the German Dioxin Regulations. However, a more recent study, using a composite sample of decabromodiphenyl ether from the three major suppliers to the EU, indicated that the levels were well below those prescribed in the German Dioxin Regulations, even after repeated recycling.

At present there is little recycling of plastic containing polybrominated diphenyl ether in the EU. Recycling of many plastics is currently at the experimental stage. This picture, however, may change in the future.

Table A24 Effects of recycling on the concentrations of lower brominated diphenyl ethers and polybrominated dibenzo-*p*-dioxins and furans (GfA, 1999)

Congener	Mean concentration in sample (µg/kg)			
	HIPS alone, extruded at 175-210°C and injection moulded at 199-227°C	**Deca alone (composite sample from three suppliers)**	**HIPS containing 12% deca and Sb_2O_3, extruded at 175-210°C and injection moulded at 199-227°C**	**HIPS containing 12% deca and Sb_2O_3, extruded at 175-210°C and injection moulded at 199-227°C, recycled 5 times by grinding and injection moulding**
Polybrominated diphenyl ethers				
3,4,4'-tri	nd (<5)	nd (<55)	nd (<5)	nd (<5)
Total tri[a]	nd	102	8	9
2,4,4',6-tetra	nd (<8)	nd (<90)	nd (8)	nd (<8)
2,3',4',6-tetra	nd (<8)	nd (<90)	nd (<8)	nd (<8)
2,2',4,4'-tetra	nd (<8)	245	39	39
2,3',4,4'-tetra	nd (<8)	nd (<90)	nd (<8)	nd (<8)
3,3',4,4'-tetra	nd (<8)	nd (<90)	nd (<8)	nd (<8)
Total tetra	nd	245	39	39
2,3',4,4',6-penta	nd (<9)	nd (<85)	nd (<9)	nd (<9)
2,2',4,4',5-penta	nd (<9)	2,227	338	341
2,2',3,4,4'-penta	nd (<9)	nd (<192)	33	30
Total penta	nd	2,227	371	371
2,2',4,4',5,5'-hexa	nd (<10)	9,279	1,150	1,195
Total hexa[a]	nd	11,705	1,507	1,554
2,3,3',4,4',5,6-hepta	nd (<180)	nd (<1,400)	nd (<180)	nd (<180)
Total hepta[a]	nd	33,541	4,623	4,449
Polybrominated dibenzo-*p*-dioxins and furans				
2,3,7,8-TeBDD	nd (<0.02)	-	nd (<0.02)	nd (<0.02)
1,2,3,7,8-PeBDD	nd (<0.04)	-	nd (<0.04)	nd (<0.04)
2,3,7,8-TeBDF	nd (<0.03)	-	nd (<0.04)	nd (<0.03)
2,3,4,7,8-PeBDF	nd (<0.04)	-	nd (<0.05)	0.07[c]
Sum of the 4 PBDD/F (limit value 1 µg/kg[b])	nd	-	nd	0.07[c]
1,2,3,4,7,8-HxBDD + 1,2,3,6,7,8-HxBDD	nd (<0.2)	-	nd (<0.2)	nd (<0.2)
1,2,3,7,8,9-HxBDD	nd (<0.2)	-	nd (<0.3)	nd (<0.3)
1,2,3,7,8-PeBDF	nd (<0.04)	-	nd (<0.04)	0.06
Sum of the 8 PBDD/F (limit value 5 µg/kg[b])	nd	-	nd	0.06

nd – not detected. Detection limit given in ( )
[a]Concentration given includes some unidentified isomers
[b]Refers to the limit value from the German Dioxin Regulations
[c]Actual value may be lower than this due to analytical interference

Polyurethane foam

The recycling of polyurethane foam is currently carried out mainly by shredding the scrap foam into small pieces and mixing with an adhesive under pressure to form a large cylinder or block. The foam product (e.g. rebond for carpet underlay) is then "peeled" from the block at the desired thickness and a suitable backing is applied. This type of recycling is common in the United States, and the EU is a net exporter of scrap foam for this process (ENDS, 1998). Other uses for scrap foam such as regrinding and subsequent use as a filler in a variety of

applications (e.g. car seats or added to virgin polyol in the manufacture of slabstock foam) have been reported (Ulrich, 1997).

As these recycling processes are generally physical in nature and do not involve the high temperatures associated with some plastic recycling processes, the potential for formation of brominated dibenzofuran and dibenzo-*p*-dioxins from recycling polyurethane foam containing pentabromodiphenyl ether is likely to be low.

Metals

Except for precious metals, the only other non-ferrous metals that are of economic importance for recycling are aluminium, copper, lead and zinc (Richardson, 1996). Of these, recycling of copper from printed circuit boards and cabling are likely to be the main processes that are associated with flame retardant use. Of the three polybrominated diphenyl ethers under consideration, decabromodiphenyl ether has been reported to be used as a flame retardant in polyester for used for printed circuit boards (Sellström, 1996) and many plastic materials, including cable, and so is likely to the one most associated with these processes. Octabromodiphenyl ether appears to be mainly used in plastics for computer/business machine housings and pentabromodiphenyl ether is used in polyurethane foam. These uses are unlikely to impinge on the recycling of metals.

Harless et al (1989) detected bromochlorinated dibenzo-*p*-dioxins and furans (containing 1 bromine) in ash from a secondary copper furnace in the United States, but these were found at much lower concentrations (6-27 times lower) the chlorinated dibenzo-*p*-dioxins and furans. In this study, the source of bromine was not identified.

Little information is reported on the potential for formation of brominated dibenzo-*p*-dioxins and furans from metal recycling as a result of use of polybrominated diphenyl ether flame retardants. However, since the process again involves relatively high temperatures, the potential for formation of these compounds exists if plastic containing them enters into the recycling process along with the metal. Again, the polybrominated diphenyl ethers are unlikely to be the only source of halogen in these processes. The possibility for formation of chlorinated dibenzo-*p*-dioxins and furans during, for example secondary copper production is well known and various emission control techniques, similar to those used in incinerators, can be used to reduce the emissions of these compounds to the environment (HMIP, 1994).

<u>Impurities present in polybrominated diphenyl ethers</u>

Another possible concern is the formation of brominated dibenzofurans and dibenzo-*p*-dioxins as impurities during the production of polybrominated diphenyl ethers. The occupational exposure aspects for this for octa- and decabromodiphenyl ether are considered in the risk assessment reports for those two substances.
Ranken et al (1994) analysed samples of commercial decabrominated diphenyl ethers for the presence of 15 brominated dibenzofurans and dibenzo-*p*-dioxins with the 2,3,7,8- substitution pattern. The analytical method used was a GC-MS method (SIM mode) but extensive sample clean-up was undertaken to allow the brominated furans to be analysed at low limits of detection free from interferences. Several analytical standards were used in the analysis (at least one pure brominated dibenzofuran and dibenzo-*p*-dioxin isomer for each degree of brominated between tetra and heptabromo). Originally, 10 samples of the commercial decabromodiphenyl ether were collected from each of 3 manufacturers. Seven out of the 10

samples from each manufacturer were randomly selected for analysis. None of the 15 dibenzofurans and dibenzo-*p*-dioxins were detected in any of the samples analysed at concentrations above the limit of quantitation specified by the USEPA.

The limits of quantitation varied from 0.1 µg/kg for 2,3,7,8-tetrabromo-*p*-dioxin to 1.0 µg/kg for 2,3,7,8-tetrabromodibenzofuran to 1,000 µg/kg for 1,2,3,4,6,7,8- and 1,2,3,4,7,8,9-heptabromodibenzofuran. Similar results were also reported by Donnelly et al (1989). The analytical method used was again based on GC-MS with extensive sample clean up before analysis. Checks were also carried out to ensure that polybrominated diphenyl ethers were not co-eluting with the PBDF peaks. Samples of octa- and decabromodiphenyl ether from commercial suppliers were analysed. In the case of octabromodiphenyl ether no brominated dibenzofurans were detected, but, since the clean up steps involve did not completely remove the potential interferences, the possibility remained that brominated dibenzofurans could still be present at very low levels. The decabromodiphenyl ether sample was found to contain very low levels of hexa- (2.3 µg/kg), hepta- (250 µg/kg) and octabromodibenzofuran (34 µg/kg). These results are consistent with the not detected results found by Ranken et al (1994).

Hileman et al (1989) also analysed several brominated diphenyl ether flame retardants for the presence of brominated dibenzofurans. Again extensive sample clean up was carried out before analysis to enable the brominated dibenzofurans to be quantified. For a flame retardant product composed of tetra- to hexabrominated diphenyl ethers (a commercial pentabromodiphenyl ether) tetrabromodibenzofurans were found at a level of approximately 2 ppm (mg/kg). The major tetrabromodibenzofuran isomers did not co-elute with either 1,2,7,8- or 2,3,7,8-tetrabromodibenzofuran.

Penta- and hexabromodibenzofurans were present at 4 and 2 ppm (mg/kg) respectively. For a product composed of hexa- to nonabromodiphenyl ether (a commercial octabromobipenyl ether), no tetrabromodibenzofurans were seen above the detection limit of 0.2 mg/kg but penta- (2-4 mg/kg), hexa- (2-4 mg/kg) and heptabromodibenzofuran isomers (detected but not quantified) were found. In a commercial decabromodiphenyl ether, tetra- and pentabromodibenzofurans were not found above the detection limit of 0.2 mg/kg, hexabromodibenzofuran isomers were just detectable at the 0.2 mg/kg detection limit and heptabromodibenzofurans were detected but not quantified. The levels of brominated dibenzofurans detected were thought to be related to the presence of trace amounts of dibenzofuran (1.7-5.3 mg/kg) in the diphenyl ether used to manufacture the flame retardants. In terms of the environmental risk assessment, as the effects data used in the assessment has been derived from the commercial supplied product, the results obtained will also account for any toxic impurities present.

Conclusions

The conclusions here only consider the processes which may lead to a significant release of decomposition products to the environment. The occupational aspects of decomposition products for octa- and decabromodiphenyl ether are considered in the risk assessment reports for those two substances. When considering the data, it should be stressed that there are considerable analytical difficulties (relating to a general lack of analytical standards, and possible interferences from the polybrominated diphenyl ethers themselves) in determining the actual levels of brominated dibenzo-*p*-dioxins and dibenzofurans found in all of the available studies.

From the available information it is clear that polybrominated diphenyl ethers can form brominated dibenzo-*p*-dioxins and furans in laboratory studies when heated to high temperatures. This means that the same or similar products have the potential to be formed in processes where similar temperatures are reached during disposal and recycling. Such processes could include waste disposal [incineration or landfill (where fires could occur)], or recycling of plastics or metals contaminated with plastics. In addition, actual fires involving articles containing the flame retardants could also be considered similarly.

In the case of incineration, landfill, metal recycling and accidental fires, the brominated diphenyl ether flame retardant is likely to represent a small part of the total halogen available in the process. The available information indicates, particularly in the case of waste incineration and landfill, that chlorine is the prevalent halogen present, and that the main dioxin and furans formed are chlorinated analogues. Monobromo-polychloro analogues have been found, but generally at lower concentrations than the analogues containing chlorine only. This indicates that the majority of the halogenated dioxins and furans in these processes are likely to be formed by *de novo* synthesis. Thus the amounts of halogenated dibenzo-*p*-dioxins formed in these processes is likely to be a function of the total amount of halogen present, of which the polybrominated diphenyl ethers will make a contribution, rather than solely on the amount of polybrominated diphenyl ether present. (The available laboratory studies using the polybrominated diphenyl ethers cannot distinguish between *de novo* synthesis and direct formation of the brominated dibenzo-*p*-dioxins and furans. It is, therefore, possible that direct formation of these products could also occur during incineration etc, followed by halogen exchange to give the mainly chlorinated species). In the case of accidental fires, many other toxic products may also be formed, for example polycyclic aromatic hydrocarbons, which will also contribute to the overall toxicity of the fire products (Spindler, 1997). These products are not related to the presence of polybrominated diphenyl ethers.

It should also be noted that halogenated dioxin and furan formation from some of these processes is well known and emission control technology is available for incinerators and metal recycling, that can be used to reduce the amounts of these substances formed in the process to acceptable levels. However, it may be possible that metal recycling and incineration could take place at installations without suitable emission reduction equipment. As landfill fires and other fires are considered to be accidental, no such emission control technology exists for these. Overall, for disposal by incineration and landfill, metal recycling and accidental fires, it can be concluded that the polybrominated diphenyl ethers, as a source of bromine, can contribute to the formation of halogenated dibenzo-*p*-dioxins and furans generated during such processes but it is not possible to quantify the amounts or assess the environmental significance of these products.

The available information available for recycling of plastics indicates that there is little or no increase in the amounts of brominated dibenzofurans and dibenzo-*p*-dioxins formed. Low levels of these products have also been measured in processed plastics (the levels in some cases exceed the German Dioxinverordnung, although a recent detailed study with decabromodiphenyl ether indicated that the levels are well below those specified in the Dioxinverordnung). The recycling of many plastics is still at an experimental stage and is not currently routinely carried out at present. In terms of the environment, the potential for environmental exposure to these substances from plastics processing and recycling appears to be lower than for some of the other processes mentioned above. The recycling of polyurethane foam containing pentaBDPE is not thought to have a potential for generating brominated dibenzofurans and dibenzo-*p*-dioxins.

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Appendix B EUSES MODELLING

In the EUSES model the use patterns refer to the following scenarios in the risk assessment:

USE Pattern 1 [processing] release from use in manufacture of polyurethanes

The disperse release of pentaBDPE from foams, etc., in use are included in the regional and continental release figures.

Appendix C SAMS MODELLING

```
Name   = PENTABROMODIPHENYL ETHER  # Substance name
SumFor = C12H5Br5O  # Chemical sum formula
MolW   = 564.7      # [g/mol] Molecular mass
SolW   = 2.4e-006   # [g/l] Solubility in water
VP     = 4.69e-005  # [Pascal] Vapor pressure at 20 centigrades
MP     = 270        # [Kelvin] Melting point
BP     = 470        # [Kelvin] Boiling point at 100000 Pascal
Koc    = 5.568e+005 # [cm3 H2O/g] Partition coefficient
                          organic carbon - water
logKow = 6.57       # Logarithm of the n-octanol - water
                          partition coefficient
BCF    = 14350      # Bioconcentration factor in Fish


Parameters for SOIL:
SOIL_Input  = 0    # [kg/m2d] Substance input rate into the
                          upper soil layer. This is the
                          default value.
SOIL_Hori   = 3    # number of soil horizons. This is the
                          default value.
SOIL_Rain   = 2.1  # [mm/d] Precipitation. This is the default
                          value.
SOIL_Evap   = 1.6  # [mm/d] Evapotranspiration. This is the
                          default value.
SOIL_Runoff = 0.2  # [mm/d] Surface water runoff. This is the
                          default value.
SOIL_Time   = 730  # [d] Current time. This value has been
                          estimated
SOIL_TEnd   = 730  # [d] End of simulation period
SOIL_TStep  = 1    # [d] Time step for output action during
                          simulation. This is the default
                          value.
SOIL_DT     = 0.01 # [d] Internal time step for simulation.
                          This is the default value.
SOIL_StartTime = 0 # [d] Starting time for mass balance. This
                          is the default value.


Boxes    Depth       Por       Disp      Dens       OrgC
           m         m3/m3     m         kg/m3      kg/kg
20        0.2        0.5       0.05      1309       0.015
20        0.6        0.5       0.05      1271       0.05
20        1.4        0.5       0.05      1271       0.05
```

OrgM kg/kg	VolW m3/m3 soil	Temp K	WFlux mm/d	pH	KD cm3 H2O/g	RDeg 1/d
0.02586	0.3	293	0.3	6.8	8352	0
0.0862	0.3	293	0.3	6.8	27840	0
0.0862	0.3	293	0.3	6.8	27840	0

```
SOIL_ConcTop =     0.9063 # [kg/m3] Concentration in top
                          layer. This value has been
                          estimated.
SOIL_ConcBot = 1.318e-217 # [kg/m3] Concentration in bottom
                          layer. This value has been
                          estimated.
SOIL_SumSorb =      547.1 # [kg/m2] Total of substance sorbed
                          to soil matrix. This value has been
                          estimated.
SOIL_SumSolv =    0.06551 # [kg/m2] Total of substance solved
                          in soil water. This value has been
                          estimated.
SOIL_SumAir =  0.0002968 # [kg/m2] Total of substance in soil
                          air. This value has been estimated.
SOIL_SumTot =   0.009456 # [kg/m2] Total of substance
                          remaining in soil. This value has
                          been estimated.
```

	Flow kg/m2/d	Balance kg/m2
Input	0	0.01
Runoff	0	0
Volatilisation	7.028e-007	0.0005439
Degradation	0	0
Leaching	1.117e-225	1.372e-224
Remaining	-7.028e-007	0.009456

Depth m	Conc kg/m3	ConcA kg/m3 air	ConcW kg/m3 H2O	ConcS kg/kg soil
0.01	0.9063	3.756e-007	8.291e-005	0.000529
0.02	0.03848	1.595e-008	3.52e-006	2.246e-005
0.03	0.0008123	3.366e-010	7.431e-008	4.742e-007
0.04	1.142e-005	4.731e-012	1.044e-009	6.664e-009
0.05	1.203e-007	4.984e-014	1.1e-011	7.021e-011
0.06	1.013e-009	4.2e-016	9.271e-014	5.916e-013
0.07	7.115e-012	2.949e-018	6.509e-016	4.153e-015
0.08	4.281e-014	1.774e-020	3.916e-018	2.499e-017
0.09	2.254e-016	9.34e-023	2.062e-020	1.316e-019
0.1	1.055e-018	4.371e-025	9.649e-023	6.157e-022
0.11	4.442e-021	1.841e-027	4.063e-025	2.593e-024

0.12	1.701e-023	7.047e-030	1.556e-027	9.927e-027
0.13	5.968e-026	2.473e-032	5.459e-030	3.484e-029
0.14	1.933e-028	8.011e-035	1.768e-032	1.129e-031
0.15	5.815e-031	2.41e-037	5.319e-035	3.394e-034
0.16	1.633e-033	6.765e-040	1.493e-037	9.53e-037
0.17	4.297e-036	1.78e-042	3.93e-040	2.508e-039
0.18	1.064e-038	4.41e-045	9.736e-043	6.213e-042
0.19	2.49e-041	1.032e-047	2.278e-045	1.453e-044
0.2	3.686e-044	1.528e-050	3.372e-048	2.152e-047
0.22	1.994e-047	2.552e-054	5.634e-052	1.234e-050
0.24	3.172e-051	4.06e-058	8.963e-056	1.963e-054
0.26	4.815e-055	6.164e-062	1.361e-059	2.98e-058
0.28	6.99e-059	8.948e-066	1.975e-063	4.326e-062
0.3	9.722e-063	1.245e-069	2.747e-067	6.017e-066
0.32	1.298e-066	1.662e-073	3.668e-071	8.033e-070
0.34	1.666e-070	2.132e-077	4.707e-075	1.031e-073
0.36	2.059e-074	2.635e-081	5.817e-079	1.274e-077
0.38	2.453e-078	3.14e-085	6.931e-083	1.518e-081
0.4	2.821e-082	3.611e-089	7.972e-087	1.746e-085
0.42	3.136e-086	4.015e-093	8.863e-091	1.941e-089
0.44	3.374e-090	4.319e-097	9.534e-095	2.088e-093
0.46	3.516e-094	4.501e-101	9.935e-099	2.176e-097
0.48	3.553e-098	4.548e-105	1.004e-102	2.199e-101
0.5	3.484e-102	4.459e-109	9.844e-107	2.156e-105
0.52	3.318e-106	4.248e-113	9.377e-111	2.054e-109
0.54	3.073e-110	3.933e-117	8.683e-115	1.902e-113
0.56	2.768e-114	3.544e-121	7.823e-119	1.713e-117
0.58	2.428e-118	3.108e-125	6.862e-123	1.503e-121
0.6	1.384e-122	1.771e-129	3.91e-127	8.564e-126
0.64	3.018e-127	3.863e-134	8.528e-132	1.868e-130
0.68	6.421e-132	8.219e-139	1.814e-136	3.974e-135
0.72	1.334e-136	1.707e-143	3.768e-141	8.253e-140
0.76	2.705e-141	3.463e-148	7.644e-146	1.674e-144
0.8	5.363e-146	6.865e-153	1.515e-150	3.319e-149
0.84	1.039e-150	1.331e-157	2.937e-155	6.433e-154
0.88	1.971e-155	2.523e-162	5.569e-160	1.22e-158
0.92	3.657e-160	4.681e-167	1.033e-164	2.263e-163
0.96	6.644e-165	8.505e-172	1.878e-169	4.112e-168
1	1.183e-169	1.514e-176	3.342e-174	7.319e-173
1.04	2.063e-174	2.64e-181	5.828e-179	1.277e-177
1.08	3.527e-179	4.515e-186	9.966e-184	2.183e-182
1.12	5.914e-184	7.571e-191	1.671e-188	3.66e-187
1.16	9.731e-189	1.246e-195	2.75e-193	6.022e-192
1.2	1.571e-193	2.011e-200	4.44e-198	9.725e-197
1.24	2.491e-198	3.189e-205	7.039e-203	1.542e-201
1.28	3.879e-203	4.965e-210	1.096e-207	2.401e-206
1.32	5.934e-208	7.596e-215	1.677e-212	3.672e-211
1.36	8.92e-213	1.142e-219	2.521e-217	5.521e-216
1.4	1.318e-217	1.687e-224	3.725e-222	8.159e-221

```
Name   = TETRABROMODIPHENYL ETHER  # Substance name
SumFor = C12H6Br4O  # Chemical sum formula
MolW   =      484.6 # [g/mol] Molecular mass
SolW   =  1.09e-005 # [g/l] Solubility in water
VP     =    0.00052 # [Pascal] Vapor pressure at 20
                        centigrades
MP     =        270 # [Kelvin] Melting point
BP     =        470 # [Kelvin] Boiling point at 100000 Pascal
Koc    =   2.8e+005 # [cm3 H2O/g] Partition coefficient
                        organic carbon - water
logKow =        6.1 # Logarithm of the n-octanol - water -
                        partition coefficient
BCF    =      31950 # Bioconcentration factor in Fish


Parameters for SOIL:
SOIL_Input  = 0    # [kg/m2d] Substance input rate into the
                        upper soil layer. This is the
                        default value.
SOIL_Hori   = 3    # number of soil horizons. This is the
                        default value.
SOIL_Rain   = 2.1  # [mm/d] Precipitation. This is the default
                        value.
SOIL_Evap   = 1.6  # [mm/d] Evapotranspiration. This is the
                        default value.
SOIL_Runoff = 0.2  # [mm/d] Surface water runoff. This is the
                        default value.
SOIL_Time   = 730  # [d] Current time. This value has been
                        estimated
SOIL_TEnd   = 730  # [d] End of simulation period
SOIL_TStep  = 1    # [d] Time step for output action during
                        simulation. This is the default
                        value.
SOIL_DT     = 0.01 # [d] Internal time step for simulation.
                        This is the default value.
SOIL_StartTime = 0 # [d] Starting time for mass balance. This is
                        the default value.


Boxes    Depth       Por       Disp      Dens       OrgC
           m         m3/m3     m         kg/m3      kg/kg
20        0.2        0.5       0.05      1309       0.015
20        0.6        0.5       0.05      1271       0.05
20        1.4        0.5       0.05      1271       0.05
```

