European Chemicals Bureau

European Union Risk Assessment Report
diphenyl ether, octabromo derivative

CAS: 32536-52-0
EC: 251-087-9
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16

Institute for Health and Consumer Protection

European Chemicals Bureau

Existing Substances

1st **Priority List**

Volume: 16

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RISK ASSESSMENT

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RISK ASSESSMENT

Final Report, 2003

France and United Kingdom

This document has been prepared by the French and UK rapporteurs on behalf of the European Union. The scientific work on the environmental part was prepared by the Building Research Establishment Ltd (BRE), under contract to the UK rapporteur.

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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.
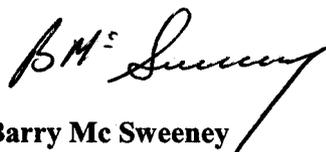
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Director-General
DG Environment

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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 Number: 32536-52-0
EINECS Number: 251-087-9
IUPAC Name   Diphenyl ether, octabromo derivative

Environment

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

This conclusion applies to the risk of secondary poisoning from all sources of octabromodiphenyl ether. It is possible that the current PEC/PNEC approach for secondary poisoning may not be appropriate in terms of both the PEC and the PNEC, and could underestimate the risk. This issue needs further investigation. Two possible areas for further work are as follows:

a)   A more widespread monitoring project to determine whether the finding in top predators (including birds' eggs) is a widespread or localised phenomenon, and trends (if possible).

b)   Further toxicity testing. The existence of a mammalian toxicity data set means that testing could be considered on birds (e.g. an avian reproduction test (OECD 206), with appropriate tissue analysis). Overall, the benefit of further vertebrate testing is open to question due to expected difficulties in achieving sufficiently high exposures. This leaves the toxicity issue with some unresolved uncertainty.

A second aspect of the concern for secondary poisoning is that although the substance is persistent, there is evidence that it can degrade under some conditions to more toxic and bioaccumulative compounds. The current database is inconclusive on this point, and further work could be done as follows:

c)   An investigation of the rate of formation of degradation products under environmentally relevant conditions over a suitably prolonged time period (e.g. years) - for example, an extended monitoring programme to determine trends in degradation product levels in various environmental compartments. This could be coupled with analysis of the parent compound to detect whether it is building up in the environment or has achieved equilibrium. A controlled field study (or studies) might be the way forward, with controlled continuous input of the substance and regular monitoring of other components.

d)   Further toxicological work on the non-diphenyl ether degradation products, to determine if they pose a hazard or risk.

There is a high level of uncertainty associated with the suitability of the current risk assessment approach for secondary poisoning and the debromination issue. The combination of uncertainties raises a concern about the possibility of long-term environmental effects that cannot easily be predicted. It is not possible to say whether or not on a scientific basis there is a current or future risk to the environment. However, given the persistent nature of the substance, it would be of concern if, once the further information had been gathered, the analysis indicated a risk to predators, since it could then be difficult to reduce exposure. In summary, although it is concluded that further information should be gathered in order to refine the risk assessment, in light of:

- the persistence of the substance,
- the time it would take to gather the information and
- the fact that there is no guarantee that the studies would provide unequivocal answers,

consideration should be given at a policy level about the need to investigate risk management options now in the absence of adequate scientific knowledge.

[N.B. A number of technical experts from EU member states consider that this uncertainty is sufficient to warrant risk reduction measures directly (conclusion (iii)) based on the information currently provided in this assessment.]

The possible long-term increase in levels as a result of releases from waste sites might need to be considered further in any future revision of this risk assessment report.

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.

This conclusion applies to the environmental assessment of risks to the aquatic (surface water, sediment and wastewater treatment plants), terrestrial and atmospheric compartments by the conventional PEC/PNEC approach for octabromodiphenyl ether itself from all sources (including the assessment of the hexabromodiphenyl ether component).

Conclusion (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 via the earthworm route for the hexabromodiphenyl ether component in the commercial octabromodiphenyl ether product from the use in polymer applications.

Human health

Human health toxicity

Workers

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

This conclusion is reached since information is needed on transthyretin-T_4 competition with OBDPO as well as information on the extent of excretion of commercial OBDPO into the breast milk and information on the effects of prolonged exposure.

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

This conclusion is reached for manufacture (bagging and cleaning activities) and for compounding and master batching (bag emptying). There are concerns for:

- systemic effects after inhalation and dermal repeated exposure,
- local effects in the respiratory tract after inhalation repeated exposure, and
- effects on female fertility after inhalation and dermal repeated exposure.

Consumers

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.

This conclusion is reached because consumer exposure is considered negligible.

Humans exposed via the environment

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

This conclusion is reached since further information is needed on emissions into the environment from use or on soil-plant transfer; on the extent of excretion of commercial OBDPO into breast milk and cow's milk. Depending upon the results submitted by Industry on milk excretion further information might be requested. There is a need for exposure information from local and regional sources on the concentration of OBDPE in cows' milk. Information is needed as well on transthyretin-T_4 competition with OBDPO and on the effects of prolonged exposure.

<u>Human health (risks from physico-chemical properties)</u>

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.

Results of discussion at the 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 secondary poisoning (section 3.3.4) and infants exposed to octabromodiphenyl ether from human breast or cows' milk (section 4.1.3.). 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 predators or breast-feeding infants. Furthermore, degradation of some of the components of the substance and their bioaccumulative properties could cause concentrations in biota and breast milk to rise while the data were 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 and health risks already identified, a risk reduction strategy for this substance has been developed. This strategy proposes a restriction on the marketing and use of octabromodiphenyl ether under Directive 76/769/EEC. If this strategy is adopted, then the proposed testing requirements listed under the conclusion (i) I n section 3.3.4 and section 4.1.3 should be adjourned in the interests of animal welfare and cost versus 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

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

TABLES

1   GENERAL SUBSTANCE INFORMATION

1.1   IDENTIFICATION OF THE SUBSTANCE

This assessment considers the following commercial flame retardant product:

CAS Number:	32536-52-0
EINECS Number:	251-087-9
IUPAC Name:	Diphenyl ether, octabromo derivative (octabromodiphenyl ether)
Molecular formula:	$C_{12}H_2Br_8O$
Molecular weight:	801.38
Structural formula:	(example component)
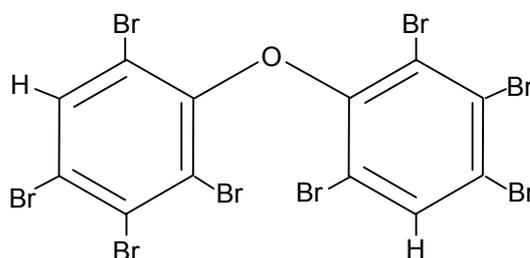
Three polybrominated diphenyl ether flame retardants are available commercially. They are referred to as penta, octa and decabromodiphenyl ether, but each product is a mixture of diphenyl ethers with varying degrees of bromination. Several synonyms and abbreviations for polybrominated diphenyl ethers 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
octabromodiphenyl ether ≡ OBBE ≡ OBBO ≡ OBDPE ≡ OBDPO
decabromodiphenyl ether ≡ DBBE ≡ DBBO ≡ DBDPE ≡ DBDPO

Other synonyms for octabromodiphenyl ether include octabromobiphenyl oxide, octabromodiphenyl oxide, octabromo phenoxybenzene and benzene, 1,1' oxybis-, octabromo derivative. The abbreviation OBDPO is used in the human health assessment.

Recently, a short hand numbering system has started to be used in the literature to identify specific polybrominated diphenyl ethers. The system is analogous to that used commonly for polychlorinated biphenyls. This system is not used in this report as, when the system is used, it is not intuitively obvious how many bromine atoms/molecule are present in a given substance, but Appendix H gives the identities of the common polybrominated diphenyl ether congeners using this system.

1.2   PURITY/IMPURITIES, ADDITIVES

1.2.1   Purity

The actual composition of octabromodiphenyl ether products from the different manufacturers/suppliers is considered to be confidential information. The actual composition specification may vary depending on the manufacturer and so only general ranges of compositions are generally reported. Example compositions of commercial products have been reported and these are shown in **Table 1.1**. These figures are broadly representative of the commercial products currently supplied. Recent physico-chemical and ecotoxicity tests have been carried out on a composite sample of octabromodiphenyl ether from three suppliers to the EU and the composition was determined as 5.5% hexabromodiphenyl ether, 42.3% heptabromodiphenyl ether, 36.1% octabromodiphenyl ether, 13.9% nonabromodiphenyl ether and 2.1% decabromodiphenyl ether. The amount of pentabromodiphenyl ether isomers present in the current octabromodiphenyl ether commercial products is thought to be <0.5%, and it is expected that this will be <0.1% in the near future (the upper limit allowable following on from the EU restrictions on the use of pentabromodiphenyl ether).

There are several components in the commercial product and so any assessment of the commercial product requires an assessment of the individual components. As can be seen from **Table 1.1**, commercial products actually contain a higher proportion of heptabromodiphenyl ether than octabromodiphenyl ether. However, the average number of bromine atoms per molecule in the products is generally around 7.5 and hence the commercial products are known as octabromodiphenyl ethers.

Table 1.1 Typical composition of commercial octabromodiphenyl ether flame retardants

Main components	% by weight			
	up to 1994 [a]	1997 [c]	2000 [d]	2001 [e]
Pentabromodiphenyl ether	10.5-12.0 [b]		1.4-12.0[b]	≤0.5
Hexabromodiphenyl ether		5.5		≤12
Heptabromodiphenyl ether	43.7-44.5	42.3	43.0-58.0	≤45
Octabromodiphenyl ether	31.3-35.3	36.1	26.0-35.0	≤33
Nonabromodiphenyl ether	9.5-11.3	13.9	8.0-14.0	≤10
Decabromodiphenyl ether	0-0.7	2.1	0-3.0	≤0.7

a)   The 1994 data are taken from WHO (1994)
b)   The value is for the total amount of pentabromodiphenyl ether + hexabromodiphenyl ether
c)   The 1997 data are from a composite sample from three suppliers to the EU at that time (Stenzel and Nixon, 1997)
d)   The 2000 data are taken from RPA (2001) and represent the composition reported to the OECD under the Voluntary Industry Commitment
e)   The 2001 data represent the mean composition based on random sampling of selected production lots from August 2000 to August 2001 (Great Lakes Chemical Corporation, 2001a)

Sondack et al. (1994) identified various components of a commercial octabromodiphenyl ether product using HPLC separation combined with NMR identification. The predominant component found was 2,2',3,4,4',5',6-heptabromodiphenyl ether. The product was also found to contain 2,2',4,4',5,5'-hexabromodiphenyl ether, along with all three possible octabromodiphenyl ether isomers and nonabromodiphenyl ether.

Most of the information in this report refers to the commercial products, and hence mixtures of polybrominated diphenyl ethers. Information provided by the three EU producers/suppliers show that the composition and physical properties of their products are similar. While the compositions given in **Table 1.1** are reasonably representative of the currently supplied products, older products or products from other countries, may have different compositions. Further information on the composition of the commercial polybrominated diphenyl ether products is given in Appendix G.

1.2.2   Additives

There were no stated additives incorporated into the commercially available forms of this substance.

1.3   PHYSICO-CHEMICAL PROPERTIES

Commercial octabromodiphenyl ether is a complex mixture and this means that the measurement of some physico-chemical properties is difficult and this difficulty is compounded by the fact that the substance has very low water solubility, vapour pressure and a very high log Kow value. These difficulties mean that there is some inherent uncertainties in the measurements of some of these values. For most applications, the approximate or limit values obtained are sufficient. However, for environmental modelling purposes reliable values are necessary. This Section reviews the available data for commercial octabromodiphenyl ethers, and these data are summarised in **Table 1.2**. Appendix E considers further the possible variability in these data and how they might influence the environmental modelling.

Table 1.2   Physico-chemical properties of octabromodiphenyl ethers

Property	Value
Chemical formula	$C_{12}H_2Br_8O$
Molecular weight	801.38
Melting point	167-257°C, 130-155°C, 70-150°C (the commercial product has a melting range depending on the composition)
Boiling point	Decomposes at elevated temperature
Vapour pressure	$6.59 \cdot 10^{-6}$ Pa at 21°C (commercial product)
Log Kow	6.29 at 25°C
Water solubility	0.5 µg/l (commercial product)
Flammability	not applicable
Autoflammability	not applicable
Explosive properties	none
Oxidising properties	none
Bromine content	79% by weight

1.3.1   Physical state (at ntp)

The commercial substance is an off-white powder or flaked material. Polybrominated diphenyl ether congeners are reported to be crystalline when pure.

1.3.2   Melting point

The melting range has been quoted as 130-155°C (Dead Sea Bromine Group, 1993), 70-150°C (Albemarle, 1997) and 167-257°C (Ethyl Corporation, 1992). Clearly the substance has a variable melting range reflecting the nature of the material and the individual manufacturing processes.

1.3.3   Boiling point

The substance does not have a boiling point. Bromine is lost as the temperature increases (i.e. the substance decomposes), with an approximate 2% loss at 330°C and 40% loss at 395°C (Dead Sea bromine Group, 1993). This is in keeping with the use of the material as a flame retardant.

1.3.4   Relative density

A specific gravity of 2.9 has been quoted (Dead Sea Bromine Group, 1993).

1.3.5   Vapour pressure

The vapour pressure of the substance has been measured as $6.59 \cdot 10^{-6}$ Pa at 21°C using a spinning rotor gauge in a study carried out according to the principles of Good Laboratory Practice (GLP). The material tested was a composite sample from three manufacturers and had the following composition: 5.5% hexabromodiphenyl ether; 42.3% heptabromodiphenyl ether; 36.1% octabromodiphenyl ether; 13.9% nonabromodiphenyl ether and 2.1% decabromodiphenyl ether. The method used was not able to separate the contributions of the individual components to the total vapour pressure and so the result 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 octabromodiphenyl ether (Stenzel and Nixon, 1997).

Watanabe and Tatsukawa (1990) determined the vapour pressures for a range of brominated diphenyl ethers at 25°C using a gas chromatographic (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 octabromodiphenyl ether, a vapour pressure of $1.2 \cdot 10^{-7}$-$2.3 \cdot 10^{-7}$ Pa was determined. The vapour pressure was found to increase as the degree of bromination decreased (see Section 3.1.1.5.1).

Wong et al. (2001) recently determined the vapour pressure of 2,3,3',4,4',5,6-heptabromodiphenyl ether (a possible component of commercial octabromodiphenyl ether) at 25°C using a GC technique. Here a GC-determined vapour pressure of $5.7 \cdot 10^{-7}$ Pa and a sub-cooled liquid vapour pressure of $9.05 \cdot 10^{-7}$ Pa was determined. These values are reasonably consistent with the values reported by Watanabe and Tatsukawa (1990). In addition, Wong et al. (2001) reported that for brominated

diphenyl ethers as a whole, each additional Br substituent caused the vapour pressure to decrease by a factor of six to nine, and that within a homologue group the vapour pressure increased by approximately 0.2 log units for each addition of a Br substituent to one of the 2,2',6, or 6' positions of the molecule (i.e. positions ortho- to the ether link).

Tomy et al. (2001) have also determined values for the sub-cooled liquid vapour pressures for two heptabromodiphenyl ethers using a GC method. The values determined were $2.3 \cdot 10^{-7}$ Pa for the 2,3,3',4,4',5,6 isomer and $6.2 \cdot 10^{-6}$ Pa for the 2,2',3,4,4',5',6-isomer.

A value of $6.59 \cdot 10^{-6}$ Pa obtained for the commercial octabromodiphenyl ether product will be used for the vapour pressure in the environmental assessment.

1.3.6   Solubility

The water solubility has been measured to be around 0.5 µg/l at 25°C using a generator column method in a GLP study (Stenzel and Markley, 1997). In the study, a composite sample of octabromodiphenyl ether from three producers was used (composition was 5.5% hexabromodiphenyl ether, 42.3% heptabromodiphenyl ether, 36.1% octabromodiphenyl ether, 13.9% nonabromodiphenyl ether and 2.1% decabromodiphenyl ether). In the test, the commercial octabromodiphenyl ether (350 mg) was dissolved in ethylacetate and added to a round bottomed flask containing 69 g of glass beads. The solvent was removed on a rotary evaporator at $43-44^{\circ}$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 pumped through the column at 0.5 ml/minute and the effluent was collected (~50 ml samples). After collection of 94 consecutive 50 ml samples 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 commercial octabromodiphenyl ether gave several groups of peaks, with the major groups corresponding to the hepta-, octa- and nonabromodiphenyl ether components. Calibration of the method was carried out by using standard solutions of the commercial octabromodiphenyl ether prepared in diphenyl ether, with the sum of the peak areas of the hepta-, octa- and nonabromodiphenyl ether being used for quantification.

Such a calibration/quantification 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 fractions (of the total peak area) for the peak areas of the main components to be derived: low-level calibration standard hepta:octa:nona 0.56:0.29:0.14; high-level calibration standard hepta:octa:nona 0.53:0.29:0.17;   5 µg/l matrix fortification (substance added in dimethylformamide solvent) hepta:octa:nona 0.54:0.31:0.15; 1 µg/l matrix fortification (substance added in dimethylformamide solvent) hepta:octa:nona 0.54:0.29:0.17; reagent fortification (substance added in dimethylformamide solvent) hepta:octa:nona 0.54:0.31:0.14; effluent water solution hepta:octa:nona 0.59:0.28:0.13. Given that the relative contribution of each peak to the total peak area used for quantification is very similar in the standards and test solution, the measured levels should accurately reflect the concentration of octabromodiphenyl ether on the commercial formulation basis. However, commercial octabromodiphenyl ether contains some components (e.g. hexabromodiphenyl ether) that would be expected to be slightly more water soluble than the higher brominated components and the method used does not allow this to be determined as the hexabromodiphenyl ether peak was not monitored.

Tomy et al. (2001) have recently reported a water solubility of 1.98 µg/l at 25°C for 2,2',3,4,4',5',6-heptabromodiphenyl ether (a possible component of decabromodiphenyl ether) using a generator column method.

A value of 0.5 µg/l will be used in the environmental risk assessment.

1.3.7   Partition coefficient

The octanol-water partition coefficient of commercial octabromodiphenyl ether has been determined as log Kow = 6.29 at 25°C using a generator column method (MacGregor and Nixon, 1997). The study was carried out to GLP and the octabromodiphenyl ether tested was a composite sample from three suppliers and had the following composition: 2.1% decabromodiphenyl ether; 13.9% nonabromodiphenyl ether; 36.1% octabromodiphenyl ether; 42.3% heptabromodiphenyl ether; 5.5% hexabromodiphenyl ether. A stock solution of the test substance was prepared by dissolving 25 mg in 25 g of octanol followed by centrifuging and filtering to remove any undissolved test material (the actual concentration of test substance in the octanol was determined by analysis). The octanol solution (15 ml) of the test substance was then added to a generator column containing an inert support material. Water that had previously been saturated with octanol was pumped through the column overnight at 0.5 ml/minute to equilibrate the system, then the flow rate was increased to 1.0 ml/minute and three consecutive 4-hour samples (volume ~255-260 ml) were collected and analysed for the presence of the test substance.

The analytical method used was GC-ECD. Calibration of the method was by standard solutions of the commercial octabromodiphenyl ether mixture made up in diphenyl ether solvent. The sum of the peak areas corresponding to the hepta-, octa- and nonabromodiphenyl ether components (several components for both hepta- and octabromodiphenyl ether were detected) were used for quantification. Such a calibration/quantification method requires the composition of the test substance in the water phase 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 areas for the hepta-, octa- and nonabromodiphenyl ether components: low level calibration standard hepta:octa:nona 0.58:0.33:0.09; high level calibration standard hepta:octa:nona 0.47:0.36:0.16; 0.2 µg/l matrix fortification standard hepta:octa:nona 0.43:0.40:0.16; 5.0 µg/l matrix fortification standard hepta:octa:nona 0.48:0.34:0.18; test aqueous solution from generator column hepta:octa:nona 0.42:0.39:0.18; octanol stock solution hepta:octa:nona 0.43:0.37:0.19. From these ratios it can be seen that the relative concentrations of the three main components used for quantification are approximately the same in all the media tested and so indicate that the concentrations obtained reflect those of the commercial product. However, it would be expected that the log Kow would increase with increasing bromination and thus the relative concentration of the three components in the water phase would be expected to differ from that in the octanol phase. The fact that this does not appear to occur may indicate that the substance detected in the aqueous phase could have been associated with dissolved octanol, which may increase the apparent solubility and hence lead to an underestimate of the octanol water partition coefficient.

Using this method the average concentrations measured in the water and octanol phase were 0.307 µg/l and 0.597 g/l respectively, giving a Kow value of $1.95 \cdot 10^{6}$.

Other values of log Kow for octabromodiphenyl ether of 8.35-8.90 (Watanabe and Tatsukawa, 1990) using a HPLC Technique have been derived. Tomy et al. (2001) reported a log Kow value

of 7.14 for 2,2',3,4,4',5',6-heptabromodiphenyl ether (a possible component of commercial octabromodiphenyl ether) using a slow stirring method at 25°C.

A log Kow value of 6.29 will be used in the environmental risk assessment as it has been carried out to GLP and the full test details are available. This value probably represents a minimum value for the octanol water partition coefficient. The effects of any uncertainties in this value in terms of environmental modelling are discussed further in Appendix E.

1.3.8 Flash point

Due to the nature of the substance (flame retardant), this parameter is not relevant. The substance does not have a flash point.

1.3.9 Autoignition

The substance does not undergo autoignition, but decomposes gradually at elevated temperatures. The decomposition properties are in line with the use of this material as a flame retardant.

1.3.10 Explosivity

Not applicable on the basis of its structure and physical properties, nor is it known to contribute 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. Commercial octabromodiphenyl ether does not contain any substance with structural alerts for oxidising effects. Octabromodiphenyl ether is not considered therefore to be an oxidiser.

1.4 CLASSIFICATION

The classification and labelling of diphenylether, octabromo derivative has been agreed at technical levels to be listed in Annex I to Directive 67/548/EEC following the adoption of the 29th Adaptation to Technical Progress, as follows:

Classification :   Repr. Cat. 2 R61   May cause harm to unborn child
                      Repr. Cat. 3 R62   Possible risk of impaired fertility

Labelling :   T R61-62
                      S 53-45

Specific concentrations limits: None

No classification is currently proposed for environmental effects.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

2.1.1 Production volumes

There were two reported producers of octabromodiphenyl ethers in the EU given in IUCLID in 1994. However, both companies have now stopped production within the EU (1996/1998) and all octabromodiphenyl ether used within the EU is now imported.

Further information on 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 in the early 1990s there were eight producers of polybrominated diphenyl ethers (penta-, octa- or deca-) in the world (although industry indicated that there were nine producers world-wide), with one in the Netherlands, one in France, two in the United States, three in Japan and one in the United Kingdom. The same total number of manufacturers was reported by KEMI (1994), but production was also reported to occur in Israel as well. According to the latest information, none of the EU sites currently manufactures octabromodiphenyl ether.

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/year (i.e. 75%) of decabromodiphenyl ether, 6,000 tonnes/year (i.e. 15%) of octabromodiphenyl ether and 4,000 tonnes/year (i.e. 10%) of pentabromodiphenyl ether (KEMI, 1994).

Arias (2001) reported that worldwide demand for octabromodiphenyl ether was 3,825 tonnes/year in 1999.

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 figures for total polybrominated diphenyl ethers in the EU (WHO, 1994)

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

Since it is known that decabromodiphenyl ether is not produced in the EU in large quantities (see the assessment on that substance (EC, 2002), then the figures in **Table 2.1** probably refer to the combined production of penta- and octabromodiphenyl ether in the EU at that time. As a worst-case approach, it will be assumed that the figures in **Table 2.1** refer solely to octabromodiphenyl ether production and so a total EU production of around 4,000 tonnes/year can be assumed at that time. Octabromodiphenyl ether is not currently produced in the EU.

2.1.2   Production methods

This information is included for completeness. The polybrominated diphenyl ethers are produced by direct bromination of diphenyl ether using a Friedel-Crafts catalyst. Two processes were used in the EU. In both processes, bromine was slowly added to diphenyl ether (either neat or dissolved in a solvent) and the temperature was allowed to rise to around 85-135°C, depending on the process used. Once the reaction was complete, residual bromine and hydrogen bromide were removed. A solution of the crude product was then filtered and the purified product was formed either by distilling off the impurities and solvent or by crystallisation. The solid product was then ground and bagged.

2.2   USES

2.2.1   Quantities used

According to the IUCLID data, octabromodiphenyl ether was imported into the EU by two companies (around 1994). As production of octabromodiphenyl ether has now ceased, all of the substance used in the EU is now imported.

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 is decabromodiphenyl ether.

Table 2.2   Import figures for total polybrominated diphenyl ethers into the EU   (WHO, 1994)

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 ether flame retardants was 10,946 tonnes/year in 1989 (WHO, 1994). An industry source (personal communication) gave a very similar figure for current (around 1996) EU usage of total polybrominated diphenyl ethers as 10,000-11,000 tonnes/year. Assuming that octabromodiphenyl ether accounts for 15% of the total EU usage of brominated diphenyl ether flame retardants, it can be estimated that up to 1,650 tonnes/year of octabromodiphenyl ether are used in the EU. This figure is slightly lower than the production/import data reported in IUCLID, although it does indicate that the EU usage figure in the mid 1990s was likely to be towards the lower end of the range given in IUCLID in 1994. A figure of 2,550 tonnes/year of octabromodiphenyl ether will be used as the EU usage figure in this assessment as an estimate of the maximum amount that has been used in the recent past. This figure is based on information reported in IUCLID in 1994.

A more recent estimate from industry (personal communication) indicates that the 1999 market demand for octabromodiphenyl ether in Europe was 450 tonnes/year, with the 1999 market demand for decabromodiphenyl ether and pentabromodiphenyl ether being 7,500 tonnes/year and 210 tonnes/year respectively.

In addition, it is possible that octabromodiphenyl ether will be imported into or exported from the EU as a component of finished articles or masterbatch (polymer pellets containing additives). Reliable figures for likely quantities involved are not available. Manufacturers estimate that a figure of around 1,350 tonnes/year is realistic for the imports of octabromodiphenyl ether into the EU in finished articles or masterbatch in 1999 (this figure then means that around 33% of the global amount of octabromodiphenyl ether produced enters the EU either as octabromodiphenyl ether itself or in finished or semi-finished articles).

The risk assessment will be based on a EU usage of 2,550 tonnes/year as estimated above. This figure overestimates the current usage of octabromodiphenyl ether in the EU, which is known to have fallen since this time, but, as such, will also account to some extent for the (unquantifiable) amount of octabromodiphenyl ether being imported into (or exported from) the EU in finished articles or masterbatch, and will also take into account any possible future increase in the usage from current levels. However, the available data for the 1999 consumption (i.e. 450 tonnes/year of octabromodiphenyl ether itself and 1,350 tonnes/year of octabromodiphenyl ether in finished or semi-finished articles) will also be considered in the risk assessment, to take into account the recent fall in consumption.

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 retardant

As can be seen from the **Table 2.3**, up to 5,000 tonnes/year of polybrominated diphenyl ethers are used in any one EU country. Assuming that this use is made up of 15% octabromodiphenyl ether, then a usage figure for a EU country can be estimated at 750 tonnes/year octabromodiphenyl ether. This figure is consistent with data reported for the individual countries below, and will be taken as being representative of reasonable worst-case usage figure for an EU country based on past usage figures. The available information indicates that current usage of octabromodiphenyl ether may be lower than this figure.

Klingenberg (1990) reported consumption figures for octabromodiphenyl ether in the Netherlands as 600-800 tonnes/year.

Watanabe and Tatsukawa (1990) reported that around 1,000 tonnes of octabromodiphenyl ether were used in Japan in 1987.

2.2.2 Uses

The polybrominated diphenyl ethers in general are used as flame retardants. They are mostly used in applications in the plastics and textile industries (decabromodiphenyl ether only). As is common with brominated flame retardants in general, a synergist is also added (frequently antimony trioxide) to increase the overall effectiveness of the flame retardant treatment.

Polybrominated diphenyl ethers are flame retardants of the additive type, i.e. they are 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.

The amount of flame retardant used in any given application depends on a number of factors such as the flame retardancy required of the finished product, the effectiveness of the flame retardant and synergist within a given polymer, the physical properties 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 (WHO, 1994).

Further information provided by industry indicates that octabromodiphenyl ether is always used in conjunction with antimony trioxide. In Europe, it is primarily used in acrylonitrile-butadiene-styrene (ABS) polymers at 12-18% weight loadings in the final product. Around 95% of the total octabromodiphenyl ether supplied in the EU is used in ABS. Other minor uses, accounting for the remaining 5% use, include high impact polystyrene (HIPS), polybutylene terephthalate (PBT) and polyamide polymers, at typical loadings of 12-15% weight in the final product. In some applications, the flame retardant is compounded with the polymer to produce pellets (masterbatch) with slightly higher loadings of flame retardant. These are then used in the polymer processing step to produce products with similar loadings as given above. The flame retarded polymer products are typically used for the housings of office equipment and business machines.