OrgM kg/kg	VolW m3/m3 soil	Temp K	WFlux mm/d	pH	KD cm3 H2O/g	RDeg 1/d
0.02586	0.3	293	0.3	6.8	4200	0
0.0862	0.3	293	0.3	6.8	14000	0
0.0862	0.3	293	0.3	6.8	14000	0

```
SOIL_ConcTop =    0.6886 # [kg/m3] Concentration in top layer.
                           This value has been estimated.
SOIL_ConcBot = 3.911e-186 # [kg/m3] Concentration in bottom
                           layer. This value has been
                           estimated.
SOIL_SumSorb =     503.4 # [kg/m2] Total of substance sorbed
                           to soil matrix. This value has been
                           estimated.
SOIL_SumSolv =    0.1199 # [kg/m2] Total of substance solved
                           in soil water. This value has been
                           estimated.
SOIL_SumAir =   0.001138 # [kg/m2] Total of substance in soil
                           air. This value has been estimated.
SOIL_SumTot =   0.008018 # [kg/m2] Total of substance
                           remaining in soil. This value has
                           been estimated.
```

	Flow kg/m2/d	Balance kg/m2
Input	0	0.01
Runoff	0	0
Volatilisation	2.224e-006	0.001982
Degradation	0	0
Leaching	6.589e-194	8.104e-193
Remaining	-2.224e-006	0.008018

Depth m	Conc kg/m3	ConcA kg/m3 air	ConcW kg/m3 H2O	ConcS kg/kg soil
0.01	0.6886	1.189e-006	0.0001252	0.0004019
0.02	0.1051	1.814e-007	1.911e-005	6.133e-005
0.03	0.007774	1.342e-008	1.414e-006	4.538e-006
0.04	0.0003807	6.572e-010	6.925e-008	2.222e-007
0.05	1.394e-005	2.407e-011	2.536e-009	8.139e-009
0.06	4.08e-007	7.043e-013	7.421e-011	2.382e-010
0.07	9.941e-009	1.716e-014	1.808e-012	5.802e-012
0.08	2.075e-010	3.582e-016	3.774e-014	1.211e-013
0.09	3.789e-012	6.541e-018	6.892e-016	2.212e-015
0.1	6.148e-014	1.061e-019	1.118e-017	3.589e-017
0.11	8.977e-016	1.55e-021	1.633e-019	5.24e-019
0.12	1.191e-017	2.057e-023	2.167e-021	6.955e-021
0.13	1.449e-019	2.502e-025	2.637e-023	8.46e-023
0.14	1.627e-021	2.81e-027	2.96e-025	9.5e-025

0.15	1.697e-023	2.929e-029	3.087e-027	9.905e-027
0.16	1.651e-025	2.85e-031	3.003e-029	9.638e-029
0.17	1.506e-027	2.6e-033	2.74e-031	8.792e-031
0.18	1.293e-029	2.232e-035	2.352e-033	7.548e-033
0.19	1.048e-031	1.81e-037	1.907e-035	6.12e-035
0.2	5.407e-034	9.335e-040	9.836e-038	3.156e-037
0.22	1.012e-036	5.398e-043	5.688e-041	6.265e-040
0.24	5.569e-040	2.97e-046	3.13e-044	3.447e-043
0.26	2.922e-043	1.558e-049	1.642e-047	1.808e-046
0.28	1.465e-046	7.814e-053	8.233e-051	9.068e-050
0.3	7.036e-050	3.752e-056	3.953e-054	4.354e-053
0.32	3.241e-053	1.728e-059	1.821e-057	2.006e-056
0.34	1.435e-056	7.651e-063	8.062e-061	8.879e-060
0.36	6.112e-060	3.26e-066	3.435e-064	3.783e-063
0.38	2.51e-063	1.338e-069	1.41e-067	1.553e-066
0.4	9.947e-067	5.304e-073	5.589e-071	6.156e-070
0.42	3.809e-070	2.031e-076	2.14e-074	2.357e-073
0.44	1.411e-073	7.525e-080	7.929e-078	8.733e-077
0.46	5.062e-077	2.7e-083	2.845e-081	3.133e-080
0.48	1.761e-080	9.389e-087	9.893e-085	1.09e-083
0.5	5.942e-084	3.169e-090	3.339e-088	3.677e-087
0.52	1.947e-087	1.039e-093	1.094e-091	1.205e-090
0.54	6.204e-091	3.308e-097	3.486e-095	3.84e-094
0.56	1.923e-094	1.025e-100	1.08e-098	1.19e-097
0.58	5.8e-098	3.093e-104	3.259e-102	3.59e-101
0.6	1.137e-101	6.062e-108	6.388e-106	7.035e-105
0.64	8.367e-106	4.462e-112	4.701e-110	5.178e-109
0.68	6.007e-110	3.203e-116	3.375e-114	3.718e-113
0.72	4.209e-114	2.245e-120	2.365e-118	2.605e-117
0.76	2.881e-118	1.536e-124	1.619e-122	1.783e-121
0.8	1.926e-122	1.027e-128	1.082e-126	1.192e-125
0.84	1.259e-126	6.715e-133	7.076e-131	7.794e-130
0.88	8.053e-131	4.294e-137	4.525e-135	4.984e-134
0.92	5.039e-135	2.687e-141	2.832e-139	3.119e-138
0.96	3.087e-139	1.646e-145	1.735e-143	1.911e-142
1	1.853e-143	9.881e-150	1.041e-147	1.147e-146
1.04	1.09e-147	5.81e-154	6.122e-152	6.743e-151
1.08	6.281e-152	3.35e-158	3.529e-156	3.887e-155
1.12	3.551e-156	1.894e-162	1.995e-160	2.198e-159
1.16	1.969e-160	1.05e-166	1.107e-164	1.219e-163
1.2	1.072e-164	5.717e-171	6.024e-169	6.635e-168
1.24	5.729e-169	3.055e-175	3.219e-173	3.546e-172
1.28	3.007e-173	1.603e-179	1.689e-177	1.861e-176
1.32	1.55e-177	8.266e-184	8.71e-182	9.593e-181
1.36	7.853e-182	4.188e-188	4.413e-186	4.86e-185
1.4	3.911e-186	2.086e-192	2.198e-190	2.421e-189

Appendix D Composition of commercial products – The presence of lower brominated diphenyl ethers in commercial octa- and decabromodiphenyl ether

Introduction

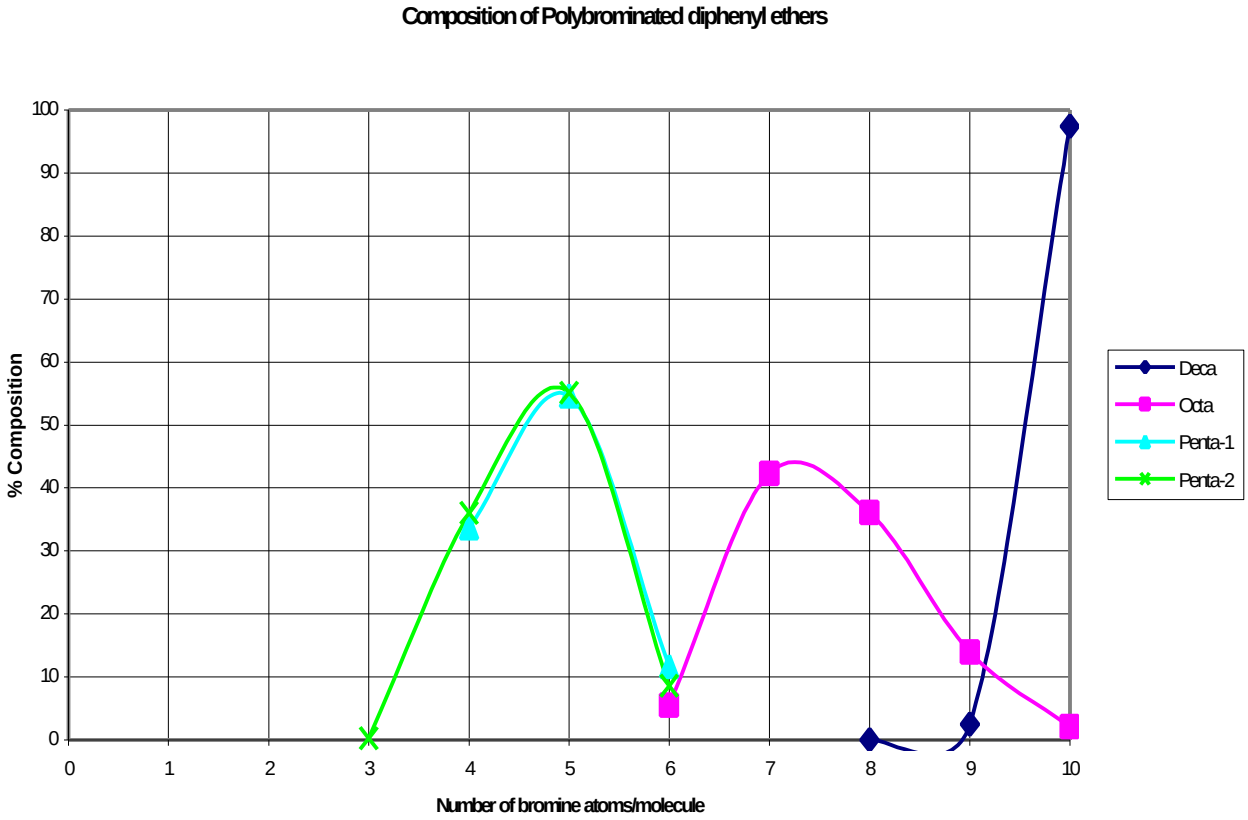
The three commercial polybrominated diphenyl ethers are all mixtures of congeners. This results from the fact that the production process involves a step-wise addition of bromine to the biphenyl ether ring and so each product has to pass through a series of lower brominated congeners until the required overall degree of bromination is obtained. As the lower brominated diphenyl ethers, particularly the tetra- and pentabromodiphenyl ether congeners, appear to be of most concern for the environment (see the main pentabromodiphenyl ether risk assessment report), it is of interest to the risk assessment process to see if significant amounts of these congeners are present in the commercial octa- and decabromodiphenyl ether products.

Composition of products

The current compositions of the commercial polybrominated diphenyl ethers are shown in **Table D1**. These are based on composite samples from the current EU suppliers and are the substances that have been used in all the recent tests. The actual raw analytical data has not been provided for these analyses. These figures are also displayed in the chart below. These data have been used as a basis for the main risk assessment reports for the three commercial substances. This data indicates that if tetra- and pentabromodiphenyl ethers are present in the commercial octabromodiphenyl ether or decabromodiphenyl ether products, they must be present only at very low levels.

Table D1 Current composition of brominated diphenyl ethers

Component	% Composition of commercial product			
	Penta-		Octa-	Deca-
	1997	2000	1997	1997
Tribromodiphenyl ether		0.23		
Tetrabromodiphenyl ether	33.7	36.02		
Pentabromodiphenyl ether	54.6	55.10		
Hexabromodiphenyl ether	11.7	8.58	5.5	
Heptabromodiphenyl ether			42.3	
Octabromodiphenyl ether			36.1	0.04
Nonabromodiphenyl ether			13.9	2.5
Decabromodiphenyl ether			2.1	97.4



Penta-1: 1997 figures
Penta-2: 2000 figures

Other information

Commercial decabromodiphenyl ether

Recently data has become available on the ultra-trace levels of lower brominated diphenyl ethers (tri- to heptabromodiphenyl ethers) present in the current decabromodiphenyl ether products supplied in the EU (GfA, 1999). The analyses were carried out in duplicate on a 1:1:1 mixture of decabromodiphenyl ether from the three current major suppliers. The results of the analyses are shown in **Table D2**.

The results of the GfA (1999) study show that the lower brominated diphenyl ethers are present in the commercial decabromodiphenyl ether product but only at trace levels. **Table D2** shows the estimated amounts of these impurities present in the 10,000 tonnes of the commercial product (the approximate amount of decabromodiphenyl ether supplied to the EU market). It should be remembered that the figures are for the total amount of these impurities present within the commercial decabromodiphenyl ether product supplied and do not represent the releases of these impurities to the environment. As only a fraction of these impurities will be released to the environment it can be concluded that the lower brominated diphenyl ether impurities present in the commercial decabromodiphenyl ether will not contribute significantly to the environmental burden, especially when compared to the releases from other sources.

Table D2 Ultra-trace analysis of amounts of lower brominated diphenyl ethers in commercial decabromodiphenyl ether (GfA, 1999).

Congener	Concentration in decabromodiphenyl ether (µg/kg)	Percentage composition	Amount present in 10,000 tonnes of commercial decabromodiphenyl ether
3,4,4'-tri	nd (<55)		
Total tri[a]	102	$1.02 \cdot 10^{5}$%	1.02 kg
2,4,4',6-tetra	nd (<90)		
2,3',4',6-tetra	nd (<90)		
2,2',4,4'-tetra	245		
2,3',4,4'-tetra	nd (<90)		
3,3',4,4'-tetra	nd (<90)		
Total tetra	245	$2.45 \cdot 10^{-5}$%	2.45 kg
2,3',4,4',6-penta	nd (<85)		
2,2',4,4',5-penta	2,227		
2,2',3,4,4'-penta	nd (<192)		
Total penta	2,227	$2.23 \cdot 10^{-3}$%	22.2 kg
2,2',4,4',5,5'-hexa	9,279		
Total hexa[a]	11,705	$1.17 \cdot 10^{-3}$%	117.05 kg
2,3,3',4,4',5,6-hepta	nd (<1,400)		
Total hepta[a]	33,541	$3.35 \cdot 10^{-3}$%	335.41 kg
Total (tri-hepta)			487.2 kg

nd – not detected. Detection limit given in ( )
[a] Concentration given includes some unidentified isomers
[b]Refers to the limit value from the German Dioxin Regulations
[c]Actual value may be lower than this due to analytical interference

Commercial octabromodiphenyl ether

There is some discrepancy between the composition of octabromodiphenyl ether given in the OECD Voluntary Industry Commitment (VIC) and the composition currently supplied (**Table D1**), particularly with regard to the levels of the pentabromodiphenyl ether congener. The composition given in the VIC is as follows:

Hexa/pentabromodiphenyl ether	1.4-12.0%
Heptabromodiphenyl ether	43.0-58.0%
Octabromodiphenyl ether	26.0-35.0%
Nonabromodiphenyl ether	8.0-14.0%
Decabromodiphenyl ether	0.0-3.0%

In the VIC it is not clear if there is any pentabromodiphenyl ether actually present. No details of the analyses used were provided. Also, at the time the VIC was set up, production of octabromodiphenyl ether was carried out in the EU. Since then, production has moved to sites outside the EU, and some producers have stopped producing octabromodiphenyl ether

altogether. This may have had some effect on the composition. From the information presented in **Table D1** above, it is clear that if pentabromodiphenyl ether is present in the commercial product, it will be at much lower levels than the 12% indicated by the VIC.

Further, perhaps more convincing evidence, for the lack of the pentabromodiphenyl ether congener in commercial octabromodiphenyl ether comes from the analyses carried out by Sondack et al (1994), mentioned in the risk assessment report. Here, commercial products were analysed for the presence of tetrabromo- to nonabromodiphenyl ether congeners by NMR analysis of material purified by preparative HPLC techniques and by GC analysis. Two commercial octabromodiphenyl ethers (one described as "high-melting" octa) were analysed; both supplied by Bromine Compounds Ltd, Israel. No peaks corresponding to tetra- or pentabromodiphenyl ether were found in the analyses of either of the two commercial octabromodiphenyl ethers.

For the high-melting octabromodiphenyl ether, three main peaks were found and identified as: 2,2',3,4,4',5,5',6-octabromodiphenyl ether; 2,2',3,3',4,4',5',6-octabromodiphenyl ether; and 2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether. For the "normal" octabromodiphenyl ether product, 6 main peaks were identified as: 2,2', 4,4', 5,5'-hexabromodiphenyl ether; 2,2',3,4,4',5',6-heptabromodiphenyl ether; 2,2',3,4,4',5,5',6-octabromodiphenyl ether; 2,2',3,3',4,4',5',6-octabromodiphenyl ether; 2,2',3,3',4,4',6,6'-octabromodiphenyl ether; and 2,2',3,3',4,4',5,6,6'-nonabromodiphenyl ether. Although in this study no information was given on the percentage composition of the congeners identified or the detection limit for the various congeners in the sample, the fact that hexabromodiphenyl ether isomers were detected but pentabromodiphenyl ether isomers were not detected does indicate that the levels of pentabromodiphenyl ether isomers in the commercial product must be very low.

As mentioned above, a possible explanation between the composition given in the VIC and the currently stated composition may be due to improvements or changes in the production methods. Another possible explanation is that at the time that the VIC was being set up the analytical methods were not able to satisfactorily distinguish between penta- and hexabromodiphenyl ether in the commercial product (analytical standards for penta- and hexabromodiphenyl ether isomers have only become available relatively recently) and so Industry were just covering themselves in the VIC. From the other available information summarised above, it appears that if pentabromodiphenyl ether is present in the commercial octabromodiphenyl ether product, it is only there in very small (trace) amounts. This is consistent with the distribution pattern found for the components of both pentabromodiphenyl ether and decabromodiphenyl ether.

In terms of the risk assessment, the hexabromodiphenyl ether component in the commercial octabromodiphenyl ether is accounted for in the assessment of octabromodiphenyl ether.

Summary

Pentabromodiphenyl ether may be present in the commercial octabromodiphenyl ether and decabromodiphenyl ether products, but only at very low (trace) levels. These levels are unlikely to contribute significantly to the environmental burden of pentabromodiphenyl ether. The main impurities present in commercial octabromodiphenyl ether and decabromodiphenyl ether are already accounted for in the respective risk assessments (see Appendix E).

References

GfA (1999). Analysis of a decabromodiphenyl oxide blend, a HIPS plastic, the HIPS plastic containing the DecaBDPO and Sb_2O_3 and the repeated recycled HIPS/Sb_2O_3/DecaBDPO plastic for partially brominated diphenyl ethers and 8 polybrominated dibenzo(p)dioxin and dibenzofuran congeners. Report 60425-001 B01, Gesellschaft für Arbeitsplatz- und Umwelanalytik mbH, August 26, 1999.

Sondack D., Ron T. and Kallos M. D. (1994). The characterization of polybrominated diphenyl ether. Advances of Organobromine Chemistry II. Proceedings of Organobrom'93, Jerusalem, June 28-July2, 1993. Elsevier Science, Amsterdam, 1994. Eds. J-R. Desmus, B. Gérard and M. J. Goldstein.

Appendix E Emvironmental modelling - Sensitivity Analysis

Introduction

This appendix looks at the predicted environmental distribution and concentrations of the individual components of the commercial mixtures. Possible variations in some of physico-chemical properties used in the environmental modelling and the likely effect on the predicted environmental concentrations for both the individual components and the commercial formulations are also discussed.

The brominated diphenyl ethers as a group are highly lipophilic substances, with low water solubilities and vapour pressures. In addition, the three commercially available substances penta-, octa- and decabromodiphenyl ether can be considered as complex mixtures. These properties mean that the measurement of some key parameters used in environmental modelling such as vapour pressure, water solubility and octanol-water partition coefficient is very difficult and so in some cases approximate or indicative values only can be obtained. The sensitivity of the environmental models to variations in these parameters are considered in the following Sections.

The modelling and PEC determinations on a commercial formulation basis are given in the main reports for the three substances.

Variation in physico-chemical properties

Available data set

The three main physico-chemical properties used in the EUSES model are water solubility, log octanol-water partition coefficient and vapour pressure. **Table E1** shows the measured and estimated values available for these properties. The EPI estimation programme (Syracuse Research Corporation) has been used to obtain estimated values from the chemical structure. **Table E2** shows some of the key measured and estimated partition coefficients used in EUSES.