Other uses that have been reported for octabromodiphenyl ether include nylon and low density polyethylene (WHO, 1994), polycarbonate, phenol-formaldehyde resins and unsaturated polyesters (OECD, 1994) and in adhesives and coatings (WHO, 1994).

For the purposes of this assessment, it will be assumed that all of the octabromodiphenyl ether used in any one country is in polymer applications (e.g. ABS). It would be expected that the releases from use in other polymers will be similar to those estimated later for use in ABS.

2.3 SUMMARY OF WORST-CASE PRODUCTION AND USAGE FIGURES FOR USE IN THE RISK ASSESSMENT

The following figures are derived for octabromodiphenyl ether from Sections 2.1 and 2.2 and will be used later in this assessment as the basis of the PEC calculations. As explained earlier, two sets of figures are considered, one reflecting the situation around 1994 and one reflecting the situation in 1999. In this way, both the recent reduction in the use of octabromodiphenyl ether and any future increase up to previous usage levels can be taken into account.

	1994 situation	**1999 situation**
Usage in any one EU country	750 tonnes/year	
Usage within EU	2,550 tonnes/year	450 tonnes/year (with a total of 1,350 tonnes/year present in finished articles)
Usage in "Region"	255 tonnes/year	45 tonnes/year (with a total of 135 tonnes/year present in finished articles
Main use	ABS and other polymers (Industry Category 11, Use Category 22)	ABS and other polymers (Industry Category 11, Use Category 22)

{Note the "Region" is as defined in the Technical Guidance Document (TGD) and it is assumed that 10% of the total amount in the EU is used in this area.}

2.4   BREAKDOWN/TRANSFORMATION PRODUCTS

There is a large body of literature that shows that, under certain combustion/pyrolysis conditions, octabromodiphenyl ether, and polybrominated diphenyl ethers in general can form brominated dibenzofurans and brominated dibenzo-*p*-dioxins. This is discussed in detail for all the commercial polybrominated diphenyl ethers in Appendix A. 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). Virtually complete destruction of octabromodiphenyl ether and any possible breakdown products appears to occur at temperatures of 800°C and above for 2 seconds.

Of possible environmental concern is the release of brominated dibenzofurans (and to a lesser extent brominated dibenzo-*p*-dioxins) from incineration of plastics containing octabromodiphenyl ether and during accidental fires involving articles containing octabromodiphenyl ether.

In the case of accidental fires, given the large amounts of toxic products known to be formed, notably chlorinated dibenzo-*p*-dioxins and dibenzofurans, but also non-halogenated products such as polycyclic aromatic compounds, the presence of octabromodiphenyl ether is unlikely to significantly affect the total release of toxic products from fires as, in most cases, octabromodiphenyl ether will only constitute a small proportion of the total halogenated material present in a fire.

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

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°C and 2 seconds. New general waste incinerators should meet 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 the brominated analogues.

Other disposal/recycling practices for articles containing octabromodiphenyl ether involving elevated temperatures may have the potential to release polybrominated dibenzofurans and dibenzo-*p*-dioxins to the environment, and these are considered further for polybrominated diphenyl ethers as a group in Appendix A.

A discussion of the breakdown/transformation products formed during production of octabromodiphenyl ether and processing of polymers containing octabromodiphenyl ether is given in Appendix D.

2.5 CONTROL MEASURES

A Proposal for a draft Directive on Waste Electrical and Electronic Equipment (WEEE Directive) was adopted on 13 June 2000 by the European Commission. The Proposal contains the following elements:

Member States shall set up separate collection schemes and ensure the proper treatment, recovery and disposal of WEEE;

The treatment, recovery and disposal of WEEE shall be financed by producers to create economic incentives to adapt the design of electrical and electronic equipment to the prerequisites of sound waste management;

Consumers shall have the possibility to return their equipment free of charge. They need to be informed about the possibilities to return WEEE.

The Commission's proposal encourages producer responsibility for waste management, separate collection of WEEE, improved treatment and reuse/recycling, and improved dissemination to users. In implementing the proposed Directive, producers would be required to set up systems to treat WEEE which would include, amongst other things, removal of plastic containing brominated flame retardants from separately collected WEEE (RPA, 2001).

In parallel a separate Directive has been proposed on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive). According to this Directive, manufacturers will be required to substitute certain brominated flame retardants, including polybrominated diphenyl ethers, in new electrical and electronic equipment in order to

prevent problems during the waste management phase. Octabromodiphenyl ether is currently included in this Proposal.

The WEEE/RoHS Proposals have been transmitted to the European Parliament, Council and other Community institutions and is currently under discussion. The Parliament adopted its first reading on 15 May 2001. A Political Agreement in view of a Common Position was adopted by the Council on 7 June 2001. The second reading is likely to start at the European Parliament before the end of 2001. It is currently proposed that the measures will come into effect in January 2007 (RPA, 2001).

Depending on how the RoHS Directive is finally implemented, it may require that octabromodiphenyl ether is no longer used in electrical and electronic equipment. The proposals for WEEE also have some indirect implications for the use of octabromodiphenyl ether in electrical and electronic equipment.

3 ENVIRONMENT

3.1 EXPOSURE ASSESSMENT

3.1.1 General discussion

It should be noted in the following sections that the estimated releases refer to the commercial octabromodiphenyl ether product. As was shown in Section 1, the commercial products are mixtures of congeners, of which octabromodiphenyl ether isomers make up approximately 31-36%. Appendix E considers the environmental release of the individual components of the commercial octabromodiphenyl ether in more detail.

3.1.1.1 Emissions from production

Production of octabromodiphenyl ether in the EU has recently stopped. Previously (up to 1996/1998) there were two production plants operating within the EU. An example calculation is shown below for a 1,000 tonnes/year production plant. This calculation is for information only.

No information was provided in IUCLID on the release of octabromodiphenyl ether to the environment from production. Proposals for emission factors from production are given in Appendix I of the Technical Guidance Document. For substances in Industry Category 2 (Chemicals Industry: Basic Chemicals) and Main Category 1C (substances produced in dedicated equipment) the following emission fractions are obtained (Table A1.1 of Appendix I): release fraction to air = 0 (vapour pressure <1 Pa); release fraction to wastewater = 0.003 (i.e. 3 kg/tonne). Releases are thought to occur over 100 days (Table B1.1 of Appendix I of the Technical Guidance).

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 diphenyls. The estimated releases of octabromodiphenyl ether vapour to air from the reactor vessel are thought to be very low, typically $1.8 \cdot 10^{-3}$ mg/tonne. The major sources of air emissions are thought to be as a result of grinding and bagging operations. The estimated emission factor for solid polybrominated diphenyl ethers was <70 g/tonne (i.e. <0.007%) (EEC, 1993). Thus the emission to air of octabromodiphenyl ether vapour from production can be considered to be negligible.

The most likely way in which octabromodiphenyl ether may reach water from its production is due to washing out of equipment. It is not clear how often this process is generally carried out or if it is carried out at all. EEC (1993) estimated that the emission of polybrominated diphenyl ether from washing out the reactor after every batch would be unlikely to exceed 0.5 kg/tonne (i.e. 0.05%). This figure does not appear, however, to include possible releases to wastewater from washing down floors etc. of bagging areas and other areas where octabromodiphenyl ether dust can be generated.

Some limited information has been provided from discussions with industry on losses from a former production site in the EU. It was estimated that around 12.0 kg octabromodiphenyl ether/tonne produced is disposed of to landfill. The major source of this waste is from filter waste and reject material. It is also thought that some material may enter the on-site effluent

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treatment system as a result of washing down floors etc., but it was not possible to put a figure on this release. Information reported in EEC (1993) indicates that around 100 kg solid waste/tonne product was generated at another former octabromodiphenyl ether production plant in the EU. This figure refers to total solids from the production process, of which brominated congeners are thought to make up a fraction. The solid waste was again disposed of to landfill.

Using the worst-case emission factor from the Technical Guidance Document of 3 kg/tonne to wastewater, the predicted loss from a 1,000 tonnes/year production site would be 3 tonnes/year to wastewater. Similarly, if the lower emission factor of 0.5 kg/tonne is used, the release to wastewater would be around 0.5 tonnes/year.

3.1.1.2   Emissions from use in polymer applications

There are various stages in polymer processing such as compounding (blending of the polymers with various additives) and conversion (production of the finished articles). The different processes are not necessarily carried out on the same site (i.e. there are firms that specialise in compounding or produce masterbatches (compounds that contain high concentrations of additives which are subsequently mixed into the main polymer matrix)). As a realistic worst-case estimate of the emissions at a local scale it will be assumed that compounding and conversion are carried out at the same site.

The Use Category Document on plastic additives (UCD, 1994) gives release factors for flame retardants for the various processes involved in the production of the plastic. These are used in the following Sections for ABS, assuming an octabromodiphenyl ether consumption of 255 tonnes/year in a region and 2,550 tonnes/year in the EU as a whole. These figures were estimated for 1994 and are higher than the current EU usage figure for octabromodiphenyl ether but do make some allowance in the regional/continental assessment for imported compound or finished articles containing octabromodiphenyl ether. Figures are also available for the consumption of octabromodiphenyl ether in 1999 (45 tonnes/year in a region and 450 tonnes/year in the EU as a whole for octabromodiphenyl ether itself, with an estimated 1,350 tonnes/year of octabromodiphenyl ether present in finished goods in the EU) and these figures will also be considered in the emission estimation.

Although the example is for use in ABS, it should be noted that the actual release estimates are independent of the type of plastic; they just depend on the type of system involved (e.g. closed or open), and the total amount of flame retardant used. From the Use Category Document on plastic additives, around 75,000 tonnes/year of ABS are processed in the United Kingdom. Of this 92% (69,000 tonnes/year) is processed in closed systems and around 40% of this (27,600 tonnes/year) is used to make brown goods (e.g. TVs, videos etc.) which may contain up to around 20% by weight of flame retardant. The remaining 8% of ABS is processed in open systems to make mainly white goods which are generally not thought to contain flame retardants. Therefore, the major applications for octabromodiphenyl ether are carried out in closed systems, as defined in the Use Category Document.

Much of the loss from polymer applications is likely to be in the form of dust. Thus much of this will be collected for re-use or disposed of to landfill/incineration. However, some of this may end up in wastewater as a result of cleaning floors and equipment etc.

3.1.1.2.1   Release during handling of raw material

Losses of powders during the handling of raw materials have been estimated as 0.21% for powders of particle size >40 µm. These losses will initially be to the atmosphere, but it is expected that the dust will rapidly settle and so losses will be mainly to solid waste, which may be recycled or disposed of, or washed to wastewater.

The release figure of 0.21% is made up three components. Firstly, it is assumed that the substance is handled in sacks or bags and some losses due to wear and tear occur. This loss has been estimated as 0.1%, independent of particle size. Secondly, it is assumed that there are problems of flow due to the presence of attractive forces between the individual particles. The origin of these forces could be mechanical interlocking, interfacial and capillary forces between adsorbed layers etc., and for very fine particles, van der Waals forces can be significant. It has been shown that such attractive forces could become significant for particles associated with adsorbed water when diameters are less than 50 µm, and for dry particles which are about two orders of magnitude smaller. Practical experience has shown that agglomeration effects are significant for particles of diameter <40 µm and such particles will not empty cleanly from a bag. For particles >40 µm diameter, retention in the bag is not significant and losses are expected to be at minimal levels e.g. 0.01% (UCD, 1994). The third source of release during handling is from dust generation. This is estimated to be around 0.1% for substances with particle sizes >40 µm (UCD, 1994).

For octabromodiphenyl ether the losses from handling of the raw material will be 0.54 tonnes/year in a region and 5.4 tonnes/year in the EU based on the 1994 consumption data or 0.0945 tonnes/year in a region and 0.945 tonnes/year in the EU based on the 1999 consumption data. It would be expected that much of this is either recycled or disposed of by a suitable method (e.g. landfill). It is possible that a small amount may enter wastewater streams as a result of cleaning down plants etc. It is assumed that such releases to wastewater will be accounted for in the emission factors that are used in the next Section.

3.1.1.2.2   Release from compounding and conversion

The compounding stage is also susceptible to dust generation but losses are thought to be lower than during the previous handling stage. Losses mainly occur early in the mixing cycle and localised containment may be used to recover the material for recycle. It is thought that losses at this stage are at least an order of magnitude lower than during the original handling stage above, and for a worst-case scenario may be of the order of 0.01% for >40 µm particles. Release will again be initially to the atmosphere but the particles would be expected to settle and so losses might ultimately be to solid waste or wastewater. In addition, as well as particulate losses, there will be an extra 0.01% loss due to the volatility of the flame retardant (giving a total loss of 0.02%) (UCD, 1994).

Release during conversion is estimated as 0.01% or less when a closed system is used. Initially, losses will be to the atmosphere due to the compound's volatility. The losses from closed systems are thought to be small (UCD, 1994).

For octabromodiphenyl ether the losses from compounding are estimated to be 0.051 tonnes/year (0.0255 tonnes/year as dust and 0.0255 tonnes/year as vapour) in a region and 0.51 tonnes/year (0.255 tonnes year as dust and 0.255 tonnes/year as vapour) in the EU based on the 1994 consumption data. The equivalent estimates based on the 1999 consumption data would be

0.009 tonnes/year (0.0045 tonnes/year as dust and 0.0045 tonnes/year as vapour) in a region and 0.090 tonnes/year (0.045 tonnes/year as dust and 0.045 tonnes/year as vapour) in the EU.

In addition, the estimated release during conversion will be around 0.0255 tonnes/year (as vapour) in a region and 0.255 tonnes/year (as vapour) in the EU based on the 1994 consumption data and 0.0045 tonnes/year (as vapour) in a region and 0.045 tonnes/year (as vapour) in the EU based on the 1999 consumption data. Thus the total release of vapour to air during compounding and conversion is 0.051 tonnes/year in a region and 0.51 tonnes/year in the EU as a whole based on the 1994 data and 0.009 tonnes/year in a region and 0.090 tonnes/year in the EU as a whole based on the 1999 data.

Table A3.11 of Appendix I of the Technical Guidance Document also gives estimates for the release of additives such as flame retardants during processing of thermoplastic polymers. For octabromodiphenyl ether the release fractions (based on a vapour pressure of <1 Pa and a boiling point of >300°C) are: release fraction to air = 0.0005 (i.e. 0.5 kg/tonne); release fraction to wastewater = 0.0005 (i.e. 0.5 kg/tonne). Assuming usage figures of 255 tonnes/year of octabromodiphenyl ether in a region and 2,550 tonnes/year in the EU as a whole (1994 consumption data), the estimated releases of octabromodiphenyl ether are 0.128 tonnes/year to air and 0.128 tonnes/year to wastewater in a region and 1.28 tonnes/year to air and 1.28 tonnes/year to wastewater in the EU as a whole. Similarly using the 1999 consumption data of 45 tonnes/year in a region and 450 tonnes/year in the EU as a whole, the equivalent emission estimates are 0.0225 tonnes/year to air and 0.0225 tonnes/year to wastewater in a region and 0.225 tonnes/year to air and 0.225 tonnes/year to wastewater in the EU as a whole.