In order to carry out an analysis of the behaviour of the different components of the commercial formulations, it is important to have a meaningful set of data as input into the model. As can be seen from **Table E1**, the EPI estimates for vapour pressure, water solubility and octanol water partition coefficient are in good agreement with the measured data for diphenyl ether itself, but the agreement gets progressively worse as the degree of bromination increases. The EPI estimates for octanol-water partition coefficients generally overestimate the measured value, whereas the water solubility and vapour pressure estimates generally underestimate the measured value.

Of the available data, there are measured values for vapour pressure, sediment-water adsorption coefficients, bioconcentration factors and water solubility for some brominated diphenyl ethers. These values will be taken as reliable and used for extrapolation to provide a reasonably consistent data set for the environmental modelling of the individual components of the commercial brominated diphenyl ethers.

Table E1 Estimated and measured physico-chemical properties for the brominated diphenyl ethers

Property	Diphenyl ether	Tetrabromo	2,2',4,4'5-Penta	2,2'4,4',6-Penta	Commercial penta	Hexa	Hepta	Octa	Commercial octa	Nona	Deca	Commercial deca
Log K_{ow}												
Measured value	4.2	5.87-6.16	6.46-6.97	6.46-6.97	6.57	6.86-7.92		8.35-8.90	6.29		9.97	6.27
Estimated-EPI	4.05	6.77	7.66	7.66		8.55	9.44	10.33		11.22	12.11	
Water solubility												
Measured value	21 mg/l	10.9 µg/l	2.4 µg/l	(2.4 µg/l)	13.3 µg/l				~0.5 µg/l			<0.1 µg/l
Estimated-EPI	15.6 mg/l	1.46 µg/l	0.079 µg/l	0.079 µg/l		0.0042 µg/l	$2.2 \cdot 10^{-4}$ µg/l	$1.1 \cdot 10^{-5}$ µg/l		$5.6 \cdot 10^{-7}$ µg/l	$2.8 \cdot 10^{-8}$ µg/l	
Vapour pressure												
Measured value	2.7 Pa	$2.5\text{-}3.3 \cdot 10^{-4}$ Pa	$2.9\text{-}7.3 \cdot 10^{-5}$ Pa	$2.9\text{-}7.3 \cdot 10^{-5}$ Pa	$4.69 \cdot 10^{-5}$ Pa	$4.3\text{-}9.5 \cdot 10^{-6}$ Pa		$1.2\text{-}2.3 \cdot 10^{-7}$ Pa	$6.59 \cdot 10^{-6}$ Pa			$4.63 \cdot 10^{-6}$ Pa
Estimated-EPI	1.04 Pa	$3.2 \cdot 10^{-5}$ Pa	$3.3 \cdot 10^{-6}$ Pa	$3.3 \cdot 10^{-6}$ Pa		$3.8 \cdot 10^{-7}$ Pa	$4.4 \cdot 10^{-8}$ Pa	$4.9 \cdot 10^{-9}$ Pa		$5.4 \cdot 10^{-10}$ Pa	$5.8 \cdot 10^{-11}$ Pa	

Table E2 Estimated and measured partition coefficients for the brominated diphenyl ethers

Property	Diphenyl ether	Tetrabromo	2,2',4,4'5-Penta	2,2'4,4',6-Penta	Commercial penta	Hexa	Hepta	Octa	Commercial octa	Nona	Deca	Commercial deca
Henry's law constant (Pa m^3/mole)												
Measured value												
Estimated-EPI (bond contribution method)	28.5	0.86	0.36	0.36		0.15	0.06	0.03		0.01 4.51	$\cdot 10^{-3}$	
Estimated from vapour pressure/water solubility	8.4, 11.3, 21.9, 29.5	10.6, 10.5-13.9, 78.6-104, 1.35	23.3, 6.8-17, 0.78, 207-522	23.3, 6.8-17, 0.78, 207-522	2	58.2, 659-1,456	144	357, 8,742-16,756, 0.19-0.37, $7.9 \cdot 10^{-3}$	10.6	849	$1.99 \cdot 10^3$, $1.58 \cdot 10^8$, >44.4, $>5 \cdot 10^{-4}$	>44.4
Fish bioconcentration factor (l/kg)												
Measured	195	28,800-35,100 [66,700][d]	~40 [1,440][d]	10,200-11,700 [17,700][d]		~1,000-5,600 [5,640][d]	(<4)	(<4)	<4	(<4)		<5
Estimated from log K_{ow}[a]	553-741	19,480-37,090; 46,050	43,061-45,880; 34,141	43,061-45,880; 34,141	44,550	46,180-27,260; 12,200	2,100	16,390-6,670; 175	39,980	7	39,560; 522; 0.14	39,560
$Kp_{sed\text{-}water}$ (l/kg)												
Measured		28,293	49,167	49,167		62,727					79,433	
Koc (l/kg)												
Measured/ experimental[c]		565,860	983,340	983,340		$1.25 \cdot 10^6$					$1.59 \cdot 10^6$	
Estimated from log K_{ow}[b]	3,180; 2,400	71,560-122,900; 383,440	215,080-556,800; $2.02 \cdot 10^6$	215,080-556,800; $2.02 \cdot 10^6$	264,060	453,520-$3.27 \cdot 10^6$; $1.06 \cdot 10^7$	$5.58 \cdot 10^7$	$7.30 \cdot 10^6$- $2.03 \cdot 10^7$; $2.93 \cdot 10^8$	156,640	$1.54 \cdot 10^9$	150,900; $1.50 \cdot 10^8$; $8.11 \cdot 10^9$	150,900

[a]For log K_{ow}<6: log BCF = 0.85 log K_{ow} - 0.70; For log K_{ow}>6: log BCF = -0.20 (log K_{ow})^2 + 2.74 log K_{ow} - 4.72
[b]log K_{oc} = 0.81 log K_{ow} + 0.10
[c]Estimated from measured sediment water partition coefficients, assuming the sediment is 5% organic carbon
[d]Value for BCF calculated following re-analysis of original study (see Risk Assessment of pentabromodiphenyl ether for further details)

With regard to the log K_{ow}, there appears to be good agreement between the values measured using the HPLC technique and direct measurements at low to moderate bromination (e.g. pentabromodiphenyl ether), but the HPLC values appear to be higher than the direct measurement values for octa- and decabromodiphenyl ether. This may reflect the fact that the direct measurements (in this case using a generator column method) for highly lipophilic, low water solubility substances are very difficult and the differences in the values obtained between the two methods probably reflect this difficulty. The predicted (EPI) values for log K_{ow} are generally higher than the measured values

For this analysis, as values for most of the key modelling parameters are available from other sources, the uncertainty in the exact values of the octanol-water partition coefficients for the higher brominated congeners can to a large extent be ignored (i.e. measured values are available for some of the partition coefficients used in EUSES and so estimation from the log K_{ow} value is not always necessary). However, to take into account this uncertainty, and the uncertainty in all the other parameters, an attempt to study the effect of variation of the key parameters on the environmental modelling will also be undertaken.

In order to obtain reasonable data sets for the congeners for which few experimental data are available, the estimated log K_{ow} values could be used as a "normaliser" for the measured values for a given property. There is some theoretical justification for doing this for end-points such as water solubility, bioconcentration factors and K_{oc} values, as correlations between these endpoints and octanol-water partition coefficient are well known. For vapour pressure, there is no theoretical justification for this approach.

In order to carry out this analysis plots of estimated log K_{ow} (from the EPI programme) against measured log K_{ow}, water solubility, vapour pressure, $Kp_{sed\text{-}water}$ (and K_{oc}) and BCF were constructed.

Based on the plots below, the following relationships were found:

$$\log K_{owmeasure,HPLC} = 0.718 \cdot \log K_{owestimated} + 1.236 \quad [N=6, R^2=0.99]$$

$$\log (\text{water solubility } \{\mu g/l\}) = -0.611 \cdot \log K_{owestimated} + 5.896 \quad [N=5, R^2 = 0.87]$$

$$\log (\text{vapour pressure } \{Pa\}) = -1.109 \cdot \log K_{owestimated} + 4.225 \quad [N=5, R^2 = 0.92]$$

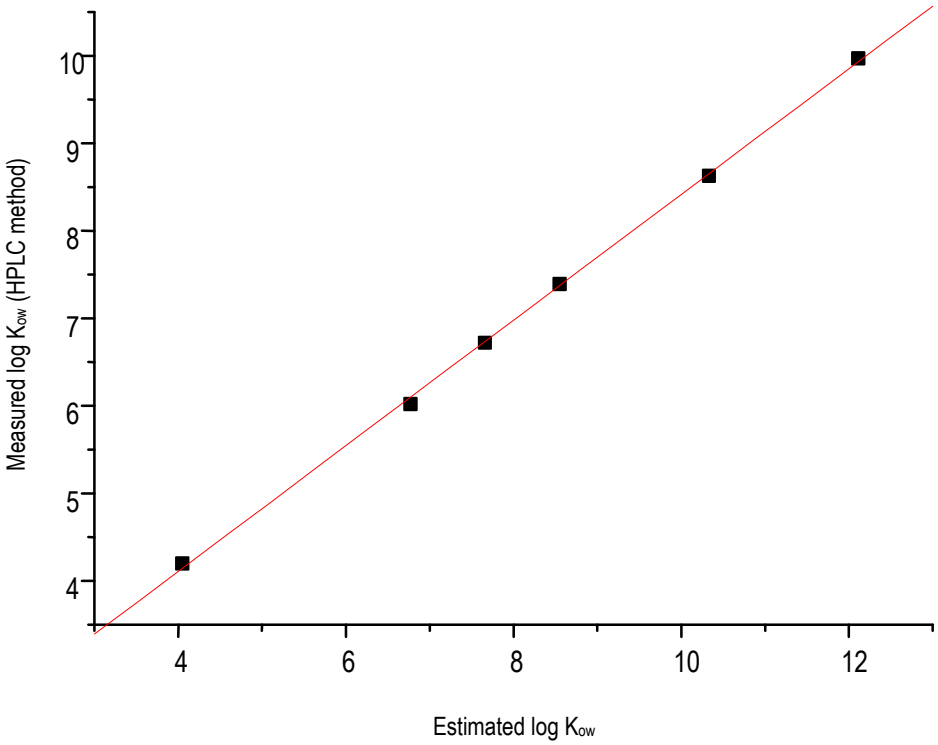
$$\log (Kp_{sed\text{-}water} \ \{l/kg\}) = 8{,}505 \cdot \log K_{owestimated} - 19{,}709 \quad [N=4, R^2 = 0.85]$$

$$\log (Koc \ \{l/kg\}) = 170{,}108 \cdot \log K_{owestimated} - 394{,}177 \quad [N=4, R^2 = 0.85]$$

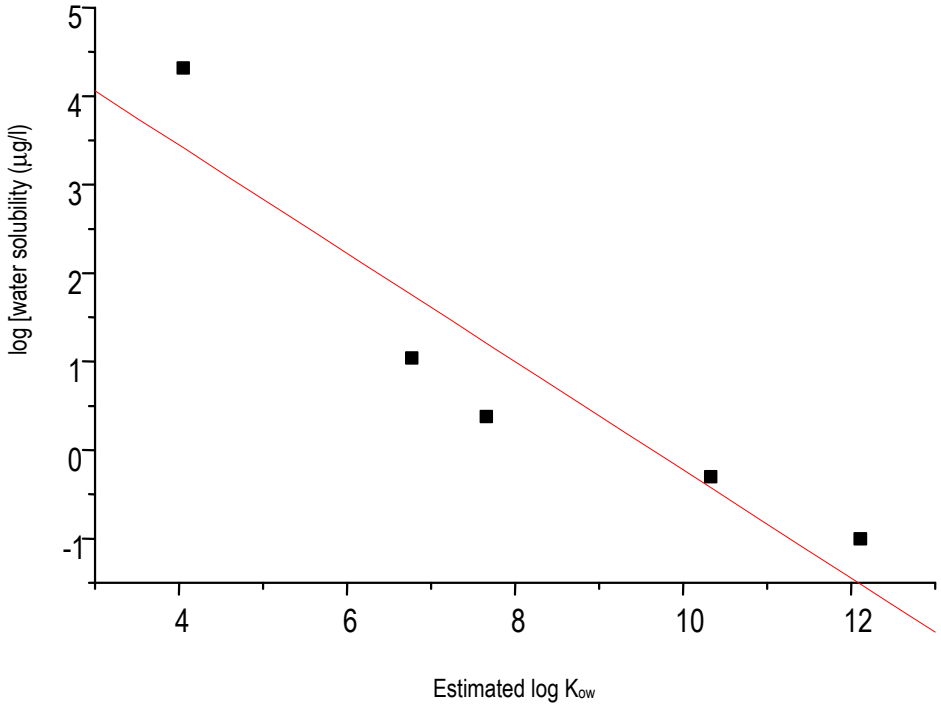
For the measured bioconcentration factors, a simple linear relationship between the BCF and estimated log K_{ow} could not be derived and so approximate values have to be estimated from the graph.

These equations then allow a value for any given property to be estimated so long as an estimated log K_{ow} is available from the EPI programme. This approach necessarily assumes that there is a (linear) relationship between the given property and the estimated log K_{ow} value. As can be seen from the plots, this appears to be a reasonable assumption.

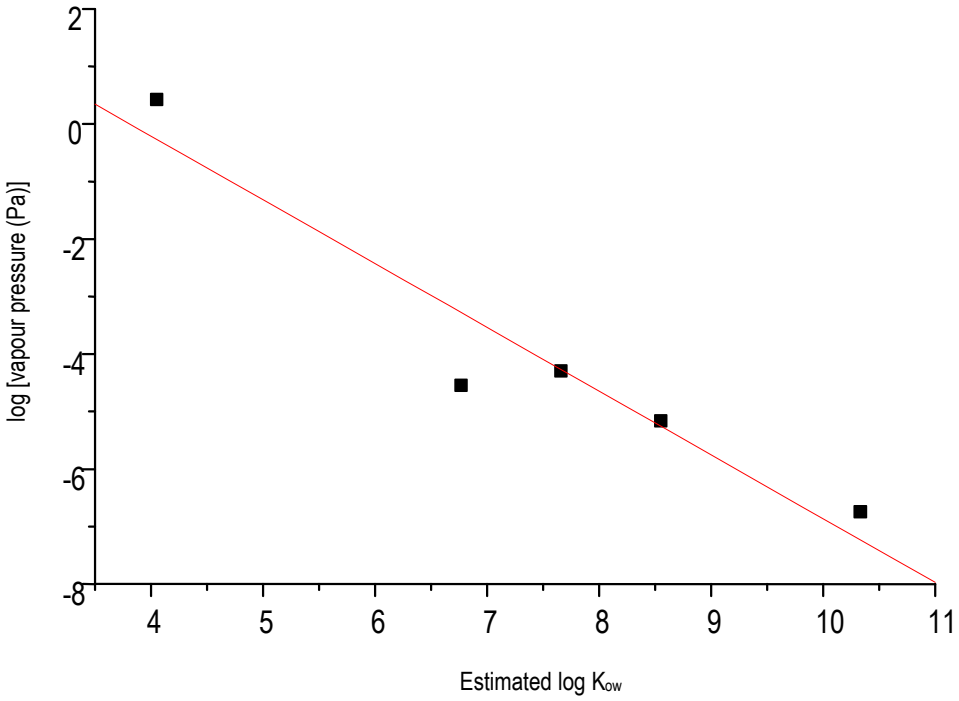
Plot 1 Relationship between measured log Kow (HPLC method) and estimated log Kow



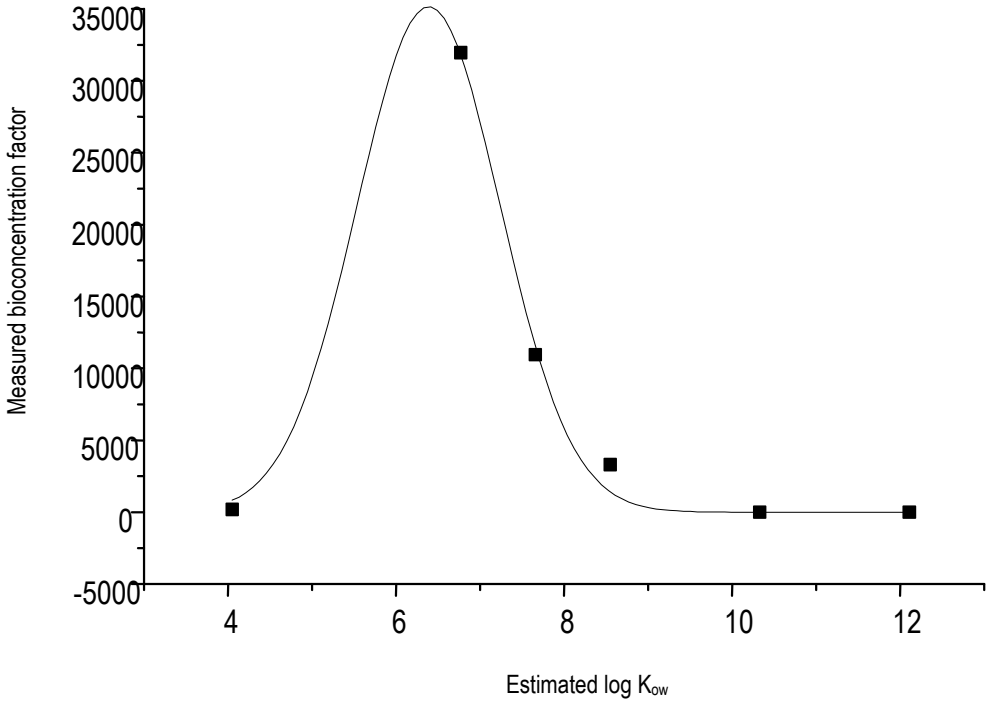
Plot 2 Relationship between log K_{ow} and water solubility



Plot 3 Relationship between estimated log K_{ow} value and measured (GC method) vapour pressure



Plot 4 Relationship between bioconcentration factor and log K_{ow}



Plot 5 Relationship between estimated log K_{ow} and measured sediment-water partition coefficient

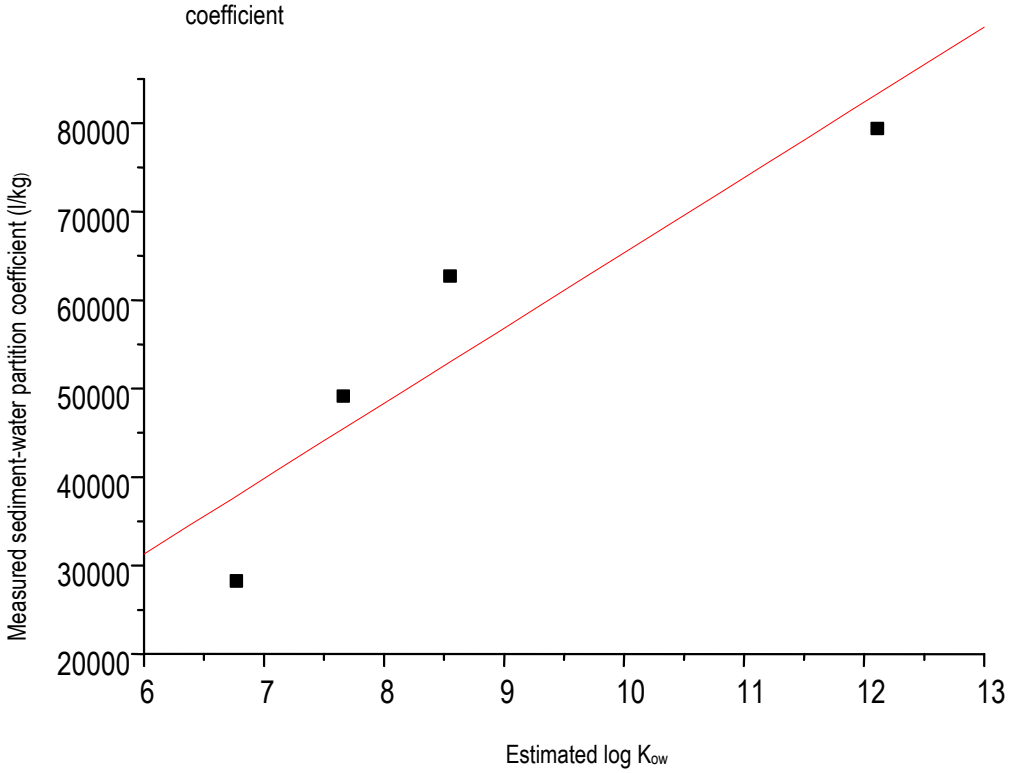


Table E3 shows the basic physico-chemical data for the brominated diphenyl ethers. The values have been derived from the equations given above using the EPI log K_{ow} estimate, except where reliable measured data was available for specific congeners (e.g. water solubility, BCFs). These values will be used as input data in the EUSES model to examine the differences in environmental behaviour between the various congeners. This analysis is carried out in Section 3.