Taken as a whole, the emissions estimated using the Technical Guidance Document are slightly higher than those estimated using the Use Category Document. However, for the worst-case assessment these higher release figures will be used for the assessment of the release to wastewater, as there is the possibility of the dust releases estimated using the Use Category Document entering wastewater due to washing down of equipment/floors, etc., and if that is the case, the two sources of estimates are in fact similar. Thus releases to wastewater are taken as 0.128 tonnes/year in a region and 1.28 tonnes/year in the EU based on the 1994 consumption data, and 0.0225 tonnes/year in a region and 0.225 tonnes/year in the EU based on the 1999 consumption data. The estimated releases to air will be taken as 0.128 tonnes/year in a region and 1.28 tonnes/year in the EU based on the 1994 consumption data, and 0.0225 tonnes/year in a region and 0.225 tonnes/year in the EU based on the 1999 consumption data.

3.1.1.2.3   Releases at a polymer processing site

In order to estimate a PEC for a polymer processing site, knowledge is needed of the size distribution of processing plants in the country. As a worst-case approach, it could be assumed that all the octabromodiphenyl ether used in a region is on one site. However, for octabromodiphenyl ether, given the wide range of finished articles that are thought to contain it, this assumption may not be correct.

According to the Use Category Document on Plastic Additives (UCD, 1994), processing of ABS containing flame retardants is carried out in closed systems only. It is thought that around 2,410 companies use closed processing systems in the United Kingdom.

From the Use Category Document, the largest estimated usage per site is obtained for a large site with between 501 and 1,000 employees, and a typical site would process around 0.62% of the total plastic processed in closed systems in the United Kingdom. The amount of ABS processed

in closed systems in the United Kingdom is 69,000 tonnes/year, thus the amount processed at a large site is 428 tonnes/year. If it is assumed that octabromodiphenyl ether is used in all this plastic at 15% concentration, the amount of octabromodiphenyl ether used at a site would be around 64 tonnes/year. This is in reasonable agreement with information obtained from a United Kingdom plastic pellets manufacturer, who is thought to use around 11-22 tonnes/year of octabromodiphenyl ether.

Appendix I of the Technical Guidance Document also gives estimates of the likely amount of substance used at a given site. From Table B3.9 of that Appendix, for a substance used in amounts of 255 tonnes/year in a region (1994 consumption data) at a concentration of 15% in the final polymer (i.e. tonnage of polymer containing octabromodiphenyl ether = 1,700 tonnes/year), it suggests that 15% of the total regional use (i.e. 38.25 tonnes/year of octabromodiphenyl ether) is used on any one site over 102 days. Similarly, using the 1999 consumption data of 45 tonnes/year in a region at a concentration of 15% in the final polymer, Table B3.9 of Appendix I of the Technical Guidance indicates that 25% of the total regional use (i.e. 11.3 tonnes/year of octabromodiphenyl ether) is used on any one site over 30 days. These figures are very similar to that obtained from a plastic pellets manufacturer, and so will be used for the local assessment.

Using the emission factors discussed in Sections 3.1.1.2.1 and 3.1.1.2.2, the following emission estimates can be obtained for a worst-case polymer processing site using octabromodiphenyl ether:

	1994 data	1999 data
No. of days of operation	102	30
Amount of octabromodiphenyl ether used	38.25 tonnes/year	11.3 tonnes/year
Quantity released as dust (handling of raw materials)	80.3 kg/year (to landfill)	23.7 kg/year (to landfill)
Quantity released to air (compounding/conversion)	19.1 kg/year	5.65 kg/year
Quantity released to wastewater (compounding/conversion)	19.1 kg/year	5.65 kg/year

These figures will be used later in the estimation of the PEC$_{local}$s.

3.1.1.2.4 Losses during service life of product

Volatilisation

The losses due to volatilisation of the additive from plastic over the lifetime of a product can be estimated from the following equation (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°C)
       N = service life of product (for brown goods N = 5-10 years)

For octabromodiphenyl ether the vapour pressure has been determined as $6.59 \cdot 10^{-6}$ Pa ($4.9 \cdot 10^{-8}$ mmHg) at 21°C (see Section 1.3.5). Using this value, the loss during the service life of a product (assuming a life of 10 years) will be 0.54% over 10 years. This corresponds to a loss of 0.138 tonnes/year in a region and 1.38 tonnes/year in the EU, based on the 1994 EU consumption figure of 2,550 tonnes/year. These figures overestimate the current EU usage of

octabromodiphenyl ether but, as a result, will also account to some extent for the (unquantifiable) amount of octabromodiphenyl ether that may be imported into (or exported from) the EU in finished articles or masterbatch. The losses will initially enter the atmosphere. It should be born in mind that since the products may be used over a 10 year lifetime or longer, and that each year new products containing octabromodiphenyl ether are likely to enter into use during this time, the actual amount of octabromodiphenyl ether present in plastic products, and hence potentially released, could be around 10 times the amount estimated above (i.e. the estimated releases would be 1.38 tonnes/year in a region and 13.8 tonnes/year in the EU as a whole).

The available information for 1999 indicates that the amount of octabromodiphenyl ether present in finished articles in the EU could be around 1,350 tonnes/year (the estimate includes both articles manufactured in the EU and imported articles containing octabromodiphenyl ether). Using a similar approach to above, the estimated emissions of octabromodiphenyl ether from volatilisation over the lifetime of the products would be 0.729 tonnes/year in a region and 7.29 tonnes/year in the EU.

Leaching

Given that the major use of plastics containing octabromodiphenyl ether appears to be in electrical applications and that the substance has a very low water solubility, the potential for leaching of octabromodiphenyl ether from the products during use appears to be small.

 "Waste remaining in the environment"

 "Waste remaining in the environment" can be considered to be particles (or dust) of polymer product, or dust generated from polymer products, that contains octabromodiphenyl ether. These particles are primarily released to the urban/industrial soil compartment, but may also end up in sediment or air. End-products with outdoor uses are most likely to be sources of this type of waste, where releases can occur over the lifetime of the product due to weathering and wear. In addition releases of this type can occur from disposal processes, particularly where articles are dismantled or subject to other mechanical processes. Air and dust monitoring data at such dismantling plants confirm that this is a source of release of polybrominated diphenyl ethers (see Section 3.1.4.2 and the risk assessment report for decabromodiphenyl ether).

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 of di-(2-ethylhexyl)phthalate (DEHP) (EC, 2000a) and a similar approach is taken here. The estimates obtained are open to a high degree of uncertainty.

Details of the approach used previously for other plastics' additives

In the draft DEHP risk assessment, "waste remaining in the environment" was identified to be produced from the following applications of PVC polymers (EC, 2000a):

    car undercoating,
    roofing material,
    coil coating,
    fabric coating,
    cable and wires,
    hoses and profile,
    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 factors 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.

In the draft DEHP assessment it was assumed that 75% of the emissions would be to industrial/urban soil and 0.1% to air, with the remainder occurring to surface water (and hence sediment).

Approach taken for octabromodiphenyl ether

A similar approach to that used for DEHP is used here as a worst case, with the same emission factors as used for DEHP. Only outdoor applications are considered to contribute significantly to the waste over the lifetime of articles, but all applications are considered to contribute at disposal. The actual amount of octabromodiphenyl ether present in plastics for outdoor applications is unknown. An estimate of 10% of the total is used in this calculation as a very conservative worst case in order to assess the potential for adverse environmental impacts from this source. Given that the known applications of plastic containing octabromodiphenyl ether are in electrical and electronic equipment, Industry (personal communication) has indicated that a figure of 0.1% of the total is likely to be more realistic for outdoor applications (they were not aware of any outdoor uses). This figure is also taken into account in the estimated emissions.

The approach assumes the following:

- The quantity of articles/products containing octabromodiphenyl ether disposed of each year is equal to the quantity of new articles/products containing octabromodiphenyl ether produced each year.
- The emission factors estimate the total release over the entire service life of the product/article (i.e. for low wear articles, 2% of the product is worn away as particles/dust over the lifetime of the product).
- Emissions can occur at disposal from dismantling etc. of articles containing octabromodiphenyl ether regardless of the method of ultimate disposal (or recycling).
- The emissions are likely to be mainly to soil, with smaller amounts going to surface water (and hence sediment) and air. In the absence of any further information, and to be consistent with the approach taken previously with DEHP, it will be assumed that these emissions are split 75% to soil, 24.9% to surface water and 0.1% to air.

In the calculations, the amount of octabromodiphenyl ether lost by volatilisation over the service life is also taken into account to avoid double counting. There are many uncertainties inherent in these emission estimates, and the approach taken may overestimate the actual releases and hence risk from this source. Further, since this type of waste is essentially polymeric particles containing octabromodiphenyl ether, it is not known if this is in a form that is "available" in the environment and so would lead to actual exposure of organisms to octabromodiphenyl ether.

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

	1994 data	1999 data
Total amount of octabromodiphenyl ether present in polymers =	2,550 tonnes/year	1,350 tonnes/year
Amount lost through volatilisation over the service life =	13.8 tonnes/year	7.29 tonnes/year
Total amount remaining in plastics =	2,536 tonnes/year	1,343 tonnes/year
Estimated fraction of plastic used for outdoor applications =	10%	0.1%
Amount of in plastic used for outdoor applications =	254 tonnes/year	1.34 tonnes/year
Estimated loss as "waste remaining in the environment" =	2% over lifetime	2% over lifetime
Emission as "waste remaining in the environment" over lifetime =	5.08 tonnes/year	0.027 tonnes/year
Total amount remaining in plastics at disposal =	2,531 tonnes/year	1,343 tonnes/year
Estimated loss as "waste remaining in the environment" at disposal =	2%	2%
Emission at disposal =	50.62 tonnes/year	26.86 tonnes/year
Amount remaining in plastics for disposal (or recycling) =	2,480 tonnes/year	1,316 tonnes/year

The estimated amount of "waste remaining in the environment" is therefore 55.7 tonnes/year for the EU as a whole using the "worst case" 1994 consumption data and 26.9 tonnes/year using the 1999 data. The regional amounts will be taken as 10% of these figures. It will be assumed that this release is to industrial/urban soil, air and surface water (and hence sediment) as follows:

	Total EU (tonnes/year)		Region (tonnes/year)	
	1994 data	1999 data	1994 data	1999 data
75% to industrial/urban soil	41.8	20.2	4.18	2.02
0.1% to air	0.0557	0.0269	0.00557	0.00269
24.9% to surface water	13.9	6.69	1.39	0.669

3.1.1.2.5   Losses during disposal

Plastics containing octabromodiphenyl ether will usually be disposed of either to landfill or by incineration. It is expected that emissions from incineration processes will be near zero, although the question of formation of brominated dibenzofurans and dibenzo-*p*-dioxins has been raised as a potential problem (this is covered in more detail in Section 2.4 and Appendix A). When plastic containing octabromodiphenyl ether is disposed of to landfill, in theory it could volatilise to the atmosphere or leach out of the plastic and into groundwater.

Using the assumption that the amount of plastic containing octabromodiphenyl ether produced each year replaces that disposed of each year then the amount of octabromodiphenyl ether disposed of in plastic articles could be around 2,480 tonnes/year (or 248 tonnes/year in a region) based on the 1994 consumption data, or 1,316 tonnes/year (or 132 tonnes/year in a region) based on the 1999 consumption data.

No experiments appear to have been carried out on the leachability of octabromodiphenyl ether from polymers in landfills, but, by comparison with the decabromodiphenyl ether (see the risk assessment report of decabromodiphenyl ether (EC, 2002)), it would not be expected to leach to a significant extent from polymers, unless the polymer itself undergoes some form of degradation, thus releasing the octabromodiphenyl ether. However, octabromodiphenyl ether is likely to adsorb strongly onto soil and this will significantly lower its leaching potential from landfills into groundwater (see also Section 3.1.1.5.2). Similarly, the low vapour pressure of the substance would limit its volatility from landfills.

3.1.1.2.6 Possibilities for recycling

It has been reported (EEC, 1993) that off-cuts and off-specification plastic material containing brominated flame retardants can theoretically be recycled. Generally the major electronics manufacturers are unwilling to accept new equipment made from recycled material such as off-cuts, since the plastic has to undergo at least two further processing steps (e.g. repelletising/compounding and reprocessing/conversion). These two extra processing steps may reduce the effectiveness of some of the additives and so such material is generally used in 'lower grade' applications. The octabromodiphenyl ether losses from any recycling of off-cuts etc. will be similar to the losses described above for the individual steps in plastics processing.

3.1.1.3 Summary of environmental releases

Table 3.1 summarises the estimated releases of octabromodiphenyl ether to the environment. Production of octabromodiphenyl ether no longer occurs in the EU and so is not included in **Table 3.1**. As can be seen, several of the release sources are likely to be as dust. Although this release is initially to air, the dust is likely to settle rapidly and be collected for recycling or disposal. Thus this release can be considered as being to solid waste. It would be expected that only a very small fraction of this dust would enter the atmosphere outside the factory. It is possible that some of this release could also end up going to wastewater as a result of washing down equipment/floors etc., but it is thought that this eventuality is covered in the worst-case release estimates for wastewater.

Table 3.1   Summary of estimated releases of octabromodiphenyl ether to the environment

Use	Octabromodiphenyl ether					
	Release at a site (local release) (tonnes/year)		Release in a region* (tonnes/year)		Release in continental model* (tonnes/year)	
	1994 data	1999 data	1994 data	1999 data	1994 data	1999 data
Polymers: handling of raw material	0.080 as dust (to landfill/incineration)	0.024 as dust (to landfill/incineration)	0.54 as dust (to landfill/incineration)	0.095 as dust (to landfill/incineration)	4.86 as dust (to landfill/incineration)	0.85 as dust (to landfill/incineration)
Polymers: compounding and conversion	0.0191 (to air) 0.0191 (to wastewater)	0.0057 (to air) 0.0057 (to wastewater)	0.128 (to air) 0.128 (to wastewater) a)	0.023 (to air) 0.023 (to wastewater) a)	1.15 (to air) 1.15 (to wastewater) a)	0.203 (to air) 0.203 (to wastewater)
Polymers: service life			1.38 (to air as vapour)	0.729 (to air as vapour)	12.4 (to air as vapour)	6.56 (to air as vapour)
Polymers:"waste remaining in the environment" (service life and disposal)			4.18 (to industrial/urban soil) 0.006 (to air) 1.39 (to surface water)	2.02 (to industrial/urban soil) 0.0027 (to air) 0.669 (to surface water)	37.6 (to industrial/urban soil) 0.050 (to air) 12.5 (to surface water)	18.18 (to industrial/urban soil) 0.024 (to air) 6.02 (to surface water)
Polymers: disposal			248 (to landfill/incineration)	132 (to landfill/incineration)	2,232 (to landfill/incineration)	1,184 (to landfill/incineration)
Maximum total emission figure for regional and continental modelling			1.51 (to air) 0.090 (to wastewater via WWTP) 1.43 (direct to surface water) 4.18 (to industrial/urban soil) 249 (to landfill/disposal)	0.755 (to air) 0.016 (to wastewater via WWTP) 0.676 (direct to surface water) 2.02 (to industrial/urban soil) 132 (to landfill/disposal)	13.60 (to air) 0.805 (to wastewater via WWTP) 12.85 (direct to surface water) 37.6 (to industrial/urban soil) 2,237 (to landfill/disposal)	6.79 (to air) 0.142 (to wastewater via WWTP) 6.08 (direct to surface water) 18.18 (to industrial/urban soil 1,185 (to landfill/disposal)

*   Release in continental model = total release in EU - estimated release in regional model
a)   In the regional and continental model a 70% connection rate to the wastewater treatment plant is assumed
Therefore, 30% of these releases are taken as going direct to surface water

3.1.1.4   Degradation

3.1.1.4.1   Abiotic degradation

There is limited information about the abiotic degradation of octabromodiphenyl ether. The available data are discussed below. It would, however, be expected to behave similarly to decabromodiphenyl ether. The degradation of decabromodiphenyl ether is discussed in more detail in the risk assessment report on that substance (EC, 2002) and the results are also considered below in terms of their significance for octabromodiphenyl ether.

Photolysis

Eriksson et al. (2001) recently reported the results of photolysis studies with 2,2'3,4,4',5,5',6-octabromodiphenyl ether (and tetra-, penta-, hexa-, hepta- and decabromodiphenyl ethers) in a mixture of methanol and water (80% methanol:20% water). The experiments were carried out in a cylindrical vessel (height 480 mm, outer diameter 85 mm and volume 1.6 l) with a fluorescent tube (λ>290 nm) placed in the middle. The initial concentration of octabromodiphenyl ether used in the study was 1 μM. The rate of photodegradation was found to generally increase with increasing degree of bromination and the octabromodiphenyl ether was found to degrade rapidly in the system with a half-life of around 5 hours (the half-lives for the tetra-, penta-, hexa-, hepta- and decabromodiphenyl ethers tested were 12-16 days, 2.4 days, 1.2 days, 1.2 days and 30 minutes respectively). The environmental significance of these findings in organic solvent mixtures is uncertain.

A possible concern is the formation of lower brominated diphenyl ethers from the photochemical degradation of octabromodiphenyl ether in the environment, since these compounds, particularly tetra- and pentabrominated diphenyl ethers have been found extensively in the environment and are potentially bioaccumulative (see the risk assessment report of pentabromodiphenyl ether (ECB, 2000) for further details). This has been studied in most detail for decabromodiphenyl ether and the data are summarised in the risk assessment report for that substance (EC, 2002). The data that are available on the direct photolysis of decabromodiphenyl ether in water generally show that it does photodegrade but that lower brominated congeners are formed only in small amounts and are not the major degradation products. There is also some uncertainty over the actual significance of the process in the environment.

As well as the studies with decabromodiphenyl ether summarised in the risk assessment report (EC, 2002), Jafvert and Hua (2001a) also carried out experiments on the photolysis of 2,2',4,4'-tetrabromodiphenyl ether using both natural sunlight and artificial sunlight. The samples for irradiation were prepared by adding 1 ml of a $2 \cdot 10^{-5}$ M solution of 2,2',4,4'-tetrabromodiphenyl ether in toluene to a series of cylindrical quartz tubes (giving a total of 9.7 μg/tube). The toluene was evaporated off as before and 2 ml of water was added to each tube and the tubes were sealed. The tubes were then either exposed to natural solar radiation from 9 am to 5 pm for 72 hours in total or exposed in a Rayonet Reactor with two 3,000 Å lamps for 16 hours. Controls and dark controls were also run in the experiments.

In the experiments with solar irradiation, approximately 30% of the initial 2,2',4,4'-tetrabromodiphenyl ether remained after 72 hours exposure. The rate of disappearance was comparable to that found for decabromodiphenyl ether under similar conditions. Accumulation of bromide ion was found to occur in the experiment. This accumulation was initially slow with the rate increasing after 24 hours. This contrasted with the disappearance of 2,2',4,4'-tetrabromodiphenyl ether, which showed an initial rapid decrease over the first

24 hours exposure. The bromine mass balance showed that around 70% of the total bromine was present as either 2,2',4,4'-tetrabromodiphenyl ether or bromide ion.

A more detailed GC-MS analysis was carried out on the possible brominated diphenyl ether products formed from this experiment using natural sunlight (Jafvert and Hua, 2001b). Two replicate exposures were carried out using the same conditions as indicated above. The results of the experiment are shown in **Table 3.2**, expressed as pg/tube. The starting concentration of 2,2',4,4'-tetrabromodiphenyl ether was nominally around 9.7 μg/tube (9,700,000 pg/tube). The actual amount found to be present in each tube at the start of the experiment by GC-MS was 9.75 μg and 9.39 μg. After 72-hours exposure these amounts had fallen to 2.48 and 3.76 μg/tube respectively, indicating 75% and 60% degradation respectively in the two replicates. The authors concluded that 2,4,4'-tribromodiphenyl ether was being formed during this reaction and that removal of bromine atoms *ortho* to the ether functionality may be a significant reaction pathway for 2,2',4,4'-tetrabromobiphenyl ether under the conditions used. In addition, when the mean and standard deviation of the concentrations found are considered (these were not given in the original paper and have been estimated here), it appears that other isomers such as 2,2',4,5'-, 2,3',4,4'-tetra and 2,4,4',6-tetrabromodiphenyl ether (and also 2,2',3,4,4',5',6-heptabromodiphenyl ether), could have been formed in small amounts, possibly by rearrangement reactions or debromination of the trace amounts of pentabromodiphenyl ether isomers present at the start of the test.

In the experiments with artificial sunlight 2,2',4,4'-tetrabromodiphenyl ether was rapidly degraded with around 20% of the original amount added remaining after 16 hours exposure. The loss was greatest over the first 4 hours exposure and this was then followed by a more gradual decline. The accumulation of bromide ion in the system mirrored the decline in the 2,2',4,4'-tetrabromodiphenyl ether concentration. The bromine mass balance indicated that around 50% of the total bromine was accounted for as either as 2,2',4,4'-tetrabromodiphenyl ether or bromide ion, with the form of the remaining 50% being unidentified.

The studies using 2,2',4,4'-tetrabromodiphenyl ether (also summarised in the risk assessment report for decabromodiphenyl ether (EC, 2002) have shown that this substance can photodegrade forming small amounts of debromination products and therefore it has to be concluded that other partially brominated congeners, including some if not all of the components of the commercial octabromodiphenyl ether product, have the potential to photodegrade in the environment to form small amounts of lower brominated congeners.

Overall, although it is clear that photodegradation of octabromodiphenyl ether could occur in the environment, it is not possible to estimate the actual amount of lower brominated congeners that may be formed from this reaction. Such a debromination reaction is by necessity a stepwise process and the amount of product formed in each step is likely to be only a fraction of that from the previous step. Each intermediate brominated diphenyl ether formed may also degrade under similar conditions as the parent compound. So far, all the available photodegradation studies are effectively "single event" studies, where there is one input of the brominated diphenyl ether into the system which is then allowed to degrade over a certain period of time. When the products formed are analysed at the end of the study, they represent the amount formed only at that time period and give no indication of whether the product was continuing to build up or decrease in the system.

Furthermore, the results are difficult to interpret in terms of a possible build up of degradation products in a more dynamic system (as would be found in the environment), where there would be multiple or continuous input of the polybrominated diphenyl ether. There is insufficient information available to estimate the actual rates of photodegradation of octabromodiphenyl

ether itself, or of these intermediate products, in the environment to determine if they are likely to build up in such situations of long-term exposures. The recent experiments by Jafvert and Hua (2001a) using 2,2',4,4'-tetrabromodiphenyl ether on solid matrices in water showed that this substance photodegraded at a similar rate to decabromodiphenyl ether when similar conditions were used (although as these studies were conducted with the solid phase, it is difficult to ensure that exactly the same exposure conditions were used owing to possible shadow effects, etc.). This finding is contradicted by the data of Eriksson et al. (2001), which showed that lower brominated congeners are more stable than the higher congeners (but these exposures were carried out using methanol:water mixtures). Therefore there is some uncertainty over whether or not the relatively small amounts of lower brominated congeners formed during these photolysis experiments would increase with continual input of the polybrominated diphenyl ether into the system. It should also be borne in mind that in the environment, where octabromodiphenyl ether is likely to be adsorbed to bulk matrices, only a small fraction of that present (i.e. that near the exposed surface) may be susceptible to photodegradation.

The results also indicate that as well as reductive debromination to form lower brominated diphenyl ethers, degradation must also be occurring by other pathways, although the products from these reactions are so far unknown.

Photodegradation of octabromodiphenyl ether is also likely to occur in the atmosphere, where decabromodiphenyl ether is likely to be adsorbed onto atmospheric particulates. It is not possible to determine if this reaction would lead to significant amounts of these substances in the environment.

Supporting evidence for the possibility of reductive debromination under environmental conditions for polybrominated diphenyl ethers as a whole is considered further in Appendix F.

Table 3.2 Detailed analysis of the products for photolysis of tetrabromodiphenyl ether with natural sunlight   (Jafvert and Hua, 2001b)

PBDE congener	Method detection limit (pg)	Level in laboratory blank (pg)			Level in 0-hour samples (pg)			Level in 72-hour samples (pg)		
		Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Mean [a]	Rep. 1	Rep. 2	Mean [a]
2-MonoBDE	18,200	nd	nd	nd	nd	nd		nd	nd	
3-MonoBDE	18,200	nd	nd	nd	nd	nd		nd	nd	
4-MonoBDE	18,200	nd	nd	nd	nd	nd		nd	nd	
2,4-DiBDE	258	nd	nd	nd	nd	nd		nd	nd	
2,4'DiBDE	258	nd	nd	nd	nd	nd		nd	nd	
2,6-DiBDE	258	nd	nd	nd	nd	nd		nd	nd	
3,3'-DiBDE	not given	nd	nd	nd	nd	nd		nd	nd	
3,4-DiBDE	258	nd	nd	nd	nd	nd		nd	nd	
3,4'-DiBDE	258	nd	nd	nd	nd	nd		nd	nd	
4,4'-DiBDE	258	nd	nd	nd	629	623	626±4	nd	925	527±563
2,2',4'-TriBDE	372	nd	nd	nd	2,120	2,940	2,530±580	2,450	3,340	2,895±629
2,3',4-TriBDE	372	nd	nd	nd	nd	nd		nd	nd	
2,4,4'-TriBDE	372	nd	nd	nd	4,880	6,990	5,935±1,492	11,600	23,600	17,600±8,485
2,4,6-TriBDE	372	nd	nd	nd	nd	nd		nd	nd	
2,4',6-TriBDE	372	nd	nd	nd	nd	nd		nd	nd	
2',3,4-TriBDE	not given	nd	nd	nd	nd	nd		nd	nd	
3,3',4-TriBDE	372	nd	nd	nd	nd	nd		nd	nd	
3,4,4'-TriBDE	372	nd	nd	nd	nd	nd		nd	nd	
2,2',4,4'-TetraBDE	415	nd	11.2	40.5	9,750,000	9,390,000	9,570,000± 254,558	2,480,000	3,760,000	3,120,000± 905,097
2,2',4,5'-TetraBDE	415	nd	nd	nd	nd	nd		928	nd	568±508
2,3',4,4'-TetraBDE	415	nd	nd	nd	nd	nd		6,070	9,400	7,735±2,355

Table 3.2 continued overleaf

Table 3.2 continued Detailed analysis of the products for photolysis of tetrabromodiphenyl ether with natural sunlight

PBDE congener	Method detection limit (pg)	Level in laboratory blank (pg)			Level in-0 hour samples (pg)			Level in 72-hour samples (pg)		
		Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Mean [a]	Rep. 1	Rep. 2	Mean [a]
2,3',4',6-TetraBDE	415	nd	nd	nd	nd	nd		nd	nd	
2,4,4',6-TetraBDE	415	nd	nd	nd	nd	nd		964	nd	586±535
3,3'4,4'-TetraBDE	415	nd	nd	nd	nd	nd		nd	nd	
2,2',3,4,4'-PentaBDE	1,680	nd	nd	nd	11,900	11,500	11,700±283	nd	4,300	2,570±2,447
2,2',4,4',5-PentaBDE	1,680	nd	nd	43.6	13,600	11,500	12,550±1,485	3,580	8,600	6,090±3,550
2,2',4,4',6-PentaBDE	1,680	nd	nd	nd	nd	nd		nd	nd	
2,3,3',4,4'-PentaBDE	1,680	nd	nd	nd	nd	nd		nd	nd	
2,3,4,5,6-PentaBDE	1,680	nd	nd	nd	nd	nd		nd	nd	
2,3',4,4',6-PentaBDE	1,680	nd	nd	nd	nd	nd		nd	nd	
3,3',4,4',5-PentaBDE	1,680	nd	nd	nd	nd	nd		nd	nd	
2,2',3,4,4',5'-HexaBDE	2,690	nd	nd	nd	nd	nd		nd	nd	
2,2',3,4,4',6'-HexaBDE	2,690	nd	nd	nd	nd	nd		nd	nd	
2,2',4,4',5,5'-HexaBDE	2,690	nd	nd	nd	nd	nd		nd	nd	
2,2',4,4',5,6'-HexaBDE	2,690	nd	nd	nd	nd	nd		nd	nd	
2,2',4,4',6,6'-HexaBDE	2,690	nd	nd	nd	nd	nd		nd	nd	
2,3,4,4',5,6-HexaBDE	not given	nd	nd	nd	nd	nd		nd	nd	
2,2',3,4,4',5,6-HeptaBDE	2,080	nd	nd	nd	nd	nd		nd	nd	
2,2',3,4,4',5',6-HeptaBDE	2,080	nd	nd	nd	nd	nd		nd	2,520	1,780±1,047
2,3,3',4,4',5,6-HeptaBDE	2,080	nd	nd	nd	nd	nd		nd	nd	
2,2',3,3',4,4',5,5',6-NonaBDE	4,260	nd	nd	nd	nd	nd		nd	nd	

Table 3.2 continued overleaf

Table 3.2 continued Detailed analysis of the products for photolysis of tetrabromodiphenyl ether with natural sunlight

PBDE congener	Method detection limit (pg)	Level in laboratory blank (pg)			Level in 0-hour samples (pg)			Level in 72-hour samples (pg)		
		Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Mean [a]	Rep. 1	Rep. 2	Mean [a]
2,2',3,3',4,4',5,6,6'-NonaBDE	4,260	nd	nd	nd	nd	nd		nd	nd	
2,2',3,3',4,5,5',6,6'-NonaBDE	4,260	nd	nd	nd	nd	nd		nd	nd	
DecaBDE	7,880	nd	nd	nd	nd	nd		nd	nd	

nd = Not detected

a)   Mean values were not reported in the original paper. The means and sample standard deviations have been estimated in this assessment. For the not detected results, the detection limit/2 has been used to estimate the mean. The shaded areas indicate isomers where there was an apparent increase in concentration during the test

Atmospheric photooxidation

A rate constant of $2.1 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} has been estimated for the atmospheric reaction of octabromodiphenyl ether with hydroxyl radicals. The value was obtained using the Syracuse Research Corporation AOP program which is based on the estimation method of Atkinson given in Chapter 4 of the Technical Guidance Document. Using this value an atmospheric half-life of around 76 days can be estimated for octabromodiphenyl ether based on an atmospheric hydroxyl radical concentration of $5 \cdot 10^5$ molecule/cm^3.