Table E3 Basic physico-chemical properties of individual congeners for modelling derived from the available data

Property	Tetrabromo	2,2',4,4',5-Pentabromo	2,2',4,4',6-Pentabromo	Hexabromo	Heptabromo	Octabromo	Nonabromo	Decabromo
Water solubility	10.9 µg/l	2.4 µg/l	2.4 µg/l	4.7 µg/l	1.3 µg/l	0.5 µg/l	0.11 µg/l 0.03 µg/l	
Log K_{ow}	6.1	6.7	6.7	7.4	8.0	8.7	9.3	9.9
Vapour pressure	$5.2 \cdot 10^{-4}$ Pa	$5.4 \cdot 10^{-5}$ Pa	$5.4 \cdot 10^{-5}$ Pa	$5.5 \cdot 10^{-6}$ Pa	$5.7 \cdot 10^{-7}$ Pa	$5.9 \cdot 10^{-8}$ Pa	$6.1 \cdot 10^{-9}$ Pa	$6.2 \cdot 10^{-10}$ Pa
Koc	757,450 l/kg 908	850 l/kg	908,850 l/kg	1,060,250 l/kg	1,211,640 l/kg	1,363,040 l/kg	1,514,430 l/kg	1,665,830 l/kg
BCF	31,950 l/kg [66,700 l/kg][a]	40 l/kg [1,440 l/kg][a]	10,950 l/kg [17,700 l/kg][a]	3,300 l/kg [5,640 l/kg][a]	<4 l/kg	<4 l/kg	<4 l/kg	<4 l/kg
Other modelling input data (estimated using EPI program)								
Melting point	162°C	183°C	183°C	197°C	211°C	226°C	240°C	255°C
Boiling point	406°C	436°C	436°C	467°C	498°C	528°C	559°C	590°C
Rate constant for reaction with atmospheric hydroxyl radicals	$1.56 \cdot 10^{-12}$ cm^3 s^{-1} $molecule^{-1}$	$1.27 \cdot 10^{-12}$ cm^3 s^{-1} $molecule^{-1}$	$1.15 \cdot 10^{-12}$ cm^3 s^{-1} $molecule^{-1}$	$9.77 \cdot 10^{-13}$ cm^3 s^{-1} $molecule^{-1}$	$5.49 \cdot 10^{-13}$ cm^3 s^{-1} $molecule^{-1}$	$2.10 \cdot 10^{-13}$ cm^3 s^{-1} $molecule^{-1}$	$1.92 \cdot 10^{-13}$ cm^3 s^{-1} $molecule^{-1}$	$1.74 \cdot 10^{-13}$ cm^3 s^{-1} $molecule^{-1}$

[a]Value for BCF calculated following re-analysis of original study (see Risk Assessment of pentabromodiphenyl ether for further details)

Environmental modelling

Congener specific

In order to carry out a congener specific analysis the releases estimated in the main assessments for the three commercial flame retardants are used as a basis (the estimates used for this analysis do not include the contribution from "waste remaining in the environment"), along with the known percentage compositions. The percentage compositions used are taken from the recent test reports, where a composite sample from several current manufacturers/suppliers was analysed and so best represent the compositions of the substances as currently used in the EU. Appendix D considers the compositions of the commercial products further.

Commercial decabromodiphenyl ether:	97%	decabromodiphenyl ether
	3%	nonabromodiphenyl ether
Commercial octabromodiphenyl ether:	2.1%	decabromodiphenyl ether
	13.9%	nonabromodiphenyl ether
	36.1%	octabromodiphenyl ether
	42.3%	heptabromodiphenyl ether
	5.5%	hexabromodiphenyl ether
Commercial pentabromodiphenyl ether:	11.7%	hexabromodiphenyl ether
	46%	2,2',4,4',5-pentabromodiphenyl ether
	8.6%	other penta- isomer (e.g. 2,2',4,4'6-)
	33.7%	2,2',4,4'-tetrabromodiphenyl ether

Tetrabromodiphenyl ether

Tetrabromodiphenyl ether is a component (33.7%) of commercial pentabromodiphenyl ether only. Using the releases estimated for commercial pentabromodiphenyl ether in the main report, the corresponding scenarios derived specifically for the tetrabromodiphenyl ether component are shown in **Table E4**.

Table E4 Estimated releases specific for the tetrabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	Tetrabromo diphenyl ether	Commercial product	Tetrabromo diphenyl ether	Commercial product	Tetrabromo diphenyl ether
Polyurethane foam manufacture	0.15 kg/day to water and 0.124 kg/day to air	0.050 kg/day to water and 0.042 kg/day to air	44.6 kg/year to water and 37.2 kg/year to air	15.0 kg/year to water and 12.5 kg/year to air	135 kg/year to water and 113 kg/year to air	45.5 kg/year to water and 38.1 kg/year to air
Polyurethane foam use			4.3 tonnes/year to air	1.45 tonnes/year to air	38.7 tonnes/year to air	13.0 tonnes/year to air
Total			44.6 kg/year to water and 4.3 tonnes/year to air	15.0 kg/year to water and 1.46 tonnes/year to air	135 kg/year to water and 38.8 tonnes/year to air	45.5 kg/year to water and 13.0 tonnes/year to air

2,2',4,4',5-Pentabromodiphenyl ether

2,2'4,4',5-Pentabromodiphenyl ether is a component (46%) of commercial pentabromodiphenyl ether only. Using the releases estimated for commercial pentabromodiphenyl ether in the main report, the corresponding scenarios derived specifically for the 2,2',4,4',5-pentabromodiphenyl ether component are shown in **Table 5**.

Table E5 Estimated releases specific for the 2,2',4,4',5-pentabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	2,2',4,4'5-pentabromo diphenyl ether	Commercial product	2,2',4,4'5-pentabromo diphenyl ether	Commercial product	2,2',4,4'5-pentabromo diphenyl ether
Polyurethane foam manufacture	0.15 kg/day to water and 0.124 kg/day to air	0.067 kg/day to water and 0.057 kg/day to air	44.6 kg/year to water and 37.2 kg/year to air	20.5 kg/year to water and 17.1 kg/year to air	135 kg/year to water and 113 kg/year to air	62.1 kg/year to water and 52.0 kg/year to air
Polyurethane foam use			4.3 tonnes/ year to air	2.0 tonnes/ year to air	38.7 tonnes/ year to air	18 tonnes/ year to air
Total			44.6 kg/year to water and 4.3 tonnes/year to air	20.5 kg/year to water and 2.0 tonnes/year to air	135 kg/year to water and 38.8 tonnes/year to air	62.1 kg/year to water and 18 tonnes/year to air

Other Pentabromodiphenyl ether isomers

2,2'4,4',6-Pentabromodiphenyl ether (or other pentabromodiphenyl ether isomers) is a component (8.6%) of commercial pentabromodiphenyl ether only. Using the releases estimated for commercial pentabromodiphenyl ether in the main report, the corresponding scenarios derived specifically for the 2,2',4,4',6-pentabromodiphenyl ether component are shown in **Table E6**.

Table E6 Estimated releases specific for the 2,2',4,4',6-pentabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	2,2',4,4'6-pentabromo diphenyl ether	Commercial product	2,2',4,4'6-pentabromo diphenyl ether	Commercial product	2,2',4,4'6-pentabromo diphenyl ether
Polyurethane foam manufacture	0.15 kg/day to water and 0.124 kg/day to air	0.013 kg/day to water and 0.011 kg/day to air	44.6 kg/year to water and 37.2 kg/year to air	3.84 kg/year to water and 3.20 kg/year to air	135 kg/year to water and 113 kg/year to air	11.6 kg/year to water and 9.7 kg/year to air
Polyurethane foam use			4.3 tonnes/ year to air	0.37 tonnes/ year to air	38.7 tonnes/ year to air	3.3 tonnes/ year to air
Total			44.6 kg/year to water and 4.3 tonnes/year to air	3.84 kg/year to water and 0.37 tonnes/year to air	135 kg/year to water and 38.8 tonnes/year to air	11.6 kg/year to water and 3.3 tonnes/year to air

Hexabromodiphenyl ether

Hexabromodiphenyl ether is a component of both commercial pentabromodiphenyl ether (11.7%) and octabromodiphenyl ether (5.5%). Using the releases estimated for these two commercial bromodiphenyl ethers in the main reports, the corresponding scenarios derived specifically for the hexabromodiphenyl ether component are shown in **Table E7**.

Table E7 Estimated releases specific for the hexabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	Hexabromo diphenyl ether	Commercial product	Hexabromo diphenyl ether	Commercial product	Hexabromo diphenyl ether
Commercial pentabromodiphenyl ether						
Polyurethane foam manufacture	0.15 kg/day to water and 0.124 kg/day to air	0.018 kg/day to water and 0.0145 kg/day to air	44.6 kg/year to water and 37.2 kg/year to air	5.2 kg/year to water and 4.4 kg/year to air	135 kg/year to water and 113 kg/year to air	15.8 kg/year to water and 13.2 kg/year to air
Polyurethane foam use			4.3 tonnes/ year to air	0.50 tonnes/ year to air	38.7 tonnes/ year to air	4.5 tonnes/ year to air
Commercial octabromodiphenyl ether						
Polymers: handling of raw material	80 kg/year dust to landfill/incin.	4.4 kg/year dust to landfill/incin.	540 kg/year dust to landfill/incin.	29.7 kg/year dust to landfill/incin.	4.86 tonnes/ year dust to landfill/incin.	0.27 tonnes/ year dust to landfill/incin.
Polymers: compounding and conversion	19.1 kg/year to air and 19.1 kg/year to water over 102 days	1.05 kg/year to air and 1.05 kg/year to water over 102 days	128 kg/year to air and 128 kg/year to water	7.0 kg/year to air and 7.0 kg/year to water	1.15 tonnes/ year to air and 1.15 tonnes/ year to water	0.063 tonnes/ year to air and 0.063 tonnes/ year to water
Polymers: service life			1.38 tonnes/ year to air	0.076 tonnes/ year to air	12.4 tonnes/ year to air	0.68 tonnes/ year to air
Total			173 kg/year to water and 5.85 tonnes/year to air	12.2 kg/year to water and 599 kg/year to air	1.41 tonnes/ year to water and 52.5 tonnes/year to air	78.8 kg/year to water and 5.26 tonnes/year to air

Heptabromodiphenyl ether

Heptabromodiphenyl ether is a component (42.3%) of commercial octabromodiphenyl ether only. Using the releases estimated for these two commercial bromodiphenyl ethers in the main reports, the corresponding scenarios derived specifically for the heptabromodiphenyl ether component are shown in **Table E8**.

Table E8 Estimated releases specific for the heptabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	Heptabromo diphenyl ether	Commercial product	Heptabromo diphenyl ether	Commercial product	Heptabromo diphenyl ether
Polymers: handling of raw material	80 kg/year dust to landfill/incin.	33.8 kg/year dust to landfill/incin.	540 kg/year dust to landfill/incin.	228 kg/year dust to landfill/incin.	4.86 tonnes/ year dust to landfill/incin.	2.06 tonnes/ year dust to landfill/incin.
Polymers: compounding and conversion	19.1 kg/year to air and 19.1 kg/ year to water over 102 days	8.1 kg/year to air and 8.1 kg/ year to water over 102 days	128 kg/year to air and 128 kg/year to water	54.1 kg/year to air and 54.1 kg/year to water	1.15 tonnes/ year to air and 1.15 tonnes/ year to water	0.486 tonnes/ year to air and 0.486 tonnes/ year to water
Polymers: service life			1.38 tonnes/year to air	0.584 tonnes/year to air	12.4 tonnes/ year to air	5.25 tonnes/ year to air
Total			128 kg/year to water and 1.51tonnes/year to air	54.1 kg/year to water and 638 kg/year to air	1.15 tonnes/ year to water and 13.6tonnes/year to air	486 kg/year to water and 5.74tonnes/year to air

Octabromodiphenyl ether

Octabromodiphenyl ether is a significant component (36.1%) of commercial octabromodiphenyl ether only.

Using the releases estimated for these two commercial bromodiphenyl ethers in the main reports, the corresponding scenarios derived specifically for the octabromodiphenyl ether component are shown in **Table E9**.

Table E9 Estimated releases specific for the octabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	Octabromo diphenyl ether	Commercial product	Octabromo diphenyl ether	Commercial product	Octabromo diphenyl ether
Polymers: handling of raw material	80 kg/year dust to landfill/incin.	28.9 kg/year dust to landfill/incin.	540 kg/year dust to landfill/incin.	195 kg/year dust to landfill/incin.	4.86 tonnes/ year dust to landfill/incin.	1.75 tonnes/ year dust to landfill/incin.
Polymers: compounding and conversion	19.1 kg/year to air and 19.1 kg/ year to water over 102 days	6.9 kg/year to air and 6.9 kg/ year to water over 102 days	128 kg/year to air and 128 kg/year to water	46.2 kg/year to air and 46.2 kg/year to water	1.15 tonnes/ year to air and 1.15 tonnes/ year to water	0.415 tonnes/ year to air and 0.415 tonnes/ year to water
Polymers: service life			1.38 tonnes/ year to air	0.498 tonnes/ year to air	12.4 tonnes/ year to air	4.48 tonnes/ year to air
Total			128 kg/year to water and 1.51 tonnes/year to air	46.2 kg/year to water and 544 kg/year to air	1.15 tonnes/ year to water and 13.6 tonnes/year to air	415 kg/year to water and 4.90 tonnes/year to air

Nonabromodiphenyl ether

Nonabromodiphenyl ether is a component of both commercial octabromodiphenyl ether (13.9%) and decabromodiphenyl ether (3%). Using the releases estimated for these two commercial bromodiphenyl ethers in the main reports, the corresponding scenarios derived specifically for the nonabromodiphenyl ether component are shown in **Table E10**.

Table E10 Estimated releases specific for the nonabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	Nonabromo diphenyl ether	Commercial product	Nonabromo diphenyl ether	Commercial product	Nonabromo diphenyl ether
Commercial octabromodiphenyl ether						
Polymers: handling of raw material	80 kg/year dust to landfill/incin.	11.1 kg/year dust to landfill/incin.	540 kg/year dust to landfill/incin.	75.1 kg/year dust to landfill/incin.	4.86 tonnes/ year dust to landfill/incin.	0.676 tonnes/ year dust to landfill/incin.
Polymers: compounding and conversion	19.1 kg/year to air and 19.1 kg/ year to water over 102 days	2.65 kg/year to air and 2.65 kg/ year to water over 102 days	128 kg/year to air and 128 kg/year to water	17.8 kg/year to air and 17.8 kg/year to water	1.15 tonnes/ year to air and 1.15 tonnes/ year to water	0.160 tonnes/ year to air and 0.160 tonnes/ year to water
Polymers: service life			1.38 tonnes/ year to air	0.192 tonnes/year to air	12.4 tonnes/ year to air	1.72 tonnes/ year to air
Commercial decabromodiphenyl ether						
Production	500 kg/year to water over 100 days	15 kg/year to waste water over 100 days	500 kg/year to water	15 kg/year to water	0 kg/year to water	0 kg/year to water
Polymers: handling of raw materials	1.6 tonnes/year dust to landfill/incin.	0.048tonnes/year dust to landfill/incin.	10.7 tonnes/year dust to landfill/incin.	0.32 tonnes/year dust to landfill/incin.	96.3 tonnes/year dust to landfill/incin.	2.9 tonnes/year dust to landfill/incin.
Polymers: compounding and conversion	51 kg/year to water and 51 kg/year to air over 268 days	1.5 kg/year to water and 1.5 kg/year to air over 268 days	340 kg/year to air and 340 kg/year to water	10.2 kg/year to air and 10.2 kg/year to water	3.06 tonnes/ year to air and 3.06 tonnes/ year to water	91.8 kg/ year to air and 91.8 kg/ year to water
Polymers: service life			2.55 tonnes/year to air	76.5 kg/year to air	22.95 tonnes/year to air	689 kg/ year to air
Textiles: compounding	600 kg/year to water over 300 days	18 kg/year to water over 300 days	600 kg/year to water	18 kg/year to water	900 kg/year to water	27 kg/year to water
Textiles: application	300 kg/year to water over 300 days	9 kg/year to water over 300 days	300 kg/year to water	9 kg/year to water	900 kg/year to water	27 kg/year to water
Textiles: washing	up to 60 kg/year to water over 365 days	up to 1.8 kg/year to water over 365 days	up to 120 tonnes/year to water	up to 3.6 tonnes/year to water	up to 240 tonnes/year to water	up to 7.2 tonnes/year to water
Total			121.9 tonnes/ year to water and 4.40 tonnes/year to air	3.67 tonnes/ year to water and 297 kg/year to air	246.0 tonnes/ year to water and 39.6 tonnes/year to air	7.50 tonnes/ year to water and 2.66 tonnes/year to air

Decabromodiphenyl ether

Decabromodiphenyl ether is a component of both commercial octabromodiphenyl ether (2.1%) and decabromodiphenyl ether (97%). Using the releases estimated for these two commercial bromodiphenyl ethers in the main reports, the corresponding scenarios derived specifically for the octabromodiphenyl ether component are shown in **Table E11**.

Table E11 Estimated releases specific for the decabromodiphenyl ether component

Scenario	Local release		Regional release		Continental release	
	Commercial product	Decabromo diphenyl ether	Commercial product	Decabromo diphenyl ether	Commercial product	Decabromo diphenyl ether
Commercial octabromodiphenyl ether						
Polymers: handling of raw material	80 kg/year dust to landfill/incin.	1.68 kg/year dust to landfill/incin.	540 kg/year dust to landfill/incin.	11.3 kg/year dust to landfill/incin.	4.86 tonnes/ year dust to landfill/incin.	102 kg/ year dust to landfill/incin.
Polymers: compounding and conversion	19.1 kg/year to air and 19.1 kg/ year to water over 102 days	0.4 kg/year to air and 0.4 kg/ year to water over 102 days	128 kg/year to air and 128 kg/year to water	0.38 kg/year to air and 0.38 kg/year to water	1.15 tonnes/ year to air and 1.15 tonnes/ year to water	24.2 kg/ year to air and 24.2 kg/ year to water
Polymers: service life			1.38 tonnes/ year to air	29.0 kg/ year to air	12.4 tonnes/ year to air	260 kg/ year to air
Commercial decabromodiphenyl ether						
Production	500 kg/year to water over 100 days	485 kg/year to water over 100 days	500 kg/year to water	485 kg/year to water	0 kg/year to water	0 kg/year to water
Polymers: handling of raw materials	1.6 tonnes/year dust to landfill/incin.	1.55 tonnes/year dust to landfill/incin.	10.7 tonnes/year dust to landfill/incin.	10.4 tonnes/year dust to landfill/incin.	96.3 tonnes/year dust to landfill/incin.	93.4 tonnes/year dust to landfill/incin.
Polymers: compounding and conversion	51 kg/year to water and 51 kg/year to air over 268 days	49.5 kg/year to water and 49.5 kg/year to air over 268 days	340 kg/year to air and 340 kg/year to water	330 kg/year to air and 330 kg/year to water	3.06 tonnes/ year to air and 3.06 tonnes/ year to water	2.97 tonnes/ year to air and 2.97 tonnes/ year to water
Polymers: service life			2.55 tonnes/year to air	2.47 tonnes/year to air	22.95 tonnes/year to air	22.26 tonnes/ year to air
Textiles: compounding	600 kg/year to water over 300 days	582 kg/year to water over 300 days	600 kg/year to water	582 kg/year to water	900 kg/year to water	873 kg/year to water
Textiles: application	300 kg/year to water over 300 days	291 kg/year to water over 300 days	300 kg/year to water	291 kg/year to water	900 kg/year to water	873 kg/year to water
Textiles: washing	up to 60 kg/ year to water over 365 days	up to 58.2 kg/year to water over 365 days	up to 120 tonnes/year to water	up to 116 tonnes/year to water	up to 240 tonnes/year to water	up to 233 tonnes/year to water
Total			121.9 tonnes/year to water and 4.40 tonnes/year to air	117.7 tonnes/ year to water and 2.83 tonnes/year to air	245.7 tonnes/ year to water and 39.6 tonnes/year to air	237.7 tonnes/ year to water and 25.5 tonnes/year to air

Results of EUSES modelling for individual components

The EUSES model was run for each individual component of the commercial products using the physico-chemical properties given in **Table E3** and the release estimates in Tables 4-11 as input data. In the model, all local releases to water were assumed to go to a waste water treatment plant, but in the regional and continental model, a waste water treatment plant connection rate of 70% was assumed (as recommended in the Technical Guidance document). Thus the results of this analysis can be compared directly with the results obtained in the main report on a commercial formulation basis. The predicted concentrations for the individual components are shown in **Table E12**.

In order to compare the predicted concentrations given in **Table E12** with the concentrations predicted in the main report for the commercial products, the sum of the individual components of any given commercial product can be used. When this is carried out (**Table E13**) it can be seen that the concentrations obtained at a local level are in reasonable agreement. This indicates that the modelling carried out in the main report is reasonably representative for the individual components of the product. This is important for the risk assessment as the effects data are all generated using the commercial product and so the PEC/PNEC has to be done on a product basis even though it is clear that individual components of the product will behave differently.

The main areas where major discrepancies occur between the two approaches are in the estimation of human intake via the environment (possible reasons for this are discussed later) and the regional modelling for octabromodiphenyl ether. The last point arises because, although nona- and decabromodiphenyl ether are components of the commercial octabromodiphenyl ether, by far the major releases the decabromodiphenyl ether component in the regional environment come from the use of the commercial decabromodiphenyl ether, and as a result these dominate the regional concentrations of the individual nona- and decabromodiphenyl ether components.

The predicted concentrations in soil and sediment depend on the K_{oc} value. The use of different K_{oc} values for the isomer specific modelling and commercial formulation modelling probably accounts for the differences seen in the predicted levels using the two methods. Even so, the predicted levels are in reasonable agreement for the two approaches. It should also be born in mind that the PNEC for soil and sediment will also depend to some extent on the K_{oc} value, and so in terms of the actual risk assessment (PEC/PNEC ratio) the two modelling approaches should give similar overall results.

Table E12 Results of EUSES modelling for individual brominated diphenyl ether components

Scenario	Compartment/endpoint	Tetra	2,2',4,4',5-Penta	2,2',4,4',6-Penta	Hexa	Hepta	Octa	Nona	Deca
Pentabromo: polyurethane foam manufacture	Air concentration (emission episode)	11.7 ng/m^3	15.8 ng/m^3	3.1 ng/m^3	4.0 ng/m^3	n/a	n/a	n/a	n/a
	PEC_{local} (water)	0.103 µg/l	0.12 µg/l	0.024 µg/l	0.030 µg/l	n/a	n/a	n/a	n/a
	PEC_{local} (sediment)	1.69 mg/kg wet wt	2.43 mg/kg wet wt	0.47 mg/kg wet wt	0.69 mg/kg wet wt	n/a	n/a	n/a	n/a
	PEC_{local} (agr. soil)	0.84 mg/kg wet wt	1.14 mg/kg wet wt	0.22 mg/kg wet wt	0.32 mg/kg wet wt	n/a	n/a	n/a	n/a
	Conc. in fish[a]	1.35 mg/kg [2.82 mg/kg][b]	0.002 mg/kg [0.073 mg/kg][b]	0.11 mg/kg [0.174 mg/kg][b]	0.041 mg/kg [0.070 mg/kg][b]	n/a	n/a	n/a	n/a
	Conc. in earthworms[a]	1.6 mg/kg	4.54 mg/kg	0.88 mg/kg	1.13 mg/kg	n/a	n/a	n/a	n/a
	Local daily human intake via food	7.8 µg/kg bw/day [12.6 µg/kg bw/day][b]	15.5 µg/kg bw/day [15.8 µg/kg bw/day][b]	3.4 µg/kg bw/day [3.6 µg/kg bw/day][b]	15.8 µg/kg bw/day [15.9 µg/kg bw/day][b]	n/a	n/a	n/a	n/a
Octabromo: polymers - compounding and conversion	Air concentration (emission episode)	n/a	n/a	n/a	2.9 ng/m^3	22.1 ng/m^3	18.8 ng/m^3	7.2 ng/m^3	1.1 ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	0.017 µg/l	0.12 µg/l	0.094 µg/l	0.039 µg/l	0.17 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	0.40 mg/kg wet wt	3.18 mg/kg wet wt	2.8 mg/kg wet wt	1.3 mg/kg wet wt	6.29 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	0.19 mg/kg wet wt	1.39 mg/kg wet wt	1.2 mg/kg wet wt	0.47 mg/kg wet wt	0.35 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	8.6 µg/kg [14.6 µg/kg][b]	0.069 µg/kg	0.054 µg/kg	0.042 µg/kg	0.68 µg/kg
	Conc. in earthworms[a]	n/a	n/a	n/a	0.69 mg/kg	4.24 mg/kg	3.26 mg/kg	4. mg/kg	102 mg/kg
	Local daily human intake via food	n/a	n/a	n/a	9.0 µg/kg bw/day [9.0 µg/kg bw/day][b]	204 µg/kg bw/day	718 µg/kg bw/day	944 µg/kg bw/day	2.37 mg/kg bw/day
Decabromo: production	Air concentration (emission episode)	n/a	n/a	n/a	n/a	n/a	n/a	$1.9 \cdot 10^{-4}$ ng/m^3	$2.3 \cdot 10^{-3}$ ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	n/a	n/a	0.20 µg/l	6.0 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	n/a	n/a	6.56 mg/kg wet wt	217 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	n/a	n/a	2.58 mg/kg wet wt	82.9 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	n/a	n/a	n/a	0.13 µg/kg	3.9 µg/kg
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	n/a	n/a	9.6 mg/kg	279 mg/kg
	Local daily human intake via food	n/a	n/a	n/a	n/a	n/a	n/a	5.18 mg/kg bw/day	561 mg/kg bw/day
Decabromo: polymers: compounding and conversion	Air concentration (emission episode)	n/a	n/a	n/a	n/a	n/a	n/a	1.6 ng/m^3	51 ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	n/a	n/a	0.013 µg/l	0.39 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	n/a	n/a	0.43 mg/kg wet wt	14.2 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	n/a	n/a	0.12 mg/kg wet wt	3.45 mg/kg wet wt

Table E12 continued overleaf

Table E12 continued

Scenario	Compartment/endpoint	Tetra	2,2',4,4',5-Penta	2,2',4,4',6-Penta	Hexa	Hepta	Octa	Nona	Deca
	Conc. in fish[a]	n/a	n/a	n/a	n/a	n/a	n/a	0.034 µg/kg	1.0 µg/kg
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	n/a	n/a	3.74 mg/kg	108 mg/kg
	Local daily human intake via food	n/a	n/a	n/a	n/a	n/a	n/a	247 µg/kg bw/day	23.4 mg/kg bw/day
Decabromo: textiles - compounding	Air concentration (emission episode)	n/a	n/a	n/a	n/a	n/a	n/a	$7.7 \cdot 10^{-5}$ ng/m^3	$9.3 \cdot 10^{-4}$ ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	n/a	n/a	0.083 µg/l	2.50 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	n/a	n/a	2.74 mg/kg wet wt	90.4 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	n/a	n/a	1.05 mg/kg wet wt	33.3 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	n/a	n/a	n/a	0.15 µg/kg	4.5 µg/kg
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	n/a	n/a	5.93 mg/kg	173 mg/kg
	Local daily human intake via food	n/a	n/a	n/a	n/a	n/a	n/a	2.10 mg/kg bw/day	226 mg/kg bw/day
Decabromo: textiles - application	Air concentration (emission episode)	n/a	n/a	n/a	n/a	n/a	n/a	$3.9 \cdot 10^{-5}$ ng/m^3	$4.6 \cdot 10^{-4}$ ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	n/a	n/a	0.045 µg/l	1.33 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	n/a	n/a	1.47 mg/kg wet wt	48.3 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	n/a	n/a	0.54 mg/kg wet wt	16.8 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	n/a	n/a	n/a	0.087 µg/kg	2.6 µg/kg
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	n/a	n/a	4.73	137 mg/kg
	Local daily human intake via food	n/a	n/a	n/a	n/a	n/a	n/a	1.08 mg/kg bw/day	114 mg/kg bw/day
All regional sources	$PEC_{regional}$ (air)	$1.1 \cdot 10^{-7}$ mg/m^3	$1.6 \cdot 10^{-7}$ mg/m^3	$3.0 \cdot 10^{-8}$ mg/m^3	$4.0 \cdot 10^{-8}$ mg/m^3	$3.3 \cdot 10^{-8}$ mg/m^3	$2.5 \cdot 10^{-8}$ mg/m^3	$1.4 \cdot 10^{-8}$ mg/m^3	$1.4 \cdot 10^{-7}$ mg/m^3
	$PEC_{regional}$ (water)	$2.6 \cdot 10^{-5}$ µg/l	$7.4 \cdot 10^{-5}$ µg/l	$1.4 \cdot 10^{-5}$ µg/l	$1.5 \cdot 10^{-4}$ µg/l	$4.0 \cdot 10^{-4}$ µg/l	$3.8 \cdot 10^{-4}$ µg/l	0.0059 µg/l	0.17 µg/l
	$PEC_{regional}$ (sediment)	0.76 µg/kg wet wt	2.6 µg/kg wet wt	0.48 µg/kg wet wt	6.2 µg/kg wet wt	18.4 µg/kg wet wt	19.7 µg/kg wet wt	341 µg/kg wet wt	10.8 mg/kg wet wt
	$PEC_{regional}$ (agr. soil)	3.5 µg/kg wet wt	9.6 µg/kg wet wt	1.79 µg/kg wet wt	12.9 µg/kg wet wt	43.4 µg/kg wet wt	43.8 µg/kg wet wt	1.46 mg/kg wet wt	46.9 mg/kg wet wt
	Regional daily human intake via food	0.017 µg/kg bw/day [0.019 µg/kg bw/day][b]	0.14 µg/kg bw/day [0.14 µg/kg bw/day][b]	0.027 µg/kg bw/day [0.027 µg/kg bw/day][b]	0.60 µg/kg bw/day [0.60 µg/kg bw/day][b]	6.4 µg/kg bw/day	26.3 µg/kg bw/day	2.93 mg/kg bw/day	318 mg/kg bw/day

[a]For secondary poisoning assessment

[b]Value estimated using the re-calculated BCF value (see Risk Assessment of pentabromodiphenyl ether for further details)

Table E13 Comparison of EUSES modelling for sum of individual brominated diphenyl ether components with the commercial product

Scenario	Compartment/endpoint	Sum of Penta components (tetra-hexa: Table 12)	Commercial Penta product (Main report)	Sum of Octa components (hexa-deca: Table 12)	Commercial Octa product (Main report)	Sum of Deca components (Nona-deca: Table 12)	Commercial Deca product (Main report)
Pentabromo: polyurethane foam manufacture	Air concentration (emission episode)	34.6 ng/m^3	34.5 ng/m^3	n/a	n/a	n/a	n/a
	PEC_{local} (water)	0.277 µg/l	0.37 µg/l	n/a	n/a	n/a	n/a
	PEC_{local} (sediment)	5.3 mg/kg wet wt	4.5 mg/kg wet wt	n/a	n/a	n/a	n/a
	PEC_{local} (agr. soil)	2.5 mg/kg wet wt	2.7 mg/kg wet wt	n/a	n/a	n/a	n/a
	Conc. in fish[a]	1.5 mg/kg [3.1 mg/kg][b]	2.2 mg/kg [4.2 mg/kg][b]	n/a	n/a	n/a	n/a
	Conc. in earthworms[a]	8.2 mg/kg	18.1 mg/kg	n/a	n/a	n/a	n/a
	Local daily human intake via food	42.5 µg/kg bw/day [47.9 µg/kg bw/day][b]	46.4 µg/kg bw/day [52.9 µg/kg bw/day][b]	n/a	n/a	n/a	n/a
Octabromo: polymers - compounding and conversion	Air concentration (emission episode)	n/a	n/a	52.1 ng/m^3	52 ng/m^3	n/a	n/a
	PEC_{local} (water)	n/a	n/a	0.53 µg/l	0.26 µg/l	n/a	n/a
	PEC_{local} (sediment)	n/a	n/a	17.0 mg/kg wet wt	7.7 mg/kg wet wt	n/a	n/a
	PEC_{local} (agr. soil)	n/a	n/a	3.61 mg/kg wet wt	3.24 mg/kg wet wt	n/a	n/a
	Conc. in fish[a]	n/a	n/a	9.8 µg/kg wet wt [15.8 µg/kg wet wt][b]	0.15 µg/kg wet wt	n/a	n/a
	Conc. in earthworms[a]	n/a	n/a	166 mg/kg wet wt	5.37 mg/kg wet wt	n/a	n/a
	Local daily human intake via food	n/a	n/a	4,345 µg/kg bw/day [4,345 µg/kg bw/day][b]	0.011 µg/kg bw/day	n/a	n/a
Decabromo: production (generic)	Air concentration (emission episode)	n/a	n/a	n/a	n/a	$2.5 \cdot 10^{-3}$ ng/m^3	4.2 ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	6.3 µg/l	6.2 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	227 mg/kg wet wt	216 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	85.5 mg/kg wet wt	84.9 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	n/a	4.3 µg/kg wet wt	3.7 µg/kg wet wt
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	340 mg/kg wet wt	149 mg/kg wet wt
	Local daily human intake via food	n/a	n/a	n/a	n/a	567 mg/kg wet wt	0.22 mg/kg bw/day
Decabromo: polymers: compounding and conversion	Air concentration (emission episode)	n/a	n/a	n/a	n/a	53 ng/m^3	52.2 ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	0.50 µg/l	0.31 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	17.6 mg/kg wet wt	10.8 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	3.6 mg/kg wet wt	3.26 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	n/a	1.3 µg/kg wet wt	0.66 µg/kg wet wt
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	164 mg/kg wet wt	40.3 mg/kg wet wt
	Local daily human intake via food	n/a	n/a	n/a	n/a	23.7 mg/kg bw/day	$9.5 \cdot 10^{-3}$ mg/kg bw/day

Table E13 continued overleaf

Table E13 continued

Scenario	Compartment/endpoint	Sum of Penta components (tetra-hexa: Table 12)	Commercial product (Main report)	Sum of Octa components (hexa-deca: Table 12)	Commercial Octa product (Main report)	Deca components (Nona-deca: Table 12)	Commercial Deca product (Main report)
Decabromo: textiles - compounding	Air concentration (emission episode)	n/a	n/a	n/a	n/a	$1 \cdot 10^{-3}$ ng/m³	1.7 ng/m³
	PEC_{local} (water)	n/a	n/a	n/a	n/a	2.6 µg/l	2.5 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	93.1 mg/kg wet wt	87.9 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	34.4 mg/kg wet wt	34 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	n/a	4.7 µg/kg wet wt	4.4 µg/kg wet wt
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	179 mg/kg wet wt	81.1 mg/kg wet wt
	Local daily human intake via food	n/a	n/a	n/a	n/a	228 mg/kg bw/day	0.088 mg/kg bw/day
Decabromo: textiles - application	Air concentration (emission episode)	n/a	n/a	n/a	n/a	$5 \cdot 10^{-4}$ ng/m³	0.8 ng/m³
	PEC_{local} (water)	n/a	n/a	n/a	n/a	1.4 µg/l	1.3 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	50 mg/kg wet wt	131 mg/kg wet wt
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	17.3 mg/kg wet wt	17 mg/kg wet wt
	Conc. in fish[a]	n/a	n/a	n/a	n/a	2.7 µg/kg wet wt	2.4 µg/kg wet wt
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	142 mg/kg wet wt	58.6 mg/kg wet wt
	Local daily human intake via food	n/a	n/a	n/a	n/a	115 mg/kg bw/day	0.044 mg/kg bw/day
All regional sources	$PEC_{regional}$ (air)	0.34 ng/m³	0.27 ng/m³	0.26 ng/m³	0.11 ng/m³	0.015 ng/m³	4.1 ng/m³
	$PEC_{regional}$ (water)	$2.6 \cdot 10^{-4}$ µg/l	$1.5 \cdot 10^{-3}$ µg/l	0.26 µg/l	$3.8 \cdot 10^{-4}$ µg/l	0.18 µg/l	0.081 µg/l
	$PEC_{regional}$ (sediment)	10.0 µg/kg wet wt	32.5 µg/kg wet wt	16.6 mg/kg	0.019 mg/kg wet wt	11.1 mg/kg wet wt	4.94 mg/kg wet wt
	$PEC_{regional}$ (agr. soil)	27.8 µg/kg wet wt	132 µg/kg wet wt	72.3 mg/kg wet wt	0.073 mg/kg wet wt	48.4 mg/kg wet wt	27.1 mg/kg wet wt
	Regional daily human intake via food	0.78 µg/kg bw/day [0.79 µg/kg bw/day][b]	1.93 µg/kg bw/day [1.96 µg/kg bw/day][b]	482 mg/kg bw/day [482 mg/kg bw/day][b]	$2.4 \cdot 10^{-4}$ mg/kg bw/day	321 mg/kg bw/day	0.073 mg/kg bw/day

[a] For secondary poisoning assessment

[b]Value estimated using the re-calculated BCF value (see Risk Assessment of pentabromodiphenyl ether for further details)

Sensitivity to variation in physico-chemical properties

As mentioned previously, the generation of reliable values for some physico-chemical properties for the polybrominated diphenyl ethers is difficult. This section looks at the effect of varying various properties on the environmental distribution and hence predicted environmental concentrations, using decabromodiphenyl ether as an example. For this purpose, EUSES was run several times varying one property at a time to look at the effect on the predicted concentrations. In order to simplify the process a single standard release scenario was chosen in all examples. Thus, although the predicted concentrations calculated have no relevance to the risk assessment, the variation of the predicted concentrations give an indication of the effect of possible errors/uncertainties in the physico-chemical properties on the concentrations predicted in the risk assessment. The results of this analysis are shown in **Table E14**.

It is clear from the data reported in **Table E14** that varying the physico-chemical properties for the brominated diphenyl ether over quite a wide range has very little effect on the predicted local concentrations in water, sediment and soil. Varying the physico-chemical properties has a much larger effect on the predicted local air concentrations. Since for these substances, the predicted air concentrations are very low, this is of minor importance in terms of the risk assessment.

At the regional level, the effect of varying the physico-chemical properties is more pronounced but the predicted levels in water, and particularly sediment and soil are relatively insensitive to the values used until the extremes of the ranges are used. Again air levels are much more sensitive to the value used for the physico-chemical properties, but in terms of the risk assessment the values predicted are always very low and so this sensitivity is less important.

The predicted concentrations in human intake at the regional level appear to be very sensitive to the value of log K_{ow}, and to a lesser extent vapour pressure, water solubility and K_{oc} value. A similar effect would also be expected to occur in the local calculations (as was found earlier: see **Table E13**). This sensitivity to K_{ow} arises due to the predictive equations used, which are very dependent on the Kow value used. In the main assessment reports for the three brominated flame retardants, the EUSES calculations for human intake indicated that root crops would account for the vast majority of the intake.

Table E14 Effect of varying physico-chemical properties on environmental modelling of decabromodiphenyl ether

Water solubility (µg/l)	Vapour pressure (Pa)	log K_{ow}	K_{oc} (l/kg)	PEClocal				Regional				
				Air (mg/m³)	Water (mg/l)	Sediment (mg/kg)	Agricultural soil (mg/kg)	Air (mg/m³)	Water (mg/l)	Sediment (mg/kg)	Agricultural soil (mg/kg)	Human intake (mg/kg bw/day)
0.1	$4.63 \cdot 10^{-6}$	6.27	$1.59 \cdot 10^{6}$	$5.6 \cdot 10^{-7}$	$8.2 \cdot 10^{-4}$	28.4	11.3	$9.6 \cdot 10^{-9}$	$1.4 \cdot 10^{-7}$	0.0083	0.045	$1.2 \cdot 10^{-4}$
1	$4.63 \cdot 10^{-6}$	6.27	$1.59 \cdot 10^{6}$	$9.3 \cdot 10^{-8}$	$8.3 \cdot 10^{-4}$	28.6	11.3	$2.8 \cdot 10^{-9}$	$2.5 \cdot 10^{-7}$	0.0151	0.074	$2.0 \cdot 10^{-4}$
0.01	$4.63 \cdot 10^{-6}$	6.27	$1.59 \cdot 10^{6}$	$3.9 \cdot 10^{-6}$	$7.8 \cdot 10^{-4}$	26.8	11.0	$1.5 \cdot 10^{-8}$	$8.6 \cdot 10^{-8}$	0.0053	0.009	$2.4 \cdot 10^{-5}$
0.001	$4.63 \cdot 10^{-6}$	6.27	$1.59 \cdot 10^{6}$	$7.7 \cdot 10^{-6}$	$7.3 \cdot 10^{-4}$	25.1	9.43	$1.6 \cdot 10^{-8}$	$7.8 \cdot 10^{-8}$	0.0047	0.001	$2.7 \cdot 10^{-6}$
0.1	$5 \cdot 10^{-7}$	6.27	$1.59 \cdot 10^{6}$	$9.3 \cdot 10^{-8}$	$8.3 \cdot 10^{-4}$	28.6	11.3	$2.2 \cdot 10^{-9}$	$2.5 \cdot 10^{-7}$	0.0152	0.074	$2.0 \cdot 10^{-4}$
0.1	$5 \cdot 10^{-8}$	6.27	$1.59 \cdot 10^{6}$	$9.3 \cdot 10^{-8}$	$8.3 \cdot 10^{-4}$	28.7	11.3	$2.4 \cdot 10^{-10}$	$3.0 \cdot 10^{-7}$	0.0184	0.079	$2.1 \cdot 10^{-4}$
0.1	$5 \cdot 10^{-9}$	6.27	$1.59 \cdot 10^{6}$	$9.3 \cdot 10^{-8}$	$8.3 \cdot 10^{-4}$	28.7	11.3	$4.8 \cdot 10^{-11}$	$3.1 \cdot 10^{-7}$	0.0188	0.079	$2.1 \cdot 10^{-4}$
0.1	$5 \cdot 10^{-10}$	6.27	$1.59 \cdot 10^{6}$	$9.3 \cdot 10^{-8}$	$8.3 \cdot 10^{-4}$	28.7	11.3	$2.6 \cdot 10^{-11}$	$3.1 \cdot 10^{-7}$	0.0188	0.079	$2.1 \cdot 10^{-4}$
0.1	$4.63 \cdot 10^{-6}$	8	$1.59 \cdot 10^{6}$	$5.6 \cdot 10^{-7}$	$8.2 \cdot 10^{-4}$	28.4	11.3	$9.6 \cdot 10^{-9}$	$1.4 \cdot 10^{-7}$	0.0083	0.045	$5 \cdot 10^{-3}$
0.1	$4.63 \cdot 10^{-6}$	9	$1.59 \cdot 10^{6}$	$5.6 \cdot 10^{-7}$	$8.2 \cdot 10^{-4}$	28.4	11.3	$9.6 \cdot 10^{-9}$	$1.4 \cdot 10^{-7}$	0.0083	0.045	0.044
0.1	$4.63 \cdot 10^{-6}$	10	$1.59 \cdot 10^{6}$	$5.6 \cdot 10^{-7}$	$8.2 \cdot 10^{-4}$	28.4	11.3	$9.6 \cdot 10^{-9}$	$1.4 \cdot 10^{-7}$	0.0083	0.045	0.396
0.1	$4.63 \cdot 10^{-6}$	12	$1.59 \cdot 10^{6}$	$5.6 \cdot 10^{-7}$	$8.2 \cdot 10^{-4}$	28.4	11.3	$9.6 \cdot 10^{-9}$	$1.4 \cdot 10^{-7}$	0.0083	0.045	31.4
0.1	$4.63 \cdot 10^{-6}$	6.27	$1 \cdot 10^{5}$	$7.6 \cdot 10^{-6}$	$3.0 \cdot 10^{-3}$	7.9	10.1	$1.8 \cdot 10^{-8}$	$2.2 \cdot 10^{-7}$	$8.4 \cdot 10^{-4}$	0.005	$2.0 \cdot 10^{-4}$
0.1	$4.63 \cdot 10^{-6}$	6.27	$1 \cdot 10^{7}$	$9.3 \cdot 10^{-8}$	$1.4 \cdot 10^{-4}$	36.5	11.4	$2.7 \cdot 10^{-9}$	$4.3 \cdot 10^{-8}$	0.0165	0.076	$4.2 \cdot 10^{-5}$
0.1	$4.63 \cdot 10^{-6}$	6.27	$1 \cdot 10^{8}$	$9.3 \cdot 10^{-8}$	$1.5 \cdot 10^{-5}$	38.4	11.4	$3.2 \cdot 10^{-10}$	$5.1 \cdot 10^{-9}$	0.0196	0.086	$1.6 \cdot 10^{-5}$

One part of the environmental modelling that might be expected to be sensitive to variations in the physico-chemical properties (log K_{ow} and Henry's Law constant) is the behaviour during waste water treatment as estimated by the Simpletreat model within EUSES. This is already accounted for in the previous calculations, but **Table E15** shows how the removal varies with physico-chemical properties in example calculations with octabromodiphenyl ether. From these results it can be seen that the actual removal during waste water treatment is relatively insensitive to the physico-chemical properties (within the most likely ranges) for the polybrominated diphenyl ethers.