Hydrolysis

No information is available on the hydrolysis of octabromodiphenyl ether. Hydrolysis is not expected to be an important process for octabromodiphenyl ether in the environment.

3.1.1.4.2   Biodegradation

Aerobic conditions

The biodegradation of octabromodiphenyl ether has been determined in a closed bottle test (OECD 301D). The test was carried out to GLP and used a composite sample of octabromodiphenyl ether obtained from three manufacturers. The inoculum for the test came from the secondary clarifier of a domestic wastewater treatment plant and the octabromodiphenyl ether was tested as a suspension at a concentration of 15 mg/l. No biodegradation, as determined by oxygen uptake, was seen over the 28-day period and so octabromodiphenyl ether is not readily biodegradable. Biodegradation of a reference substance (sodium benzoate) was >60% by day 7 of the test, indicating that the inoculum used was viable and the test was valid (Schaefer and Haberlien, 1996).

Anaerobic conditions

No data on biodegradation of octabromodiphenyl ether under anaerobic conditions are available. From the data generated for other halogenated aromatic substances, there is a possibility for reductive dehalogenation to occur under some conditions (see Appendix F). If such a process occurs for octabromodiphenyl ether, this could lead to the formation of more toxic and bioaccumulative congeners.

An anaerobic biodegradation test has recently been carried out with decabromodiphenyl ether. Full details of the test are given in the risk assessment report of that substance (EC, 2002). The potential for formation of significant amounts of lower brominated congeners from decabromodiphenyl ether appears to be low.

A further similar anaerobic degradation study has been carried out with 2,2',4,4'-tetrabromodiphenyl ether (Schaefer and Flaggs, 2001). The substance tested was a mixture of ^{14}C-labelled 2,2',4,4'-tetrabromodiphenyl ether (radiochemical purity 96.5%) and unlabelled 2,2',4,4'-tetrabromodiphenyl ether (purity ~99%), and was tested at concentrations of 5 and 500 mg/kg dry weight. A positive control using ^{14}C-labelled glucose was also run. The test was carried out using the same sample preparation method, a similar sediment and the same test system as used for decabromodiphenyl ether outlined above. The mass balance results from the experiment are shown in **Table 3.3**.

Table 3.3   Anaerobic degradation of ^{14}C-labelled 2,2',4,4'-tetrabromodiphenyl ether

Nominal concentration	Mass balance at week 32			
	% as $^{14}CO_2$	% as $^{14}CH_4$	% ^{14}C in solids	Total % recovery of ^{14}C
5 mg/kg	0.5±0.34	0.01±0.01	134.3±5.0	134.8±5.2
500 mg/kg	0.2±0.02	0.01±0.02	124.8±7.7	125.0±7.7
Positive control (glucose at 5 mg/kg)	73.4±8.5	7.8±4.7	19.6±4.0	100.9±0.25

The total recovery of ^{14}C from the positive control was 101%, with 81.2% being converted to $^{14}CO_2$ and ^{14}C and 19.6% being associated with the sediment-phase. The degradation seen in the positive control indicates that the sample pre-treatment methods using tetrahydrofuran solvent appear to have had little effect on the viability of the microbial community present.

In the experiments with 2,2',4,4'-tetrabromodiphenyl ether, <1% of the total radioactivity was recovered as $^{14}CO_2$ and $^{14}CH_4$, indicating that essentially no mineralisation had occurred. Parent compound analysis using an HPLC method (mean of 7 replicates) indicated that the measured concentration in the 5 mg/kg treatment was 6.49±1.35 mg/kg at day 0 and 7.53±1.67 mg/kg at week 32. The measured parent compound concentrations in the nominal 500 mg/kg treatment were 832±69 mg/kg at day 0 and 771±127 mg/kg at week 32. There was no statistically significant difference between these results at day 0 and week 32. The composition of the sediment cores was found to account for some of the variability seen within the measured concentrations, with sediments containing a greater number of stones leading to a higher variability between replicate measurements of concentrations. Therefore, in addition to the measured concentrations, the concentrations were also converted to a mass of 2,2',4,4'-tetrabromodiphenyl ether present and these were compared to the actual mass of the test substance added at the start of the test. For the 5 mg/kg treatment the mean difference between the measured mass and the mass added was 0.059 mg and 0.276 mg at day 0 and week 32 samples respectively. For the 500 mg/kg treatment these differences were 59.9 mg and 46.5 mg at day 0 and week 32 respectively. The differences between the mass weighed into the test chamber on day 0 and the mass calculated to be present at week 32 were not statistically significantly different.

Therefore, based on the measured mass and concentrations of 2,2'4,4'-tetrabromodiphenyl ether during the study it appears that no significant degradation had occurred during this study. However, the HPLC analytical method using radiometric detection indicated that some products had been formed in the 32-week samples that eluted before the parent compound. Between 1 and 3 such peaks were identified in 26 of the 42 samples analysed, and at least one significant peak was observed in all of the 32-week samples from the 500 mg/kg treatment. Work is currently in progress to try to identify these products.

From these results, it is clear that 2,2',4,4'-tetrabromodiphenyl ether has the potential to degrade slowly under anaerobic conditions. Information on the products from this process is not available but, from knowledge of the transformation processes of other halogenated aromatic compounds under anaerobic conditions (see Appendix F), reductive debromination, to form congeners with a lower degree of bromination, is at least a possibility.

Although it is not possible to apply the results from 2,2',4,4'-tetrabromodiphenyl ether to octabromodiphenyl ether directly, they do provide some evidence that other partially brominated diphenyl ethers, such as some of the components of the commercial octabromodiphenyl ether products, may also have the potential to biodegrade under anaerobic conditions in the

environment. There is insufficient information available to assess the significance of this process in the environment, in terms of the formation of more toxic and accumulative lower brominated congeners from octabromodiphenyl ether.

3.1.1.4.3 Summary of degradation rates used for environmental modelling

From the preceding Sections there is some evidence that octabromodiphenyl ether may photodegrade in the environment under certain conditions, but it is not possible to estimate the rate or extent of this reaction. Octabromodiphenyl ether is predicted to adsorb strongly onto sediment and soil and only a fraction of this, that exposed to sunlight, will have the potential to photodegrade. Thus, although photodegradation of octabromodiphenyl ether is a possibility, the rate of reaction will be assumed to be effectively zero for environmental modelling purposes.

The rate of degradation of octabromodiphenyl ether under aerobic conditions and anaerobic conditions (by analogy with other brominated diphenyl ethers) would be expected to be very low, although there are some indications that degradation may occur for some components of the commercial product under anaerobic conditions, albeit at a very slow rate. The rate of biodegradation will be assumed to be effectively zero for environmental modelling purposes.

Octabromodiphenyl ether is predicted to react with atmospheric hydroxyl radicals, and a reaction rate constant of $2.1 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} will be used for this reaction in the environmental modelling.

Octabromodiphenyl ether is considered to be stable to hydrolysis. Therefore the rate of hydrolysis will be assumed to be zero in the environmental modelling.

Despite the assumption of an overall rate of degradation of zero, the implications of possible degradation will be discussed in the risk characterisation section (Section 3.3).

3.1.1.5 Distribution

Since octabromodiphenyl ether is a mixture of compounds of differing degrees of bromination (ranging from penta-/hexa- to nona-/decabrominated 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 to be considered in order to identify trends and extrapolations have to be made from one chemical to the other in the absence of data. Appendix E considers this further, and looks for 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 for the polybrominated diphenyl ethers 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.

3.1.1.5.1 Volatilisation

The vapour pressure of octabromodiphenyl ether has been determined as $6.59 \cdot 10^{-6}$ Pa using a composite sample from three manufacturers (see Section 1). This vapour pressure is likely to reflect the vapour pressure of the most volatile components of the commercial product and not

necessarily that of the octabromodiphenyl ether component. This value has been used in the EUSES modelling for the commercial octabromodiphenyl ether.

Brominated diphenyl ethers as a group 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°C using a GC technique. 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 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 approximate vapour pressures of the most and least volatile components in the products tested.

Low vapour pressures have been determined for all the components of octabromodiphenyl ether and so they are unlikely to volatilise from spillage to land. However, given the very low water solubility of these substances, volatilisation from solution may still be significant, particularly for the moderately brominated components. Once in the atmosphere, they are likely to adsorb strongly onto atmospheric particles and subsequently get removed by wet or dry deposition. This could provide a transport mechanism for these compounds in the environment.

Table 3.4   Vapour pressures (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	$1.2 \cdot 10^{-7}$-$2.3 \cdot 10^{-7}$

3.1.1.5.2   Adsorption

The octanol-water partition coefficient for octabromodiphenyl ether has been determined as log Kow = 6.29 using a composite sample from three manufacturers (see Section 1). This is considered as a minimum value for the commercial substance.

High octanol-water partition coefficients (Kow) have also been determined for polybrominated diphenyl ethers using a HPLC technique (Watanabe and Tatsukawa, 1990). The results are shown in **Table 3.5**. 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 3.5 Octanol-water partition coefficients   (Watanabe and Tatsukawa, 1990)

Polybrominated diphenyl ether	Log Kow
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

The results indicate that all components of commercial octabromodiphenyl ether are expected to adsorb strongly onto soil and sediment since they have high octanol-water partition coefficients, this tendency increasing with increasing bromination.

According to the Technical Guidance Document, soil organic carbon - water partition coefficients (Koc) can be estimated for hydrophobic chemicals from $\log Koc = 0.81 \cdot \log Kow + 0.10$. Thus for octabromodiphenyl ether a Koc value of 156,640 l/kg can be estimated from the log Kow value of 6.29.

A Koc value of 144,544 l/kg has been estimated for an octabromodiphenyl ether from the chemical structure using the EPI estimation program (see Section 3.1.1.5.4). This is very similar to the value estimated above from the octanol-water partition coefficient.

No measured Koc value is available for octabromodiphenyl ether. Values have been estimated from structure and from the Kow value, both of which give similar values. Measured values for adsorption coefficients are available for both commercial decabromodiphenyl ether and pentabromodiphenyl ether (see their assessments for further details). These values indicate that a Koc value of around 1,363,040 l/kg would be expected for commercial octabromodiphenyl ether (see Appendix E). This is higher than the predicted values by a factor of 10. However, it should be born in mind that the log Kow value of 6.29 measured for commercial octabromodiphenyl ether probably represents a minimum value, and that higher values (see **Table 3.5**) have been determined by other methods, which would lead to higher predictions for the Koc (e.g. 7,302,978-20,370,421 l/kg) as estimated by the equation given in the Technical Guidance Document.

A value for Koc of 1,363,040 l/kg will be used in this assessment as this is extrapolated from measurements with other brominated diphenyl ethers. Using this value of Koc, adsorption coefficients can be estimated as Kp = 27,261 l/kg for soil, = 68,152 l/kg for sediment and = 136,304 l/kg for suspended sediment, assuming organic carbon contents of 2, 5, and 10% respectively (default values from the Technical Guidance Document). The equivalent partition coefficients on a m^3/m^3 basis are $K_{soil-water}$ = 40,892 m^3/m^3, $K_{sed-water}$ = 34,076 m^3/m^3 and $K_{susp-water}$ = 34,076 m^3/m^3. These values will be used later as representative values for modelling/PEC calculation. Appendix E considers how the uncertainties in these values will affect the environmental modelling.

From the above information, octabromodiphenyl ether can be considered to be immobile in soil and it is unlikely to leach into groundwater. Results obtained using the SAMS soil model 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 in the soil was assumed and a Koc of 1,363,040 l/kg was used in the model. The model indicated that the majority of the octabromodiphenyl 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.

It is possible that some of the lesser brominated components of commercial octabromodiphenyl ether may be more mobile in soil than octabromodiphenyl ether itself. For instance, a Koc value of 983,340 l/kg can be estimated for a pentabromodiphenyl ether (see Appendix E). However, the estimated Koc value is still very high and so the other components of commercial octabromodiphenyl ether are also likely to be immobile in soil.

3.1.1.5.3   Accumulation

A single study on a mixed commercial octabromodiphenyl ether product indicated essentially no bioaccumulation in carp (*Cyprinus carpio*) (CBC, 1982). The material tested was a mixture of brominated diphenyl ether congeners containing between 6 and 9 bromine atoms (86% of the material had between seven and nine bromine atoms; consisting of 47% heptabromodiphenyl ether, 17% octabromodiphenyl ether (isomer 1), 11% octabromodiphenyl ether (isomer 2) and 7% nonabromodiphenyl ether). The test was carried out using a flow-through system in 100 l glass aquaria and a flow rate of 582 l/day. The octabromodiphenyl ether was tested at two concentrations, 10 µg/l and 100 µg/l. A dispersing agent (polyoxyethylene hydrogenated castor oil) was present at 400 and 4,000 µg/l at the two test concentrations respectively. The test fish had an average body weight of 23.7 g, an average body length of 9.8 cm and a lipid content of 4.8%. The bioconcentration factor was <4 after 8 weeks exposure for all of the main components of the commercial product, although there was some indication of low to moderate accumulation of a hexabromodiphenyl ether component of the mixture (the BCF for the hexabromodiphenyl ether components of commercial pentabromodiphenyl ether have been measured at around 1,000-5,600 l/kg in fish (see the assessment of pentabromodiphenyl ether)). The water concentrations used in the test are above the reported water solubility of octabromodiphenyl ether (around 0.5 µ/l). The actual solubility of the substance in the test medium is unknown but it is possible that the actual dissolved concentration present was lower than indicated by the test concentrations of 10 and 100 µg/l. If it is assumed that the octabromodiphenyl ether isomers were present at around 0.5 µg/l, then the upper limit for the BCF would be around <9.5 l/kg for this component. For the heptabromodiphenyl ether component, some uptake by the fish was seen at some exposure periods, leading to a BCF of the order of <1.1-3.8 l/kg. Again, if it is assumed that the actual concentration of octabromodiphenyl ether in the water was around 0.5 µg/l, these BCFs would be of the order of <10-36 l/kg. The results indicate that no significant bioconcentration of octabromodiphenyl ether is expected, unless the commercial product contains significant amounts of lower (≤6 bromines) brominated diphenyl ether components.