Table E15 Variation in predicted behaviour during waste water treatment as predicted using EUSES for octabromodiphenyl ether

log K_{ow}	H (Pa m^3/mol)	K_{oc} (l/kg)	Predicted distribution during waste water treatment		
			Air	Water	Solids
a) Fixed K_{oc} value					
6.29	10.6	$1.363 \cdot 10^6$	0.094%	8.46%	91.4%
7.29	10.6	$1.363 \cdot 10^6$	0.094%	8.46%	91.4%
8.29	10.6	$1.363 \cdot 10^6$	0.094%	8.46%	91.4%
9.29	10.6	$1.363 \cdot 10^6$	0.094%	8.46%	91.4%
6.29	1.06	$1.363 \cdot 10^6$	0.011%	8.48%	91.5%
6.29	0.106	$1.363 \cdot 10^6$	0.0010%	8.49%	91.5%
6.29	0.0106	$1.363 \cdot 10^6$	0.00011%	8.49%	91.5%
6.29	106	$1.363 \cdot 10^6$	0.81%	8.27%	90.9%
b) K_{oc} estimated from K_{ow}					
6.29	10.6	$1.57 \cdot 10^5$	0.77%	11.8%	87.5%
7.29	10.6	$1.01 \cdot 10^6$	0.10%	8.62%	91.3%
8.29	10.6	$6.54 \cdot 10^6$	0.020%	8.10%	91.9%
9.29	10.6	$4.22 \cdot 10^7$	0.0031%	8.02%	92.0%
6.29	1.06	$1.57 \cdot 10^5$	0.091%	12.0%	87.9%
6.29	0.106	$1.57 \cdot 10^5$	0.0094%	12.1%	87.9%
6.29	0.0106	$1.57 \cdot 10^5$	0.00094%	12.1%	87.9%
6.29	106	$1.57 \cdot 10^5$	5.9%	10.0%	84.1%

Overall conclusions

The environmental modelling behaviour of the three commercial polybrominated diphenyl ethers has been considered in detail. Overall, it can be concluded that the predicted concentrations estimated on a commercial formulation basis in the main report are reasonably representative for all components of the commercial mixtures. The isomer specific modelling does show, however, that the relative contribution of each component of the commercial mixture to the total concentration varies from media to media. Such partitioning behaviour can also be expected to occur in the toxicity tests and so comparison of PECs and PNECs generated on a commercial formulation basis directly is a reasonable approach.

The environmental modelling for surface water, soil and sediment has been shown to be insensitive to possible uncertainties in the physico-chemical properties measured for these complex mixtures. However, the estimation of exposure for man via the environment has been shown to be very dependent on the log K_{ow}. This is a particular problem for the congeners with very high log K_{ow} values but that generally show low uptake in biota (e.g. octa-, nona- and decabromodiphenyl ether), as the current estimation methods may seriously overestimate the likely environmental exposure via food.

Appendix F Demobrination of Brominated Diphenyl Ethers in the Environment – Supporting Information

Introduction

This appendix discusses the possibility of the highly brominated diphenyl ether congeners undergoing a reductive debromination process in the environment to form brominated diphenyl ethers with lower degrees of bromination. This process is particularly relevant for the risk assessments of octa- and decabrominated diphenyl ethers, where the formation of the more toxic and bioaccumulative tetra- and pentabromodiphenyl ether congeners could result if reductive debromination occurs to a significant extent in the environment.

The main processes that could lead to reductive debromination considered in this appendix are photodegradation and anaerobic biodegradation. This appendix discusses some of the supporting data available for various halogenated aromatic compounds, from which the potential for debromination of polybrominated diphenyl ethers may be inferred. The information reported is not intended to be comprehensive, but to give an indication of the data available.The data available for the three polybrominated diphenyl ethers is discussed in detail in the main reports.

Anaerobic biodegradation

Brominated diphenyl ethers

No anaerobic biodegradation tests have been carried out using brominated diphenyl ethers.

Other relevant brominated substances

Morris et al (1992) studied the reductive debromination of polybrominated biphenyls using anaerobic microorganisms derived from three sites [a contaminated sediment from near a polybrominated biphenyl production site and two sediments contaminated with chlorinated biphenyls (Aroclor 1242 or Aroclor 1260)], as well as non-contaminated sediments. The sediments were placed in a flask under a N_2:CO_2 atmosphere (80:20 vol/vol) and mixed with an equal volume of reduced anaerobic mineral medium. After shaking, the flask contents were allowed to settle and the supernatants were used as inocula for the debromination experiments.

The degradation cultures were prepared by adding 5 ml of the inoculum to 1 g of air dried non-contaminated sediment and the polybrominated biphenyl was added as a solution in acetone to give a concentration of either 500 and 50 µg/g sediment for a polybrominated biphenyl mixture (Firemaster; >50% 2,4,5,2',4',5'-hexabromobiphenyl, with 2,4,5,2',5'-pentabromobiphenyl, 2,4,5,3',4'-pentabromobiphenyl, 2,4,5,3',4',5'-hexabromobiphenyl, and 2,3,4,5,2',4',5'-heptabromobiphenyl being the other major components) or 250 and 50 µg/g sediment for the pure compound 2,4,5,2',4',5'-hexabromobiphenyl. The cultures were incubated at 25^{o}C in the dark. Analysis of the degradation products was carried out by gas chromatography with electron capture detection (GC-ECD) using authentic standards of individual polybrominated biphenyl isomers, or standards purified from the commercial mixture used. However, several new peaks were seen in the chromatograph. For these compounds the number of bromine atoms present/molecule was determined by mass spectrometry and the most probable identity of the compound was determined by the relative retention times and the assumption that the corresponding polybrominated biphenyl and polychlorinated biphenyl congeners have the same relative retention times and response factors.

In the experiments using the inocula derived from Aroclor 1242-contaminated sediment, 29% of the *meta*- and *para*-bromines present in the polybrominated biphenyl mixture (Firemaster) were removed during 40 weeks incubation at a concentration of 500 µg/g sediment. The same sediment system had previously been shown to dechlorinate polychlorinated biphenyls and 59% of the *meta*- and *para*-chlorines of added Aroclor 1242 were removed under the same conditions. No asymptote was reached in the degradation curve for the polybrominated biphenyl mixture, indicating that further debromination could have occurred over a longer incubation period. No debromination of the polybrominated biphenyl mixture was seen with the inocula derived from Aroclor 1260 (when Aroclor 1260 itself was incubated at 500 µg/g sediment 18% removal of *meta*- and *para*-chlorines was seen over 40 weeks incubation, but a 24-week acclimation period was seen before dechlorination occurred).

In a second series of experiments, 32% removal of *meta*- and *para*-bromines using the inocula from polybrominated biphenyl-contaminated sediment, 12% removal of *meta*- and *para*- bromines using inocula from Aroclor 1242-contaminated sediment and 3% removal of *meta*- and *para*-bromines using inocula from Aroclor 1260-contaminated sediment was seen over 32 weeks. In these experiments, the polybrominated biphenyl mixture (Firemaster) was incubated at a concentration of 500 µg/g sediment. No debromination was seen in incubations at a polybrominated biphenyl concentration of 50 µg/g sediment. A similar pattern was seen when the pure compound 2,4,5,2',4',5'-hexabromobiphenyl was incubated in the same system.

The authors concluded that debromination or dechlorination was greatest in those systems that had previously been exposed to the brominated or chlorinated biphenyl under investigation. The results indicated that adaptation of the microorganisms present (enzyme induction) was needed for debromination to occur, and this was further supported by the fact that no debromination was seen at lower polybrominated biphenyl concentrations of 50 µg/g. A similar concentration dependence for the reductive dechlorination of polychlorinated biphenyls had previously been seen (Morris et al, 1992).

Other relevant chlorinated substances

The reductive dechlorination of polychlorinated biphenyls has been studied using two freshwater sediments and an estuarine sediment under both methanogenic and sulfidogenic conditions. All sediments had been previously contaminated with polychlorinated biphenyls. A 35% (v/v) sediment inoculum was used in the experiments and incubations were carried out at 30^{o}C in the dark over a 17 month period. The polychlorinated biphenyls (PCB) used in the experiments were either Aroclor 1242 at 100 mg/kg or Aroclor 1260 at 400 mg/kg (these correspond to the contamination levels found in the sediments). In general, reductive dechlorination started within 1-2 months in the experiments carried out under methanogenic conditions, with a decrease in the concentrations of tri-, tetra- and pentachlorobiphenyls and a corresponding increase in the mono- and dichlorobiphenyls (dechlorination of the ortho chlorine atoms did not occur). The half-life for the reaction was found to be slow in the laboratory experiments (of the order of several months). No dechlorination was seen under sulfidogenic conditions (Alder et al, 1993).

A similar experiment has been carried out by Sokol (1998). Here the ability of polychlorinated biphenyl-contaminated sediments to dechlorinate PCBs was investigated in laboratory incubations over a 39 month period. The sediment used had an average PCB concentration of 300 mg/kg dry weight and these, along with PCB-free sediments spiked with Aroclor 1248 at 300 mg/kg were used to prepare inocula for the experiments. The results indicated that the majority of the dechlorination occurred during the first 4 months of

incubation, but there was some indication of further dechlorination of the initial products after a further lag period. The results agreed with those of earlier studies in that dechlorination appears to be congener specific, with *meta*- and *para*-chlorines being removed more easily than ortho-chlorines. The results also indicated that a threshold concentration may exist, below which no dechlorination of PCBs is observed.

Factors affecting anaerobic dehalogenation

Several factors have been put forward as being important in considering the dehalogenation of aromatic compounds under anaerobic conditions. These include:

- microbial populations present (position of dehalogenation may be population specific)
- adsorption of the substrate to sediment/soil
- availability of co-metabolites/electron donors/carbon source
- concentration of substance

Peijnenburg et al (1991) carried out a series of tests on the rate of both biotic and abiotic transformation of halogenated hydrocarbons in anoxic sediments. The object of the tests was to provide a database in order to assess the factors that were important in determining the rate of degradation. Reductive dehalogenation was seen to occur for halogenated aromatic compounds but the rate and selectivity of the reaction was found to depend on both compound specific factors and environmental factors (such as nature and location of the substituents on the carbon skeleton, redox potential of the system, temperature, sediment composition and microbial habitat). For most compounds considered in the study the rate of degradation was seen to increase after a lag period. This was thought to be due to acclimation as treatment with γ-radiation reduced the rate back to that seen at the start. The results were interpreted in terms of an underlying abiotic process occurring at the start of the experiment (although the nature of the actual reducing agent in the sediment was unknown), then, after a lag phase, biodegradation becoming the dominant removal process. For halogenated aromatic compounds, the abiotic process was found to be a minor removal process compared to biotic dehalogenation. The rates of dehalogenation were found to correlate with molecular structural parameters such as bond strength, Hammett σ-constants (a descriptor of charge distribution within the molecule), inductive effects of substituents and steric parameters.

In an experiment with PCBs, dechlorination has been demonstrated under methanogenic but not sulfidogenic conditions. Methanogenic conditions in sediments are usually associated with the deeper layers of the sediment, where direct exchange with the aerobic upper layers is minimal. Sulfidogenic aerobic conditions usually exist between the aerobic surface layers and the methanogenic lower layers and some exchange between the sulfidogenic and aerobic surface layers can occur. Thus, if anaerobic debromination of the polybrominated diphenyl ethers occurs in the environment under similar conditions to the dechlorination of PCBs, any products formed are more likely to be present in the deeper methanogenic layers of the sediment, and rapid exchange between this layer and the aerobic sediment and water phases would be expected to be limited (Ten Berge, 1995).

Conclusion on anaerobic biodegradation regarding brominated diphenyl ethers

The available data for halogenated aromatic compounds indicate that reductive dehalogenation can occur under some anaerobic conditions. The rate of reaction is generally found to be slow, with the rate depending on several factors, one of which appears to be

carbon-halogen bond strength. Most of the data reported above is for chlorinated organics, with a moderate degree of chlorination. Given that the C-Br bond is weaker than the C-Cl bond, then dehalogenation of brominated diphenyl ethers in the environment under anaerobic conditions is a possibility, and indeed has been seen with other brominated aromatic compounds (e.g. polybrominated biphenyls). It is not clear from the available information whether dehalogenation would occur for fully halogenated substances (such as decabromodiphenyl ether), as little experimental data has been generated for other fully halogenated substances. There is also evidence that dehalogenation requires an adaptation period during which enzyme induction occurs in the microorganisms, and that this process may be dependent on the presence of a high concentration of the halogenated compound.

Photodegradation

Polybrominated diphenyl ethers

The photodegradation of decabromodiphenyl ether has been carried out mainly in organic solvents. Here lower brominated diphenyl ethers (reductive debromination products) were generally observed as reaction products. In aqueous systems, the available tests with decabromodiphenyl ether indicate that little or no lower brominated diphenyl ethers are formed, but identification of the actual products formed has not been fully established. Experiments recently carried out with decabromodiphenyl ether on solid matrices indicated that a very small amount of debrominated products (such as nona-, octa- and heptabromodiphenyl ether) where formed in a step wise process but no lower brominated congeners (e.g. tetrabromodiphenyl ether) were found. The available tests are discussed in more detail in the main report.

No photodegradation studies have been carried out with octa- and pentabromodiphenyl ether.

Other supporting information

Stegeman et al (1993) carried out a series of photolysis experiments in water at 20^{o}C using 300 nm lamps on a range of halogenated benzene derivatives in water and used the results obtained to identify the parameters that were important in the reactions involved. In most cases, photohydrolysis was the only reaction pathway observed. They identified that photohydrolysis occurred in two steps. After light adsorption and excitation of the molecule to the excited state, the first rate determining step was cleavage of the carbon-halogen bond having the lowest bond strength, which was then followed by formation of the corresponding hydroxylated derivative. Both the carbon-halogen bond strength and steric factors in the molecule were considered to be important in determining the site of photohydrolysis.

Many other photolysis studies have been carried out with halogenated aromatic compounds under a variety of conditions and a selection of these are summarised in **Table F1**. From the available information, reductive dehalogenation occurs most prevalently in organic solvents. Where tests are carried out in aqueous solution using wavelengths >290 nm (conditions more relevant to the environment), the main initial reaction products are hydroxylated products, which can react further by ring cleavage to give mineralisation products. It is not possible from the available information to assess the significance of these processes in the environment.

Table F1 Summary of photolysis experiments for halogenated compounds

Substance	Solvent	Radiation	Comments	Reference
Polybrominated dibenzo-*p*-dioxins and furans	methanol or n-hexane	low-pressure mercury lamps (λ>280 nm)	Rate of degradation increased with increasing number of bromine atoms. Rate was faster in n-hexane than methanol. Sequential substitution of bromine with hydrogen occurred along with other unidentified reactions. Rate with bromine compounds was faster than that with chlorine compounds.	Lenoir et al, 1991
4-chlorobiphenyl and Aroclor 1254	methanol/water (10:3)	300 nm or 254 nm	Sodium methyl siliconate enhanced the reaction. Substitution of halogen with hydrogen occurred. Preferential loss of *ortho*-, followed by *meta*- chlorine over *para*- chlorines.	Hawari et al, 1991[a]
4-chlorobiphenyl and Aroclor 1254	alkaline 2-propanol	λ>300 nm	In presence of acetone, dechlorination to biphenyl occurred.	Hawari et al, 1991[b]
Polybromo dibenzo-*p*-dioxins and bromochloro dibenzo-*p*-dioxins	dodecane	natural sunlight	Debromination to lower brominated congeners occurred. Similar pattern of degradation was seen in soil. Other degradative routes than reductive debromination were also occurring.	Chatkittiunwong and Creaser, 1994
2,3,7,8-, 1,3,6,8- and 1,2,3,4-tetrachloro dibenzo-*p*-dioxin	1.4-doxane	xenon lamp - various wavelengths between 199.8 nm and 397.9 nm	Reductive dechlorination was observed. Rate varied with wavelength. Two maximal rate peaks were seen, one around 252 nm and the other in the region of 292-332 nm.	Koshioka et al, 1989
Aroclor 1232, 1242, 1254 and 1260	90% acetonitrile/water with and without sodium borohydride	254 nm	Rate faster with sodium borohydride. Reductive dechlorination observed. Hydroxybiphenyls were not observed.	Epling et al, 1988
2-chloro- and 2,7-dichlorodibenzo-*p*-dioxin and 3,3'-dichlorobiphenyl	aerated aqueous suspensions of semiconductors (TiO_2, WO_3, CdS, Fe_2O_3, and ZnO)	simulated sunlight - xenon lamp with a 340 nm cut-off filter	Catalytic activity was TiO_2>WO_3>ZnO, with CdS and Fe_2O_3 being poor catalysts. Suggests mineralized into CO_2 and HCl. A reaction pathway involving hydroxy intermediates is given based on results from other chloroaromatic compounds.	Pelizzetti et al, 1988
Pentachlorobenzene and methoxychlor	various types of purified water with and without humic acid	eight 350 nm lamps	In unpurified water, rate faster in presence of humic acid. In pure water, pentabromobenzene does not disappear - this was expected since does not absorb at 350 nm and reaction was put down to presence of photosensitising trace impurity. Decrease in pentabromobenzene was apparently second order. Methoxychlor appeared to be stable under the conditions used. No details of products formed	van Noort et al, 1988

Table F1 continued overleaf

Table F1 continued

Substance	Solvent	Radiation	Comments	Reference
Bromo- and bromo/chloro tetra- and penta-halogenated dibenzo-*p*-dioxins	i-octane or as a thin solid film (no solvent)	natural sunlight	Fast photochemical decomposition of the bromo- and bromo/chloro-derivatives in solution, much slower in the solid phase experiments. Reductive dehalogenation was occurring in solution but there was evidence of other degradation routes in the solid phase experiments (not identified).	Buser, 1988
3,4-Dichlorobiphenyl	aqueous suspensions of TiO_2	Xenon/mercury lamp (λ 300-380 nm)	Degrades but no information on products is given.	Tunesi and Anderson, 1987
Brominated biphenyls	90% acetonitrile/water with and without sodium borohydride	λ = 254 nm	Rate of degradation enhanced by sodium borohydride. Reductive debromination occurring. A chain mechanism is thought to occur in presence of borohydride.	Epling et al, 1987
Chlorinated dioxins, biphenyls, phenols and benzenes	aqueous suspensions of semiconductor materials (TiO_2)	λ 310-830 nm	Decomposition occurs. No details of products formed, although reported to be CO_2 and HCl for chlorophenols.	Barbeni et al, 1986
Polychlorodibenzo-*p*-dioxins	water/acetonitrile (2:3 v/v)	λ 290-310	Degradation occurs, no details of products formed.	Choudhry and Webster, 1986
Polychlorinated biphenyls	-	-	Explains photolysis rates in terms of preferential photodissociation of chlorine from a lateral vs. a non-lateral position to yield the corresponding aryl radical and/or aryl cation-aryl carbene intermediate.	Mamantov, 1985a
Polychlorinated diphenyl ethers and chloroanisoles	-	-	Postulates that photolysis of polychlorinated diphenyl ethers to give chlorinated dibenzofurans may proceed via a carbene insertion reaction. Also photosubstitution of chloroanisoles and diphenyl ethers may proceed via an aryl carbene/aryl cation, whereas the photoreduction may proceed via an aryl radical.	Mamantov, 1985b
Polychlorinated dibenzo-*p*-dioxins	-	-	Photolysis rates of tetrachlorodibenzo-*p*-dioxins are explained by the preferential photodissociation of chlorine from a lateral vs. non-lateral position to yield the corresponding aryl radical and/or aryl cation-aryl carbene intermediate.	Mamantov, 1985c.
1,2,3,4,7-pentachloro- and 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	water/acetonitrile (4:6 v/v)	λ = 313 nm	Degradation but no information on products.	Choudhry and Webster, 1985

Table F1 continued overleaf.

Table F1 continued

Substance	Solvent	Radiation	Comments	Reference
Chlorobenzene	water	λ = 254 nm and around 300 nm	Phenol is the product. Previously photoreduction was seen in cyclohexane, isopropanol and methanol (photosubstitution competes with photoreduction in methanol). Reaction photosensitized by acetone.	Tissot et al, 1984
Biphenyl, 2-chlorobiphenyl and 4,4'-dichlorobiphenyl	adsorbed onto silica gel	λ>290	Hydroxylated products formed.	Kotzias et al, 1984
Aroclor 1254	aqueous 2-propanol	λ>300 nm or natural sunlight	Dechlorination enhanced by presence of photosensitiser (hydroquinone), increasing aqueous solvent (1:1 water:alcohol) and maintaining neutral pH. Some evidence for photonucleophilic displacement by 2-propyl groups	Chaudhary et al, 1984
Tetrachlorodibenzofurans	tetradecane or hexane	λ = 254 nm	Trichlorodibenzofurans formed. General rules: 1) chlorines on the same aromatic ring tend to stabilise the loss of chlorine from that ring; 2) vicinal chlorines stabilise the loss of a particular chlorine (i.e. the greater the number of adjacent chlorines about a given chlorine, the greater the likelihood of initially losing that particular chlorine; 3) given an equal number of vicinal chlorines, the 3-chlorine will be lost before the 2-chlorine.	Mazer and Hileman, 1982
Decachlorobiphenyl	hexane, methanol, acetone or benzene	30 different wavelengths between 199 and 358 nm	Observed reductive dechlorination in methanol and hexane. In benzene the product was a terphenyl derivative of decachlorobiphenyl, where a chlorine atom was replaced by a benzene molecule.	Koshioka et al 1987
Chlorobenzene, 2- and 4-chlorobiphenyl and 2- and 4-chlorodiphenyl ether	water	250-300 nm	Produced corresponding phenols or, in the case of 2-chlorodiphenyl ether, dibenzofuran. Quantum yields very similar to those reported in hexane for reduction processes (some speculation that higher chlorinated biphenyls and diphenyl ethers, if have Cl and OH present in the 2 and 2' positions, could cyclise to give chlorinated dibenzofurans and dibenzo-*p*-dioxins).	Dulin et al, 1986
Tetra-, penta- and hexachlorobenzenes	various acetonitrile/water mixtures with and without acetone sensitisers	λ >285 nm	Reductive dechlorination occurred. Also got formation of chlorinated biphenyls.	Choudhry and Hutzinger, 1984
4-Bromodiphenyl ether	water with and without hydrogen peroxide	λ 254-546 nm (with 32 % of total radiation at λ<313 nm)	3 types of reaction seen: dehalogenation to form diphenyl ether and p-hydroxydiphenyl ether; decomposition of the (bromo) diphenyl ether to form benzene and phenol; opening of aromatic rings to form carboxylic acids leading to mineralisation.	Milano et al, 1992

Conclusion on photolysis regarding brominated diphenyl ethers

From the available information it is clear that polybrominated diphenyl ethers have the potential to photodegrade in the environment. In water, and at environmentally relevant wavelengths, the most likely initial reaction products from these reactions are hydroxylated diphenyl ethers, which possibly then react further. The first step in the reaction is probably cleavage of a C-Br following the absorption of radiation, followed by reaction of the radical (radical cation intermediates species may be formed in water) intermediate with oxygen and/or water to give substituted (e.g. hydroxylated) products (Larson and Weber, 1994; Mill and Mabey, 1985). The formation of lower brominated diphenyl ethers during direct photolysis in the environment would require the presence of H-atom donors at concentrations sufficiently high to compete with other oxidants for the aromatic radical intermediate formed. It is not possible to say anything about the significance or rates of these reactions for polybrominated diphenyl ethers in the environment.

Evidence from measured levels

If debromination to lower brominated diphenyl ethers was a significant process in the environment then it would be expected that where high levels of decabromodiphenyl ether or octabromodiphenyl ether were detected there would also be detectable levels of lower brominated congeners as a result of debromination. To enable this analysis to be carried out, all available measured data for the various brominated diphenyl ethers in sediment (**Table F2**) and biota (**Table F3**) has been combined on a site by site basis (these are the two most complete datasets available; data taken from: Law et al, 1996; Environment Agency, 1997; de Boer and Dao, 1993; de Boer et al, 1998; Haglund et al, 1997; Nylund et al, 1992; Sellström et al, 1990, 1993 and 1998; Jansson et al, 1987 and 1993; Anderson and Blomkvist, 1981; van Zeijl, 1997; Watanabe et al, 1987; Lonaganathan et al, 1995; Kuehl et al, 1991; de Wit, 1999; Sellström et al, 1999; Andersson and Wartanian, 1992; Burreau et al, 1999; Srandman et al, 1999; van Bavel et al, 1999; Lindström et al, 1999; Alaee et al, 1999; Asplund et al, 1999a and 1999b). The interpretation of the results is complicated by the fact that a much more extensive data set exists for commercial pentabromodiphenyl ether than the two other commercial products.

The sediment levels (**Table F2**) indicate that decabromodiphenyl ether and octabromodiphenyl ether are detected mainly at sites near to sources of release, whereas the commercial pentabromodiphenyl ether is found widespread throughout the environment, with the higher levels again being associated with sites of release. This means that it is very difficult to determine from the measured data if there is any pattern in the measured levels with regards to the debromination issue as deca- and octabromodiphenyl ether are found only near to sources, and it is likely that pentabromodiphenyl ether will also be released by similar sources. Thus for the locations where high levels of e.g. decabromodiphenyl ether are detected, there are some sites where high levels of commercial pentabromodiphenyl ether are also found and some sites where low (background) levels are found. Thus, it appears that there is little or no evidence in the measured data for reductive debromination of the higher brominated diphenyl ethers to form the lower brominated diphenyl ethers being a significant process.

A similar problem exists for the biota data in **Table F3**, where it is clear that commercial pentabromodiphenyl ether is found widespread through the environment, but there is little or no indication for the presence of decabromodiphenyl ether in biota. From this it can be

concluded that the levels of pentabromodiphenyl ether found in biota are as a result of uptake of pentabromodiphenyl ether rather than uptake and subsequent metabolism of decabromodiphenyl ether, but the results do not allow any conclusions to be drawn over whether decabromodiphenyl ether or octabromodiphenyl ether undergo reductive debromination in the sediment to a significant extent.

With this aim in mind, four of the sediments taken as part of the Mersey estuary study, were recently reanalysed to a) confirm the original levels found and b) to look for the presence of other congeners not originally covered in the study. The results obtained confirmed the earlier concentration of decabromodiphenyl ether (concentrations of <50, 169, 215 and 817 µg/kg dry weight) and the commercial pentabromodiphenyl ether components (tetrabromodiphenyl ether concentrations 3.07, 0.83, 2.02 and 1.61 µg/kg dry weight; pentabromodiphenyl ether concentrations 0.51, 1.20, 4.10 and 2.90 µg/kg dry weight), but hexabromodiphenyl ether (detection limit 0.5 µg/kg dry weight), heptabromodiphenyl ether (detection limit 1 µg/kg dry weight), octabromodiphenyl ether (detection limit 2 µg/kg dry weight) and nonabromodiphenyl ether (detection limit 40 µg/kg dry weight) were not detected in any sample (GFA, 1998). In these samples, if reductive dehalogenation was a significant environmental fate process for decabromodiphenyl ether, then as well as detecting pentabromodiphenyl ether components and decabromodiphenyl ether, it would also be expected that significant levels of the hexa-, hepta-, octa- and nona- components would also be present. This is clearly not the case in these samples.

KEMI (1999) have also tried to find a relationship between the levels of decabromodiphenyl ether and those of tetra- and pentabromodiphenyl ether found in the Swedish environment. They suggest that debromination of decabromodiphenyl ether in sediment is one possible explanation for the levels of tetra- and pentabromodiphenyl ether found in sediments and biota near to industry in the Rivers Viskan and Häggån (reported in Table 2), where high levels of decabromodiphenyl ether were also found. The industry in the area was known to have included 3 sites where decabromodiphenyl ether was used to for back-coating of textiles (this use was phased-out in the area in the early 1990s), but did not include polyurethane foam production sites where pentabromodiphenyl ether may have been used. An alternative explanation to debromination would be that pentabromodiphenyl ether was used in the textile industry in the area.

Although the available monitoring data are insufficient to rule out that reductive debromination of the highly brominated diphenyl ethers occurs in the environment, they do indicate that if it does occur at all, it is not likely to be a significant process and that it is unlikely to account for all the levels of commercial pentabromodiphenyl ether currently found in the environment. A more likely explanation for the pattern and levels of commercial pentabromodiphenyl ether are as a result of widespread environmental distribution following release to the environment, with higher levels being associated with sites of release.

Table F2 Levels of polybrominated diphenyl ethers in sediments

Location	Comments	Pentabromodiphenyl ether components				Penta	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4' PeBDPE/ otter penta[a]	Approx. total	(product basis)			
River Tweed at Tweedmouth	Background site	0.4	<0.6	<0.4	0.4	<0.38	<0.44	<0.6	µg/kg dry wt
River Tweed at Berwick on Tweed bridges	Background site	<0.3	0.6	<0.4	0.6	<0.38	<0.44	<0.6	µg/kg dry wt
River Nith, upstream of wwtp	Near rubber producer	<0.3	<0.6	<0.4	nd	<0.38	<0.44	<0.6	µg/kg dry wt
River Nith, downstream of wwtp	Near rubber producer	1.7	3.5	<0.4	5.2	0.6	<0.44	<0.6	µg/kg dry wt
River Nith at Glencaple	Near rubber producer	0.7	1	<0.4	1.7	<0.38	2	<0.6	µg/kg dry wt
Avonmouth	Near flame retardant producer/user	2.4-3.6	2.9-4.7	<0.4-9.2	7.1-16.6	0.6-1.0	<0.44	<0.6-7	µg/kg dry wt
River Tees, upstream of confluence with River Skerne	Near a producer of penta/octabromodiphenyl ether	<0.3	<0.6	<0.4	nd	<0.38		<0.6	µg/kg dry wt
River Tees, downstream of confluence with River Skerne	Near a producer of penta/octabromodiphenyl ether	8	11	2.9	21.9	35	<0.44-25	<0.6	µg/kg dry wt
River Skerne at Croft-on-Tees	Near a producer of penta/octabromodiphenyl ether	51	85	3.5	139.5	34	129	7	µg/kg dry wt
River Skerne at Newton Aycliffe	Near a producer of penta/octabromodiphenyl ether	239	319	2.7	560.7	130	397	64	µg/kg dry wt
Howden Beck	Near a producer of penta/octabromodiphenyl ether	86	111	1.8	198.8	45	264	23	µg/kg dry wt
River Skerne, upstream of Howden Beck	Near a producer of penta/octabromodiphenyl ether	68	126	0.7	194.7	51	333	294	µg/kg dry wt
River Skerne, downstream of Howden Beck	Near a producer of penta/octabromodiphenyl ether	112	159	<0.4	271	68	1,405	95	µg/kg dry wt
River Calder at Cock Bridge	Near a foam manufacturer	2.3	0.6	4.2	7.1	<0.38	9	399	µg/kg dry wt
Hyndburn Brook, upstream of wwtp	Near to foam manufacturer	7.6	16	<0.4	23.6	6.1	3	<0.6	µg/kg dry wt
River Calder, downstream of wwtp	Near to foam manufacturer	24	46	0.5	94.1	18	17	3,190	µg/kg dry wt
Elstow landfill	Landfill receiving brominated wastes	0.8-2.4	2.9-5.7	<0.4	5.3-6.5	<0.38-1.5	<0.44-13	<0.6	µg/kg dry wt
Elstow Brook	Downstream of landfill site	0.4	<0.6	1.2	1.6	<0.38	1	<0.6	µg/kg dry wt
Tees Estuary	Portrack wwtp	8.9	16	9.1	34	19	29	5	µg/kg dry wt
	Bamlett's Bight	368	898	4.8	1,271	366	164	<0.6	µg/kg dry wt
	No. 23 buoy	49	99	14	162	77	263	9	µg/kg dry wt
	Phillips approach buoy	103	201	72	372	81	1,348	8	µg/kg dry wt
Great Ouse at Kings Lynn	Downstream of landfill site	4.2	4.6	<0.4	8.8	<0.38	7.9	<0.6	µg/kg dry wt
River Ribble at Freckleton saltings	Near foam manufacturing site	1.2	1.7	<0.4	2.9	<0.38	4.4	111	µg/kg dry wt
River Humber at Paull		21	36	<0.4	57	6.6	29	17	µg/kg dry wt
Upstream of a plastics processor	Decabromodiphenyl ether used					<50	<200	<200	µg/kg dry wt
Downstream of a plastics processor	Decabromodiphenyl ether used					<50	<200	<200	µg/kg dry wt
Upstream of warehouse	Decabromodiphenyl ether stored					<100	1,480	<500	µg/kg dry wt
Downstream of warehouse	Decabromodiphenyl ether stored					<100	3,030	<500	µg/kg dry wt
Industrial area	Upstream of site possibly using pentabromodiphenyl ether					<100	<500	<500	µg/kg dry wt
Industrial area	Downstream of site possibly using pentabromodiphenyl ether					<100	<500	<500	µg/kg dry wt
Mersey estuary	Industrial area, upstream of polymer processing site					<100	<500	<500	µg/kg dry wt
Mersey estuary	Downstream of polymer processing site					<100	<500	<500	µg/kg dry wt

Table F2 continued overleaf

Table F2 continued

Location	Comments	Pentabromodiphenyl ether components				Penta	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]	Approx. total	(Product basis)			
Upstream of a plastic compounder.	Decabromodiphenyl ether used.					5.9	<200	<200	µg/kg dry wt
Downstream of a plastic compounder	Decabromodiphenyl ether used.					<5	<200		µg/kg dry wt
Landfill site.	Pentabromodiphenyl ether waste disposed on-site					<100	<500	<500	µg/kg dry wt
Haringvliet-east	River sediment from 1992	6.7	7.3		14				µg/kg wet wt
Nieuwe Merwede	River sediment from 1992	17			17				µg/kg wet wt
Meuse	River sediment from 1992	6.9	8.2		15.1				µg/kg wet wt
Waal	River sediment from 1992	23	21		44				µg/kg wet wt
Sediments from near a factory	Upstream	3.5	8.2		11.7				µg/kg lG
	Downstream	840	1,200		2,000				µg/kg lG
Lake Marsjön	Upstream from industry	<2	<1	<0.4	<3			<20	µg/kg lG
Lake Öresjö	Downstream from industry	7.4	3.5	1.2	12.1			<40	µg/kg lG
River Viskan	Downstream from town	12	12	3.5	27.5			150	µg/kg lG
River Viskan	At Moga	13	9.2	3.6	25.8			220	µg/kg lG
River Viskan	Upstream from Skene	23	43	8.9	74.9			3400	µg/kg lG
River Viskan	Downstream from Skene	50	53	19	122			12,000	µg/kg lG
River Häggån	Upstream from Fritsla	1.3	1.1	0.31	2.7			<20	µg/kg lG
River Häggån	Downstream from Fritsla	2	2.7	0.69	5.4			<20	µg/kg lG
Lake Skäresjön		<2	<2	0.63	<4.6			<30	µg/kg lG
Sediment core, Baltic Sea	0-5 mm depth	1.6	0.98	0.31	2.89				µg/kg lG
	5-10 mm depth	0.76	0.2	0.07	1.03				µg/kg lG
	10-15 mm depth	0.68	0.36	<0.04	1.04				µg/kg lG
	15-20 mm depth	0.5	0.13	<0.04	1.67				µg/kg lG
	80-90 mm depth	0.06	<0.04	<0.04	0.06				µg/kg lG
Liffey River		0.61	0.73					40.3	µg/kg dry wt
Clyde		0.74	1.03					8.4	µg/kg dry wt
Mersey		2.2	2.27					1,700	µg/kg dry wt
Southampton		0.19	0.23					2.1	µg/kg dry wt
Thames		0.64	0.7					18.3	µg/kg dry wt
Humber		5.8	6.93					39	µg/kg dry wt
Tyne		0.7	0.99					4.3	µg/kg dry wt

Table F2 continued overleaf

Table F2 continued

Location	Comments	Pentabromodiphenyl ether components				Penta	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]	Approx. total	(product basis)			
Forth		0.39	0.36					3.3	µg/kg dry wt
Seine		0.69	0.83					12.2	µg/kg dry wt
North sea (off Belgium)		<0.17	<0.20					11.6	µg/kg dry wt
Schelde		0.42	0.32					200	µg/kg dry wt
Rijn		1.4	1.3					15.7	µg/kg dry wt
Noordwijk		0.9	1					11.3	µg/kg dry wt
Waddensee		0.19	0.42					1.1	µg/kg dry wt
Ems		0.38	0.44					4.9	µg/kg dry wt
Weser		0.17	0.2					3.4	µg/kg dry wt
Elbe		<0.17	<0.20					0.83	µg/kg dry wt
Göta		<0.17	<0.20					2.6	µg/kg dry wt
Glomma		<0.17	<0.20					<0.52	µg/kg dry wt
Skiens		<0.17	<0.20					1	µg/kg dry wt
Otria		<0.17	<0.20					0.71	µg/kg dry wt
100 km off Terschdling (reference site)		0.18	0.2					<0.51	µg/kg dry wt
Baltic Sea	Surficial sediments				nd-1.1				µg/kg dry wt
Near manufacturing site, USA								nd-14,000	µg/kg
Japan	1977							nd	µg/kg
Japan	1987						8-21	10-1,370	µg/kg
Japan	1988						15-22	4-6,000	µg/kg
Japan	River sediment, 1981-1983							33-375	µg/kg dry wt
Japan	Estuary sediment, 1981-1983							nd-20	µg/kg dry wt
Japan	Marine sediment, 1981-1983							<5	µg/kg dry wt
Osaka, Japan	River sediment, 1983							200	µg/kg dry wt
Osaka, Japan	River sediments, 1983							120-310	µg/kg dry wt
Osaka bay, Japan	Marine sediments, 1983							<5	µg/kg dry wt

[a]Other penta isomer is probably 2,2'4,4',6-pentabromodiphenyl ether (Sellström et al, 1998)

Table F3 Levels of polybrominated diphenyl ethers in biota

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]				
Dab liver	Off River Tees; 12% lipid	129	9.4	<1	13	325	<1.2	µg/kg wet wt
	Off Wash; 31% lipid	117	23	<1	34	18	<1.2	µg/kg wet wt
	Tees Bay; 23.6% lipid	601	29	55	236	179	<1.2	µg/kg wet wt
	Bideford Bay; 33.6% lipid	37	11	11	33	<1	<1.2	µg/kg wet wt
Dab muscle	Bideford Bay; 1% lipid	<1	<1	<1	1	9.7	<1.2	µg/kg wet wt
	Tees Bay; 1.2% lipid	7	1	1.6	11	6	<1.2	µg/kg wet wt
Whiting liver	Bristol Channel; 45% lipid	102	21	<1	48	<1	<1.2	µg/kg wet wt
Flounder liver	Off Lune/Wyre; 12% lipid	49	6.5	<1	12	14	<1.2	µg/kg wet wt
	Off River Humber; 14% lipid	217	22	<1	16	126	<1.2	µg/kg wet wt
	Nith Estuary; 18.8% lipid	19	3.6	<1	9	<1	<1.2	µg/kg wet wt
	Nith Estuary; 19.2% lipid	14	3.1	<1	9	16	<1.2	µg/kg wet wt
	Bideford Bay; 18.8% lipid	69	4.9	22	22	19	<1.2	µg/kg wet wt
	Tees Bay; 13.6% lipid	1,294	108	130	169	115	<1.2	µg/kg wet wt
Flounder muscle	Nith Estuary; 1% lipid	1.4	<1	<1	1.2	<1	<1.2	µg/kg wet wt
	Nith Estuary; 1% lipid	1.2	<1	<1	1	<1	<1.2	µg/kg wet wt
	Bideford Bay; 0.8% lipid	1.4	<1	<1	0.8	<1	<1.2	µg/kg wet wt
	Tees Bay; 1.2% lipid	22	4.4	1.1	13	7	<1.2	µg/kg wet wt
Plaice muscle	Bideford Bay; 0.6% lipid	0.6	<1	<1	1	3.3	<1.2	µg/kg wet wt
	Tees Bay; 1.6% lipid	8.3	1.6	2.2	15	12	<1.2	µg/kg wet wt
Plaice liver	Bideford Bay; 16% lipid	15	3	3.6	15	<1	<1.2	µg/kg wet wt
	Tees Bay; 3.3% lipid	161	12	14	35	41	<1.2	µg/kg wet wt
Winkles	River Tweed; 2.6% lipid	1.9	1.8	1.5	25	<1	<1.2	µg/kg wet wt
Mussels	Gat Sand/Hunstanton, the Wash; 1.8% lipid	3.5	3.9	2	18	16	<1.2	µg/kg wet wt
Rabbit	Pooled muscle samples, 1986	<1.8	<0.34	<0.21				µg/kg lipid
Moose	Pooled muscle samples, 1985-1986	0.82	0.64	0.24				µg/kg lipid
Reindeer	Pooled suet samples, 1986	0.17	0.26	0.04				µg/kg lipid
Whitefish	Pooled muscle samples, 1986	15	7.2	3.9				µg/kg lipid
Arctic char	Pooled muscle samples, 1987	400	64	51				µg/kg lipid
Herring	Pooled and individual samples, 1986-1987	12-450	3.4-46	1.6-32				µg/kg lipid
Ringed seal	Pooled blubber samples, 1981	47	1.7	2.3				µg/kg lipid
Grey seal	Pooled blubber samples, 1979-1985	650	40	38				µg/kg lipid
Osprey	Pooled muscle samples, 1982-1986	1,800	140	200				µg/kg lipid
Starling	Muscle samples, 1988	2.7-7.8	2.3-4.2	0.62-1.1				µg/kg lipid
Guillemot eggs	Pooled and individual samples, 1970-1989	130-1,500	24-330	4.2-79				µg/kg lipid
Bream	Muscle samples, 1987	250-750	2.3-2.4	11-37				µg/kg lipid