Based on its octanol-water partition coefficients (see **Table 3.5**) octabromodiphenyl ether would be expected to be bioaccumulative. However, the experimental result indicates that the octabromodiphenyl ether does not bioconcentrate, probably due to its large size precluding crossing of cell walls in organisms.

The uptake of octabromodiphenyl ether by earthworms has been studied as part of a toxicity study. Full details of the toxicity test are given in Section 3.2.2.2. The soil used in the test was an artificial soil and had an organic carbon content of 4.7% and a pH of 6.0. The water content was maintained at around 26% on a dry weight soil basis. Groups of 4 month old worms (weights 300.6-435.4 mg/worm) were exposed to octabromodiphenyl ether concentrations of 84.9, 166

361, 698 and 1,470 mg/kg dry weight (mean measured concentrations) for 28-days. After this time, the worms were removed from the soil, allowed to purge their guts for 48 hours, and then analysed for the presence of octabromodiphenyl ether using a gas chromatographic method with electron capture detection. The method used for quantification involved the summing of the peak areas from the two largest peaks from the octabromodiphenyl ether product. The actual identities of these peaks were not given, but, based on the known composition of commercial octabromodiphenyl ether products (see Section 1.2.1), it is likely that these were from the heptabromodiphenyl ether and octabromodiphenyl ether components. No octabromodiphenyl ether was found in any of the earthworm samples analysed. The limit of quantification of the method used was 0.75 mg/kg. Based on this limit of quantification, the upper limit for the earthworm bioaccumulation factor (expressed as concentration in worm/concentration in dry soil) would be $5 \cdot 10^{-4}$. As the study only analysed the two main peaks from the commercial product, it is not possible to extrapolate the results to other components of the commercial product (for example the hexabromodiphenyl ether component).

There is little information on the accumulation potential for octabromodiphenyl ether through other (e.g. dietary) routes of exposure (the available toxicokinetic, metabolism and distribution data in mammalian systems are shown in Section 4). The available monitoring data (see Section 3.1.5.2) indicate that, as well as hexabromodiphenyl ethers, some heptabromodiphenyl ethers have recently been found to be present in organisms in the environment. This shows that uptake of some of the main components of the commercial octabromodiphenyl ether is occurring in the environment. These results are considered in the Risk Characterisation.

3.1.1.5.4   Structure-Activity Relationship (SAR) data

Since few data are available on the environmental fate of polybrominated diphenyl ethers the Syracuse Research Corporation EPI estimation program 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 3.6**.

As can be seen from **Table 3.6**, the estimated octanol-water partition coefficient (Kow) and soil organic carbon-water partition coefficient (Koc) 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.

Bioaccumulation potential would also be expected to increase with increasing bromination, however, the measured results given in Section 3.1.1.5.3 indicate that the octabromodiphenyl ether commercial products do not bioconcentrate, probably due to their large size precluding crossing of cell walls in organisms.

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 decrease with increasing bromination.

The model estimates that all of the compounds are not 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.

Table 3.6 Results of EPI estimation program for some representative polybrominated diphenyl ethers

Property	Bromo diphenyl ether [d]	Dibromo diphenyl ether [d]	Tribromo diphenyl ether [d]	Tetrabromo diphenyl ether [d]	Pentabromo diphenyl ether [d]	Hexabromo diphenyl ether [d]	Heptabromo diphenyl ether[d]	Octabromo diphenyl ether [d]	Nonabromo diphenyl ether [d]	Decabromo diphenyl ether [d]
Log Kow	4.94	5.83	5.88	6.77	7.66	8.55	9.44	10.33	11.22	12.11
Log Koc	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/mol)	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)	1,010 hours (42.1 days)	2,564 hours (106.8 days)	270 days	678 days	1,698 days
Volatilisation half-life from lake	236 hours (9.8 days)	409 hours (17 days)	825 hours (34.4 days)	1,869 hours (77.9 days)	4,518 hours (188 days)	468 days	1,175 days	2,953 days	7,405 days	18,530 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 WWTP:	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 1.5×10^6 molecules/cm^3 and 12 hours sunlight/day
d) 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 and so the actual isomers used in the estimates are not shown

3.1.1.6 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 ring. 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 be 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 mis-identification 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 unlikely to be a consideration in the determination of the levels of the commercial octabromodiphenyl ether flame retardant.

3.1.2 Aquatic compartment

3.1.2.1 Calculation of PECs

It should be born in mind in the following sections that the PECs estimated refer to the commercial octabromodiphenyl ether products. As was shown in Section 1, the commercial products are mixtures of congeners, of which octabromodiphenyl ether isomers make up around 31-36%.

3.1.2.1.1   Production

An example calculation is given below for information only. The release of octabromodiphenyl ether from a 1,000 tonnes/year production site is estimated to be 3 or 0.5 tonnes/year to wastewater. It will be assumed that all of this release occurs to a wastewater treatment plant (wwtp). No production of octabromodiphenyl ether currently occurs in the EU and so the significance of the PECs will not be considered further in this report.

Using the Technical Guidance Document for Risk Assessment of Existing Substances, the size of the wwtp is 2,000 m^3/day and the removal of octabromodiphenyl ether is 91.54% due mainly to adsorption onto sewage sludge (91.4%), with a very small amount to air (from EUSES, assuming log Kow = 6.29, water solubility = 0.5 µg/l, vapour pressure = 6.59 · 10^{-6} Pa, and no biodegradation occurs).

> Amount released to wwtp = 3 or 0.5 tonnes/year
> No of days of operation = 100
> Amount released daily = 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 = 91.54%
> Concentration in effluent = 1.27 or 0.212 mg/l
> Dilution in receiving water = 10
> Concentration in receiving water (Clocal$_{water}$) = 127 or 21.2 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 octabromodiphenyl ether. Using the equation given in the Technical Guidance Document:

$$PEC_{local}(water) = Clocal_{water}/(1 + Kp_{susp} \cdot C_{susp}) + PEC_{regional}$$

> where Kp$_{susp}$ = suspended matter-water partition coefficient = 136,304 l/kg
> C$_{susp}$ = concentration of suspended matter in the river = 1.5 · 10^{-5} kg/l
> PEC$_{regional}$ = 7.5 ng/l (1994 consumption data) or 3.6 ng/l (1999 consumption data).

Hence, PEC$_{local}$(water) from production = 41.7 or 7.0 µg/l.

The yearly average PEC$_{local}$(water) can be estimated as 11.4 or 1.6 µg/l.

The PEC$_{local}$s estimated are well above the water solubility of octabromodiphenyl ether.

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

$$PEC_{local}(sed) = \frac{Ksusp \text{-} water}{\rho_{susp}} \times PEC_{local}(water) \times 1000$$

> where Ksusp-water = suspended matter - water partition coefficient = 34,076 m^3/m^3
> ρ$_{susp}$ = bulk density of suspended matter = 1,150 kg/m^3.

Thus, the PEC$_{local}$(sed) from production can be estimated as 1,236 mg/kg (wet weight) or 207 mg/kg (wet weight).

3.1.2.1.2 Polymers

In Section 3.1.1.2.2 it was estimated that 19.1 kg/year of octabromodiphenyl ether may be released to wastewater at an ABS processing site over 102 days using the 1994 consumption data. The equivalent estimates using the 1999 consumption data are 5.65 kg/year of octabromodiphenyl ether over 30 days.

It will be assumed that all of this release occurs to a wastewater treatment plant (wwtp). Using the same approach as in Section 3.1.2.1.1, the size of the wwtp is 2,000 m^3/day and the removal of octabromodiphenyl ether is 91.54%, mainly due to adsorption onto sewage sludge.

	1994 data	1999 data
Amount released to wwtp =	19.1 kg/year	5.65 kg/year
No of days of operation =	102	30
Amount released daily =	187 g/day	188 g/day
Size of wwtp =	2,000 m^3/day	2,000 m^3/day
Concentration in influent to wwtp =	0.094 mg/l	0.094 mg/l
Removal in wwtp =	91.54%	91.54%
Concentration in effluent =	8.0 µg/l	8.0 µg/l
Dilution in receiving water =	10	10
Concentration in receiving water (Clocal$_{water}$) =	0.80 µg/l	0.80 µg/l

Using the same values as in Section 3.1.2.1.1, the PEC$_{local}$ for water and sediment can be calculated as follows (for both the 1994 and 1999 consumption data):

> PEC$_{local}$(water) for polymer production = 0.27 µg/l.
> PEC$_{local}$(sed) for polymer production = 8.0 mg/kg wet weight.

The yearly average PEC$_{local}$(water) can be estimated as 0.08 µg/l using the 1994 consumption data and 0.025 µg/l using the 1999 consumption data.

Note that the estimated PEC$_{local}$(water) is close to the water solubility of the substance.

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

The calculation of PECs on a regional and continental scale can be done using the EUSES model.

A direct release of octabromodiphenyl ether to soil from "waste remaining in the environment" was assumed to occur to industrial soil in the model. A summary of the release estimates used in the model is given in **Table 3.1**.

The results of the model are shown in **Table 3.7**. No biodegradation was assumed in the model, but a rate constant for atmospheric reaction with hydroxyl radicals of $2.1 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} was assumed. The following physical chemical properties were used: water solubility 0.5 µg/l, vapour pressure $6.59 \cdot 10^{-6}$ Pa, log Kow 6.29, Henry's law constant 10.6 Pa m^3/mol (estimated from ratio of vapour pressure and water solubility). A full summary of the modelling results is given in Appendix B.

Table 3.7   Summary of regional and continental concentrations estimated using EUSES

	$PEC_{regional}$		$PEC_{continental}$	
	1994 data	**1999 data**	**1994 data**	**1999 data**
Concentration in surface water (dissolved)	7.5 ng/l	3.6 ng/l	1.2 ng/l	0.56 ng/l
Concentration in sediment	0.39 mg/kg wet weight	0.19 mg/kg wet weight	0.06 mg/kg wet weight	0.029 mg/kg wet weight

3.1.2.1.4   Summary of predicted levels for the aquatic compartment

Concentrations of octabromodiphenyl ether in the aquatic compartment have been estimated using a variety of methods. The concentrations are summarised in **Table 3.8**.

Table 3.8   Summary of predicted environmental concentrations for the aquatic compartment

Media	Source	Type	Concentration	
			1994 data	**1999 data**
Water	[Production *]	PEC_{local}	[7.0 or 41.7 µg/l] [yearly average 1.6 or 11.4 µg/l]	[7.0 or 41.7 µg/l] [yearly average 1.6 or 11.4 µg/l]
	Polymer processing	PEC_{local}	0.27 µg/l (yearly average 0.08 µg/l)	0.27 µg/l (yearly average 0.025 µg/l)
	Regional scale	$PEC_{regional}$	7.5 ng/l	3.6 ng/l
	Continental scale	$PEC_{continental}$	1.20 ng/l	0.56 ng/l
Sediment	[Production *]	PEC_{local}	[20.7 or 1,236 mg/kg wet weight]	[20.7 or 1,236 mg/kg wet weight]
	Processing	PEC_{local}	8.0 mg/kg wet weight	8.0 mg/kg wet weight
	Regional scale	$PEC_{regional}$	0.39 mg/kg wet weight	0.19 mg/kg wet weight
	Continental scale	$PEC_{continental}$	0.06 mg/kg wet weight	0.029 mg/kg wet weight

*   Production no longer occurs in the EU

The predicted concentrations of octabromodiphenyl ether 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 octabromodiphenyl ether are predicted to occur in the aquatic environment. For the local production scenario (based on the default release assumptions), the estimated concentration in water is above the water solubility of the substance.

3.1.2.2   Measured levels in water and sediment

This Section reports the levels of octabromodiphenyl ether measured in water and sediment. The analysis of octabromodiphenyl ether is complicated by the fact that the commercial product is a mixture and that there is a lack of analytical standards for individual isomers/congeners of the mixture (although these are becoming increasingly available). This means that in most of the early analyses, the levels found are referenced against the commercial products. Using this approach uncertainties arise in the analysis due to the fact that the individual components of the

mixture will behave differently in the environment, leading to a different distribution of congeners to that of the commercial product. This could lead to large errors in determining the actual levels found in the environment and so the measured levels should be treated as indicative of the presence of commercial octabromodiphenyl ether rather than absolute values at present. This situation is improving as more pure standards of individual isomers/congeners become available.

In addition to the levels of commercial octabromodiphenyl ether products reported in earlier studies, more recent studies have also investigated the concentrations of some of the major components of the commercial products, including hexabromodiphenyl ether and heptabromodiphenyl ether isomers. As hexabromodiphenyl ethers are also a major component of the commercial pentabromodiphenyl ether product, the levels of the hexabromodiphenyl ether isomers are reported in the risk assessment report of pentabromodiphenyl ether (EC, 2000b). The levels of heptabromodiphenyl ethers (which are major components of the commercial octabromodiphenyl ether product) are reported in the following Sections.

3.1.2.2.1 Water

The levels of octabromodiphenyl ethers measured in water are shown in **Table 3.9**. As can be seen, in all cases, the levels in water are below the limit of detection (i.e. <0.07-<0.1 μg/l). The samples are thought to be representative of industrial, urban and rural areas of Japan and the "not detected" results are reasonably consistent with the regional (3.6-7.5 ng/l) and continental (0.56-1.2 ng/l) surface water levels obtained by EUSES. It is not known if any of the sampling sites were in the vicinity of a polybrominated diphenyl ether production site or a polymer processing site, so it is not possible to compare the levels with the PEC$_{local}$ calculated at such sites.

Table 3.9   Levels of octabromodiphenyl ether in water

Location	Comments	Level	Reference
Japan, 1987	Detection limit 0.1 μg/l	Not detected in 75 samples	Environment Agency Japan, 1991
Japan, 1988	Detection limit 0.07 μg/l	Not detected in 147 samples	Environment Agency Japan, 1991

The Environment Agency (2002) investigated the concentrations of several components of commercial octabromodiphenyl ether in effluent and surface water near to a former polybrominated diphenyl ether production site in the United Kingdom. The site was known to produce both commercial pentabromodiphenyl ether and octabromodiphenyl ether up until the late 1990s but neither product was being manufactured at the site at the time of sampling (March 2002), although octabromodiphenyl ether may now be imported to the site. It is also possible that other sources of these substances may exist in the area. The samples (two from each location) were filtered (0.45 μm) before analysis and the concentration of the polybrominated diphenyl ether in both the water phase and suspended sediment was measured.