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]	(product basis)			
Pike	Pooled and individual muscle samples, 1987-1988	94-6,500	60-1,100	25-640				µg/kg lipid
	Muscle samples, Lake Marsjön, 1995	40-63b	<52-<70	9.3-16			nd-trace	µg/kg lipid
	Muscle samples, Lake Öresjö, 1995	240-2,000	68-1,600	60-1,000			nd	µg/kg lipid
	Muscle samples, River Viskan, downstream from Borås 1995	330-510	<48-<59	65-98			nd	µg/kg lipid
	Muscle samples, River Viskan at Moga, 1995	150-200	<37-<56	24-43			nd-trace	µg/kg lipid
	Muscle samples, Lake Skäresjön, 1995	130-190	<37-58	20-49			nd	µg/kg lipid
Perch	Muscle samples, 1987	2,200-24,000	380-9,400	230-3,500				µg/kg lipid
Trout	Pooled and individual muscle samples, 1988	120-460	64-590	33-150				µg/kg lipid
Harbour seal from the Baltic	Blubber sample				90			µg/kg lipid
Harbour seal from the Kattegat	Blubber sample				10			µg/kg lipid
Ringed seal from the Arctic Ocean	Blubber sample				40			µg/kg lipid
Guillemot from the Baltic	Pectoral muscle sample				370			µg/kg lipid
Guillemot from the North Sea	Pectoral muscle sample				80			µg/kg lipid
Guillemot from the Arctic Ocean	Pectoral muscle sample				130			µg/kg lipid
Sea eagle	Pectoral muscle sample				350			µg/kg lipid
Pike muscle from the Viskan River system	Mean levels, 1979-1981				nd-24,000			µg/kg lipid
Pike liver from the Viskan River system	Mean levels, 1979-1981				nd-88,000			µg/kg lipid
Bream muscle from the Viskan River system	Mean levels, 1979-1981				9,700			µg/kg lipid
Tench muscle from the Viskan River system	Mean levels, 1979-1981				950			µg/kg lipid
Eel muscle from the Viskan River system	Mean levels, 1979-1981				900-16,000			µg/kg lipid
Sea trout muscle from the Viskan River system	Mean levels, 1979-1981				1,400			µg/kg lipid
Harbour seal from the Skagerrak	Composite blubber samples				160-250			µg/kg lipid
Harbour seal from the Kattegat	Composite blubber samples				210-390			µg/kg lipid
Harbour seal from the Baltic, Kalmarsund	Composite blubber samples				450-570			µg/kg lipid

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]	(product basis)			
Hake liver	Atlantic, 1986	<20	<10					µg/kg wet wt
	Bay of Biscay, 1983	70						µg/kg wet wt
	English Channel, 1982	11	<10					µg/kg wet wt
	Irish Sea, 1982	18	<10					µg/kg wet wt
Cod	Central North Sea, 1985-1991	0.2-1	<0.1					µg/kg wet wt
	Northern North Sea, 1986	0.4	<10					µg/kg wet wt
Cod liver	Central North Sea, 1983-1989	12-73	3.9-13					µg/kg wet wt
	Northern North Sea, 1983-1989	14-30	1.3-5.1					µg/kg wet wt
	Southern North Sea, 1981-1991	45-460	1.7-17					µg/kg wet wt
Herring	Central North Sea, 1985	1	<10					µg/kg wet wt
	Northern North Sea, 1985	0.7	<10					µg/kg wet wt
	Skagerrak, 1991	4.3	1.7					µg/kg wet wt
	Southern North Sea, 1985-1991	1.6-11	<10					µg/kg wet wt
	Southern North Sea (Vlaamse Bank), 1992	28	17					µg/kg wet wt
	Straits of Dover, 1985	0.9-7.6	<10					µg/kg wet wt
Herring liver	Southern North Sea (Vlaamse Bank), 1992	2.4	1.3					µg/kg wet wt
Plaice	Danish West Coast, 1989	<0.1						µg/kg wet wt
	English Channel, 1989	0.4						µg/kg wet wt
	English East Coast, 1989	<0.1						µg/kg wet wt
	German Bight, 1989	0.1						µg/kg wet wt
	Skagerrak, 1989	0.1						µg/kg wet wt
	Straits of Dover, 1989	0.2						µg/kg wet wt
Plaice liver	Danish West Coast, 1989	1.1						µg/kg wet wt
	English Channel, 1989	4.5						µg/kg wet wt
	English East Coast, 1989	6.6						µg/kg wet wt
	German Bight, 1989	2.1						µg/kg wet wt
	Skagerrak, 1989	1.3						µg/kg wet wt
Sprat	English Channel, 1982	1.8						µg/kg wet wt
Grey seal from the Baltic.	Composite blubber samples				280-1,500			µg/kg lipid
Ringed seal from the Baltic.	Composite blubber samples				190-320			µg/kg lipid
Hake	Atlantic, 1987	0.8	0.4					µg/kg wet wt
	Bay of Biscay, 1983	69						µg/kg wet wt

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]				
Blenny	Southern North Sea, 1992	1	0.2					µg/kg wet wt
Brill	Southern North Sea, 1992	0.4	<0.1					µg/kg wet wt
Brill liver	Southern North Sea, 1992	13	0.7					µg/kg wet wt
Dab	German Bight, 1991	0.19	<0.1					µg/kg wet wt
	North Sea (IJmuiden), 1990	3.5	<0.3					µg/kg wet wt
	Wadden Sea, 1991	0.4	<0.1					µg/kg wet wt
Dab liver	German Bight, 1991	3						µg/kg wet wt
	Wadden Sea, 1991	11	<1					µg/kg wet wt
Whiting	Southern North Sea, 1992	0.4	0.1					µg/kg wet wt
	Southern North Sea, 1984-1991	0.3-1	<0.1					µg/kg wet wt
Twaite shad	Southern North Sea, 1987	77	<4					µg/kg wet wt
Twaite shad liver	Southern North Sea, 1987	15	1.7					µg/kg wet wt
Turbot	Southern North Sea, 1992	0.2	<0.1					µg/kg wet wt
Sole	German Bight, 1990	<0.1	<0.1					µg/kg wet wt
	Southern North Sea, 1991-1992	0.1-0.5	<0.1					µg/kg wet wt
Sole liver	German Bight, 1990	2	<2					µg/kg wet wt
Mackerel	Shetland Islands, 1991	3.1	<1					µg/kg wet wt
Smelt	Southern North Sea, 1992	1.2	0.2					µg/kg wet wt
Dolphin blubber	Atlantic, 1983	590	<10					µg/kg wet wt
	Southern North Sea, 1990	2,600-3,000	220					µg/kg wet wt
Dolphin muscle	Atlantic, 1983	18						µg/kg wet wt
	Southern North Sea, 1990	57	12					µg/kg wet wt
Dolphin liver	Southern North Sea, 1990	45-180	5.3-30					µg/kg wet wt
Dolphin kidney	Southern North Sea, 1990	44	7.9					µg/kg wet wt
Dolphin spleen	Southern North Sea, 1990	43	8.7					µg/kg wet wt
Porpoise blubber	Southern North Sea, 1990	830	79					µg/kg wet wt
Silver Eel	Ketelmeer, 1987	7.4-81	4.3-14					µg/kg wet wt
	Waal, 1987	55	4.4					µg/kg wet wt
Yellow Eel	Aar Kanaal (Ter Aar), 1992	6.2	<1					µg/kg wet wt
	Amstel Drecht Kanaal, 1991	<1	0.5					µg/kg wet wt
	Amsterdam-Rijnkanaal, 1992	3.5						µg/kg wet wt
	Apeldooms Kanaal, 1991	5	1.3					µg/kg wet wt
Turbot liver	Southern North Sea, 1992	7	1					µg/kg wet wt

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]				
	Bergsche plas, 1991	1.6	1					µg/kg wet wt
	Binnen Liede, 1983	<10	<10					µg/kg wet wt
	Boven Merwede (Gorinchem), 1989	9.7-120	1.8-11					µg/kg wet wt
	Buiten Liede, 1983	<10	<10					µg/kg wet wt
	Callandkanaal, 1985	9.7	<10					µg/kg wet wt
	Delfzijl, 1984	3.5 and <10						µg/kg wet wt
	Diemerzeedijk, 1985	<10	<10					µg/kg wet wt
	Geul (Meersen), 1992	6.8	0.7					µg/kg wet wt
	Haringvliet-east, 1977-1992	6.7-190	<2-7.3					µg/kg wet wt
	Haringvliet-west, 1989-1992	22-62	<2-2.1					µg/kg wet wt
	Hollands Diep, 1979-1992	32-190	1-4					µg/kg wet wt
	Hollandse IJssel (Gouderak), 1984-1987	52-91	<10					µg/kg wet wt
	IJ, Amsterdam, 1992	4.3						µg/kg wet wt
	Ketelmeer, 1977-1992	16-120	<2-7.9					µg/kg wet wt
	Lauwersmeer, 1988-1992	1.7-3.4	<1-2.2					µg/kg wet wt
	Lek, 1988-1992	34-97	2.4-3.8					µg/kg wet wt
	Maas-Waalkanaal (Malden), 1992	40	2.2					µg/kg wet wt
	Markermeer, 1991-1992	4-6.2	<1					µg/kg wet wt
	Meuse, 1983-1992	1.3-110	<1-2.8					µg/kg wet wt
	Niers, 1984	<10						µg/kg wet wt
	Nieuwe Maas, 1989	18-55	1.1-4.3					µg/kg wet wt
	Nieuwe Merwede, 1987-1992	40-97	2.4-8.7					µg/kg wet wt
	Nieuwe Waterweg, 1991	25	1.3					µg/kg wet wt
	Noordhollands kanaal, 1992	2.4						µg/kg wet wt
	Noordzeekanaal, 1992	3.3-5.2	<0.5-1.1					µg/kg wet wt
	Oostvaardersplassen, 1984	<10	<10					µg/kg wet wt
	Oude Rijn Sprangen, 1986	3.9	<4					µg/kg wet wt
	Oude Maas, 1989-1990	77-110	<5					µg/kg wet wt
	Paterswoldermeer, 1991	1.9	<4					µg/kg wet wt

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]				
Yellow Eeel (continued)	Prinses Margrietkanaal, 1992	1.1	<1					µg/kg wet wt
	Rhine (Lobith), 1984-1992	18-250	0.9-7.5					µg/kg wet wt
	Ringvaart (Haarlemmermeer), 1983	<10	<10					µg/kg wet wt
	Linge (Rhenoij), 1991	12	0.6					µg/kg wet wt
	Roer (Vlodrop), 1983-1992	68-260	<4-32					µg/kg wet wt
	Rottige Meenthe, 1988	1.1	<1					µg/kg wet wt
	Tjeukemeer, 1988-1991	<2-5.3	<2					µg/kg wet wt
	Tongelreep (Bruggerhuizen), 1992	7.6	<2					µg/kg wet wt
	Twentekanaal, 1987-1992.	4.7-49	<1-2.9					µg/kg wet wt
	Vecht (Ommen), 1991-1992	6.6-7.7	0.5					µg/kg wet wt
	Vliet (Rijswijk), 1988	<3	<5					µg/kg wet wt
	Volkerak, 1986-1992	4.9-14	<1-3.4					µg/kg wet wt
	Waal, 1983-1992	43-340	6.1-22					µg/kg wet wt
	Wadden Sea-east (Eems), 1992	1.5	1.5					µg/kg wet wt
	Wadden Sea (Steendiep), 1991-1992	5.5-9.7	0.68					µg/kg wet wt
	Western Scheldt, 1983-1992	3.5-6.3	0.8					µg/kg wet wt
	Yssel (Deventer), 1988-1992	33-110	<3-5.4					µg/kg wet wt
	Yssel Lake, 1984-1992	4.8-40	<1-2.1					µg/kg wet wt
	Zoommeer, 1987-1992	3.1-3.8	<4					µg/kg wet wt
	Zuid-Willemsvaart, 1989-1992	3-3.7	0.6-1.5					µg/kg wet wt
Yellow Eel liver	Nieuwe Merwede, 1989	5.7	0.61					µg/kg wet wt
Sea Trout	Meuse, 1989	1.8-2.1	0.2-0.6					µg/kg wet wt
	Waal, 1989	2.9-3.3	0.5-0.7					µg/kg wet wt
Roach	Boven Merwede (Gorinchem), 1990	2.8						µg/kg wet wt
	Haringvliet-east, 1990	16						µg/kg wet wt
	Ketelmeer, 1990	1.8						µg/kg wet wt
	Rhine (Lobith), 1990	2.4						µg/kg wet wt
	Twentekanaal, 1987	15	<1					µg/kg wet wt
	Waal, 1990	2.1						µg/kg wet wt

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]				
Mussel	Eastern Scheldt, 1984-1991	0.3-0.7	<1					µg/kg wet wt
	Wadden Sea-east, 1984	0.4	<10					µg/kg wet wt
	Wadden Sea, 1984	0.4	<10					µg/kg wet wt
	Western Scheldt, 1984	1.5	<10					µg/kg wet wt
Oyster	Eastern Scheldt, 1991	0.7	0.7					µg/kg wet wt
	Zuidlaardermeer, 1992	1.5	1.3					µg/kg wet wt
Shrimp	Eastern Scheldt, 1984	0.3	<10					µg/kg wet wt
	Egmond, 1984	0.7-1.5	<10					µg/kg wet wt
	IJmond, 1991	0.1						µg/kg wet wt
	Maasvlakte, 1984	1	<10					µg/kg wet wt
	Rijnmond, 1984	2.5	<10					µg/kg wet wt
	Southern North Sea, 1989-1992	<0.1-0.4	<0.1-0.1					µg/kg wet wt
	Wadden Sea-east, 1984	<10	<10					µg/kg wet wt
	Wadden Sea, 1984	0.6	<10					µg/kg wet wt
	Western Scheldt, 1984	1	<10					µg/kg wet wt
Shrimp liver	Southern North Sea, 1985	4	<4					µg/kg wet wt
Cormorant liver	Biesbosch, 1981	25,000	4,000					µg/kg wet wt
Cormorant kidney	Biesbosch, 1981	18,000	2,000					µg/kg wet wt
Human Milk	Utrecht, 1983	0.4						µg/kg wet wt
Sperm whale	3 blubber samples, Dutch coast, 1995	61-95	10-26	7.5-15			<3-<5	µg/kg wet wt
	Liver sample, Dutch coast, 1995	2.7	0.91	0.54			<3	µg/kg wet wt
Whitebeaked dolphin	Blubber sample, Dutch coast, 1995	5,550	1,000	1,200			<10	µg/kg wet wt
	Liver sample, Dutch coast, 1995	22	3.0	5.8			<1	µg/kg wet wt
Pike-perch	Hollands Diep, 1990-1991	5.1-5.5	1.3					µg/kg wet wt
	Hollandse IJssel, 1990	5.6-25	1-4.7					µg/kg wet wt
	Yssel Lake, 1991	1.1						µg/kg wet wt
Pike-perch liver	Hollands Diep, 1990	61	19					µg/kg wet wt
	Hollandse IJssel, 1990	25	4.7					µg/kg wet wt

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]				
Minke whale	Blubber sample, Dutch coast, 1995	88	23	11			<1	µg/kg wet wt
Harbour seal	3 blubber samples, Dutch coast, 1995	280-1,200	40-160	18-110			<10-<15	µg/kg wet wt
	3 liver samples, Dutch coast, 1995	12-21	0.07-0.93	0.53-5.1			<1-<2	µg/kg wet wt
Mackerel	Muscle, Dutch coast, 1995	5.4	1.9	1.8			<2	µg/kg wet wt
Herring	2 year old, Baltic	3.2	<0.1	<0.1				µg/kg lipid
	3 year old, Baltic	10	1.0	1.3				µg/kg lipid
	4 year old, Baltic	13	<0.1	<0.1				µg/kg lipid
	5 year old, Baltic	27	2.9	1.9				µg/kg lipid
Grey seal	Liver, Baltic	16	1.3	0.8				µg/kg lipid
	Blubber, Baltic	308	54	57				µg/kg lipid
Ringed seal	Liver, Baltic	33	3.0	2.9				µg/kg lipid
	Blubber, Baltic	256	33	61				µg/kg lipid
Salmon	Muscle, Baltic	167	52	44				µg/kg lipid
Fish oil	Baltic	0.1-23	0.1-2.8	<0.1-3.8				µg/kg lipid
Human adipose tissue	Baltic area	8.8	1.1	1.8				µg/kg lipid
Sprat	Baltic area	4.32	0.71	0.8				µg/kg lipid
Herring	Baltic area	6.21	0.62	0.81				µg/kg lipid
Salmon	Baltic area	46.29	7.27	6.37				µg/kg lipid
Herring	Baltic Sea	7.46-23.76	3.89-4.28					µg/kg lipid
Sprat	Baltic Sea	17.48-140-84	1.89-9.51					µg/kg lipid
Human adipose	Finland	3.07-16.75	0.74-5.51					µg/kg lipid
Long-finned pilot whales	Adult males, Faroe Islands, 1997	271-486.6	54.5-92.9	nd-50.4				µg/kg lipid
	Adult females, Faroe Islands, 1997	66.0-211.7	23.9-51.1	nd-26.0				µg/kg lipid
	Juvenile males, Faroe Islands, 1997	249.4-557.1	67.1-112.5	nd-59.9				µg/kg lipid
	Juvenile females, Faroe Islands, 1997	247.1-749.1	67.3-169.3	nd-97.7				µg/kg lipid
	9 Females from Hvannasund, 1994	411.9	164.1	nd-87.1				µg/kg lipid
	19 Females from Vestmanna, 1996	529.4	209.0	nd-104.4				µg/kg lipid
	8 Males from Vestmanna, 1996	862.4	292.0	0.2-153.6				µg/kg lipid
	4 Young females from Vestmanna, 1996	1,727.4	562.2	0.4-281.1				µg/kg lipid
	13 Yound males from Vestmanna, 1996	1,782.1	603.6	0.5-280.5				µg/kg lipid

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/ other penta[a]				
Trout	Lake Ontario				545			µg/kg lipid
	Lake Huron				237			µg/kg lipid
	Lake Superior				135			µg/kg lipid
Ringed seal	Female blubber, Canada				25.8			µg/kg lipid
	Male blubber, Canada				50.0			µg/kg lipid
Beluga	Female blubber, Canada				81.2			µg/kg lipid
	Male blubber, Canada				160			µg/kg lipid
Baltic salmon	Muscle, River Daläven	180-200	50-54	45-47				µg/kg lipid
	Eggs, River Daläven	63-66	16	18-19				µg/kg lipid
	Blood, River Daläven	180-200	45-64	52-65				µg/kg lipid
	Muscle, River Daläven	110	35	26				µg/kg lipid
Steel head trout	Muscle, Lake Michigan	1,700	600	360				µg/kg lipid
Mussels	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	nd-14.6	nd-2.8				nd (<0.5)-1.4	µg/kg wet wt
Mullet	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	nd	nd				nd (<0.5)	µg/kg wet wt
Goby	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	nd	nd				nd (<0.5)	µg/kg wet wt
Sardine	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	nd-0.8	nd				nd (<0.5)	µg/kg wet wt
Sea bass	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	0.1	nd				nd (<0.5)	µg/kg wet wt
Horse Mackerel	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	nd	nd				nd (<0.5)	µg/kg wet wt
Mackerel	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	0.3	nd				nd (<0.5)	µg/kg wet wt
Hairtail	Japan, 1981-1985. Detection limit 0.1 mg/kg wet weight	0.1	nd				nd (<0.5)	µg/kg wet wt
Carp	Buffalo River, United States, 1991. Young fish	12.3	0.63					µg/kg wet wt
	Buffalo River, United States, 1991. Middle aged fish	19.3	0.65					µg/kg wet wt
	Buffalo River, United States, 1991. Old fish	21.3	1.17					µg/kg wet wt
Bottlenose dolphin	United States, 1987				180-220			µg/kg lipid

[a]Other penta isomer is probably 2,2'4,4',6-pentabromodiphenyl ether (Sellström et al, 1998)

Conclusion

The available information indicates that the brominated diphenyl ethers have the potential to undergo biodegradation by reductive dehalogenation to form lower brominated congeners under anaerobic conditions. Photolysis may also occur but the products formed are most likely to be hydroxylated products which may react further. The environmental significance of these processes is unknown but the available monitoring data would suggest that reductive dehalogenation of decabromodiphenyl ether or octabromodiphenyl ether in the environment is only a minor source of the lower brominated congeners (e.g. tetra- and pentabromodiphenyl ether). However, such data is only suggestive and not conclusive. It is therefore recommended that an anaerobic degradation experiment is undertaken with either octabromodiphenyl ether or decabromodiphenyl ether under environmentally relevant conditions to further elucidate this matter.

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European Commission

EUR 19730 – European Union Risk Assessment Report
Dinephenyl ether, pentabromo derivative, Volume 5

Editors: B.G. Hansen, S.J. Munn, S. Pakalin, C.J.A. Heidorn, R. Allanou, S. Scheer, G. Pellegrini, S. Vegro, M. Luotamo, J. De Bruijn, F. Berthault, H. Loonen, K. Vormann, A. Naughton, V. Anfossi, L. Praderio

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The report provides the comprehensive risk assessment of the substance Diphenyl ether, pentabromo derivate. It has been prepared by the United Kingdom in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation considers the emissions and the resulting exposure to the environment and the human populations in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined. For human health the scenarios for occupational exposure, consumer exposure and humans exposed via the environment have been examined and the possible risks have been identified.

The human health risk assessment for Diphenyl ether, pentabromo derivate concludes that there is at present concern for workers and no concern for consumers. For humans exposed via the environment and for infants exposed via (breast)milk additional information is needed in order to characterise the risks. The environmental risk assessment for Diphenyl ether, pentabromo derivate concludes that there is at present concern for the aquatic and terrestrial ecosystems, whereas further information is needed in order to characterise the risk micro-organisms in the sewage treatment plant. There is no concern for the atmosphere.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commissions committee on risk reduction strategies set up in support of Council Regulation (EEC) No. 793/93.

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