The concentrations of the substances found in the water (dissolved phase) were generally very low. Samples of influent water to the sewage treatment plant were found to contain around 0.009 μg/l of 2,2',3,4,4',5',6-heptabromodiphenyl ether (and also <0.002 μg/l of 2,2',3,4,4',5'-hexabromodiphenyl ether, 0.007 μg/l of 2,2',4,4',5,5'-hexabromodiphenyl ether and 0.004 μg/l of 2,2',4,4',5,6'-hexabromodiphenyl ether). The concentration of the hexabromodiphenyl ether isomers in the effluent from the sewage treatment plant was <0.002 μg/l, but heptabromodiphenyl ether was

present at 0.003 µg/l in these samples. No hexa- or heptabromodiphenyl ethers were found in samples taken from both upstream and downstream of the effluent discharge point from the sewage treatment plant (detection limit 0.002 µg/l).

A similar pattern of occurrence was found in the suspended sediment levels. The influent water to the sewage treatment plant was found to contain 0.95 µg/l of 2,2',3,4,4',5',6-heptabromodiphenyl ether, 0.20 µg/l of 2,2',3,4,4',5'-hexabromodiphenyl ether, 0.33 µg/l of 2,2',4,4',5,5'-hexabromodiphenyl ether and 0.093 µg/l of 2,2',4,4',5,6'-hexabromodiphenyl ether, with the concentration in the effluent from the sewage treatment plant being 0.006, <0.002, 0.003 and <0.002 µg/l for the four substances respectively. The four substances were also detected in river water at one site upstream from the effluent discharge point from the sewage treatment plant at 0.009, <0.002, 0.004 and 0.002 µg/l for the four substances respectively, but were not found at a further two sites upstream of the effluent discharge point and two sites downstream of the effluent discharge point (detection limit 0.002 µg/l).

3.1.2.2.2   Sediment

The levels of octabromodiphenyl ether in sediments in the United Kingdom are shown in **Table 3.10**. **Table 3.11** shows levels of octabromodiphenyl ether measured in other parts of the world.

As well as the above measurements of octabromodiphenyl ether itself, several studies have investigated the concentrations of some of the major components of commercial octabromodiphenyl ether products in the environment (a detailed review of the levels of hexabromodiphenyl ether congeners is given in ECB (2000)).

Table 3.10 Levels of octabromodiphenyl ether in sediment in the United Kingdom

Location	Comment	Level	Ref.
River Tweed at Tweedmouth	Background site	<0.44 µg/kg dry wt.	a
River Tweed at Berwick upon Tweed bridges	Background site	<0.44 µg/kg dry wt.	a
River Nith, upstream of wwtp	Near rubber producer	<0.44 µg/kg dry wt.	a
River Nith, downstream of wwtp	Near rubber producer	<0.44 µg/kg dry wt.	a
River Nith at Glencaple	Near rubber producer	2 µg/kg dry wt.	a
Avonmouth	Near a possible flame retardant producer/user	<0.44 µg/kg dry wt.	a
River Tees at Croft-on-Tees	Near to a manufacturer of octabromodiphenyl ether	<0.44-25 µg/kg dry wt.	a
River Skerne at Croft-on-Tees	Near to a manufacturer of octabromodiphenyl ether	129 µg/kg dry wt.	a
River Skerne at Newton Aycliffe	Near to a manufacturer of octabromodiphenyl ether	397 µg/kg dry wt.	a
Howden Beck	Near to a manufacturer of octabromodiphenyl ether	264 µg/kg dry wt.	a
River Skerne, upstream of Howden Beck	Near to a manufacturer of octabromodiphenyl ether	333 µg/kg dry wt.	a
River Skerne, downstream of Howden Beck	Near to a manufacturer of octabromodiphenyl ether	1,405 µg/kg dry wt.	a
River Calder at Cock Bridge	Near to a foam manufacturing site	9 µg/kg dry wt.	a
Hyndburn Brook, upstream of wwtp	Near to a foam manufacturing site	3 µg/kg dry wt.	a
River Calder, downstream of sewage treatment works	Near to a foam manufacturing site	17 µg/kg dry wt.	a
Elstow landfill	Landfill receiving brominated wastes	<0.44-13 µg/kg dry wt.	a
Elstow Brook, downstream of landfill site	Landfill receiving brominated wastes	1 µg/kg dry wt.	a
Tees estuary, Portrack wwtp	Industrial area	29 µg/kg dry wt.	a
Tees estuary, Bamlett's Bight	Industrial area	164 µg/kg dry wt.	a
Tees estuary, No. 23 buoy	Industrial area	263 µg/kg dry wt.	a
Tees estuary, Philips approach buoy	Industrial area	1,348 µg/kg dry wt.	a
Great Ouse, The Point, Kings Lynn	Downstream of landfill site	7.9 µg/kg dry wt.	a
River Ribble, Freckleton saltings	Near to a foam manufacturing site	4.4 µg/kg dry wt.	a
River Humber, Paull		29 µg/kg dry wt.	a
Upstream of plastics processor	Decabromodiphenyl ether used	<200 µg/kg dry wt.	b
Downstream of plastics processor	Decabromodiphenyl ether used	<200 µg/kg dry wt.	b
Upstream of warehouse	Decabromodiphenyl ether stored	1,480 µg/kg dry wt.	b
Downstream of warehouse	Decabromodiphenyl ether stored	3,030 µg/kg dry wt.	b

Table 3.10 continued overleaf

Table 3.10 continued Levels of octabromodiphenyl ether in sediment in the United Kingdom

Location	Comment	Level	Ref.
Industrial area, Stockport	Upstream of a site possibly using pentabromodiphenyl ether	<500 µg/kg dry wt.	b
Industrial area, Stockport	Downstream of a site possibly using pentabromodiphenyl ether	<500 µg/kg dry wt.	b
Mersey estuary	Industrial area, upstream of polymer processing site	<500 µg/kg dry wt.	b
Mersey estuary	Industrial area, downstream of polymer processing site	<500 µg/kg dry wt.	b
Wales, upstream of a plastics compounder	Decabromodiphenyl ether used	<200 µg/kg dry wt.	b
Wales, downstream of a plastics compounder	Decabromodiphenyl ether used	<200 µg/kg dry wt.	b
Landfill site	Pentabromodiphenyl ether waste disposed on-site	<500 µg/kg dry wt.	b

References: a) Law et al., 1996; Allchin et al., 1999.
                      b) Environment Agency, 1997.

Table 3.11 Levels of octabromodiphenyl ether in sediment from the rest of the world

Location	Comments	Level	Reference
Japan, 1987	Detection limit 7 µg/kg	Detected in 3/51 samples at 8-21 µg/kg	Environment Agency Japan, 1991
Japan, 1988	Detection limit 5 µg/kg	Detected in 3/135 samples at 15-22 µg/kg	Environment Agency Japan, 1991

The Environment Agency (2002) reported the levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether (and 2,2,3,4,4',5'-hexabromodiphenyl ether, 2,2',4,4',5,5'-hexabromodiphenyl ether and 2,2',4,4',5,6'-hexabromodiphenyl ether) in sediments near to a octabromodiphenyl ether production site. Production of the substance (and pentabromodiphenyl ether) at the site ceased in the late 1990s, but octabromodiphenyl ether may currently be imported to the site. It is also possible that other sources of these substances may exist in the area. The samples were taken from the River Skerne area of the United Kingdom. The concentrations measured were in the range 0.019 to 2.33 mg/kg dry weight for 2,2',3,4,4',5',6-heptabromodiphenyl ether, 0.010 to 0.56 mg/kg dry weight for 2,2,3,4,4',5'-hexabromodiphenyl ether, 0.010 to 0.85 mg/kg dry weight for 2,2',4,4',5,5'-hexabromodiphenyl ether and 0.003 to 0.73 mg/kg dry weight for 2,2',4,4',5,6'-hexabromodiphenyl ether.

Heemken et al. (2001) found that heptabromodiphenyl ethers (major components of commercial octabromodiphenyl ether) were not present in 20 sediments from the River Elbe. Few other details of this study were given.

Kemmlein (2000) reported results from analysis on sediment samples from the Berlin area in Germany. In most samples, heptabromodiphenyl ethers, octabromodiphenyl ethers and nonabromodiphenyl ethers were not detectable. At one location the sediment contained a non-identified heptabromodiphenyl ether isomer at 1.35 µg/kg dry weight, three non-identified octabromodiphenyl ether isomers at 11.53 and 13.69 µg/kg dry weight (two isomers together), and three non-identified nonabromodiphenyl ether isomers at 2.8, 5.4 and 7.6 µg/kg dry weight

respectively (all concentrations were reported on a sediment wet weight basis). Three other locations provided samples where the three octabromodiphenyl ether isomers were present, but below the limit of quantitation of the method used (in one sample one isomer was present at 0.26 µg/kg dry weight). A number of other samples contained one or more of the nonabromodiphenyl isomers at levels up to 1.5 µg/kg dry weight.

A recent detailed investigation into the levels of 2,3,3',4,4',5,5'-heptabromodiphenyl ether in sediment from the Western Scheldt, the Netherlands and River Tees, the United Kingdom has been reported (de Boer et al., 2001). For the Western Scheldt, 19 samples (each sample was a composite of 9 sub-samples) were collected and 2,3,3',4,4',5,5'-heptabromodiphenyl ether was not found in any of the samples analysed (the detection limit ranged from 0.11 to 0.78 µg/kg dry weight. For the Tees, a total of 50 samples were analysed representing the upper Tees (source to Croft on Tees), middle Tees (Croft on Tees to the Tees Barage), lower Tees (Tees Barage to Tees mouth) and Tees estuary (Tees mouth and Tees bay). 2,3,3',4,4',5,5'-Heptabromodiphenyl ether was not found (<0.2 µg/kg dry weight) in samples from the upper Tees. The level in the middle Tees was generally <0.2 µg/kg dry weight, but levels of 0.45 and 0.71 µg/kg dry weight were measured at two sites upstream of the confluence with the River Skern. In the lower Tees the concentration found was again <0.2 µg/kg dry weight. Finally in the Tees Estuary 2,3,3',4,4',5,5'-heptabromodiphenyl ether was generally not found (<0.05 - <0.2 µg/kg dry weight), with a level of 0.11 µg/kg dry weight being reported for one site.

In addition to these, de Boer et al. (2001) also carried out analysis of several sediment cores (German Bight, Skagerak, Birkat Ram, Meerfelder Maar, Eifel, Drammenfjord, Wester Wadden Sea, Lake Woserin in order to determine any time trends in the levels of 2,3,3',4,4',5,5'-heptabromodiphenyl ether (and other polybrominated diphenyl ethers) present. The results from the cores showed that generally the majority of the polybrominated diphenyl ethers became present from the late nineteen sixties, with decabromodiphenyl ether becoming present around a decade later. However, no 2,3,3',4,4',5,5'-heptabromodiphenyl ether was detected in any sample (detection limits were in the range 0.1-2 µg/kg dry weight).

The final part of the de Boer et al. (2001) study investigated recent trends in the levels of 2,3,3',4,4',5,5'-heptabromodiphenyl ether in sediments from locations in the Netherlands (Roer, Rhine, Waal, Hollands Diep, Haringvliet East, Nieuwe Merwede, Meuse (Eijsden and Keisersveer), United Kingdon (Clyde, Humber, River Tyne, River Skern, Liverpool Bay and River Mersey and Ireland (Liffey). No 2,3,3',4,4',5,5'-heptabromodiphenyl ether was found in any sample (detection limits were 0.05-0.75 µg/kg dry weight), except for a sample from the Clyde (0.48 µg/kg dry weight) and River Skern (2.6 µg/kg dry weight)

A recent study has measured the concentration of 2,2',3,4,4',5',6-heptabromodiphenyl ether in sediments from Hamburg Harbour and the Danube River. The first part of the study (Sawal et al., 2002a) investigated the levels in sediment from Hamburg Harbour as part of the analytical method development. In all, eight samples were analysed and the heptabromodiphenyl ether was found in all eight samples at a concentration of 0.14-0.31 µg/kg dry weight.

The second part of the study (Sawal et al., 2002b) determined the levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether in sediments from the Danube River and its main tributaries. In all, 26 samples were analysed from sites in Germany, Austria, Slovakia, Hungary, Croatia, Yugoslavia, Bulgaria, Romania, Moldova and Ukrane during the summer of 2001. The heptabromodiphenyl ether was found at levels from not detected to 0.82 µg/kg dry weight (the detection limit of the method was around 0.01-0.05 µg/kg dry weight). The median level found was 0.11 µg/kg dry weight.

The measured levels for octabromodiphenyl ether show that elevated concentrations occur in areas near to a manufacturing site (production of octabromodiphenyl ether no longer occurs at this site). The levels detected (up to 1.4 mg/kg dry weight (~0.53 mg/kg on a wet weight basis, assuming the sediment is 62% water by weight (80% water by volume) (TGD defaults))), are lower than the predicted concentration for a production site of 1,236 or 207 mg/kg wet weight by around a factor of 400-2,500. This may be due to the actual releases being lower or dilution at the site being higher than those used in the assessment. Nevertheless, the monitoring data show that octabromodiphenyl ether is present in sediments in the vicinity of the site. Recent monitoring data from 2002 from the same area show that the components of the commercial octabromodiphenyl ether are present at similar levels (up to 2.3 mg/kg dry weight).

The measured levels octabromodiphenyl ether in other industrial areas are generally around 20-200 µg/kg dry weight (~8-76 µg/kg wet weight assuming sediment is 62% water by weight). The predicted regional concentration of 190-390 µg/kg wet weight is slightly higher than these levels. Higher levels, up to 3,000 µg/kg dry weight (~1,140 µg/kg wet weight assuming sediment is 62% water by weight) have been measured. It is not clear what the source of octabromodiphenyl ether is in these samples, but it could be as a result of polymer processing activity. The PEC_{local} of 8.0 mg/kg wet weight, calculated for releases from polymer processing, is in reasonable agreement with this level.

The measured background level of octabromodiphenyl ether is typically <0.44 µg/kg dry weight, indicating that octabromodiphenyl ether does not appear to be transported far from the source of release. This is consistent with the physical chemical properties of the substance that indicate that the substance would adsorb strongly on to sediment and would not be very mobile in the environment.

3.1.3 Terrestrial compartment

3.1.3.1 Predicted concentrations

No information is available about the direct application/disposal of octabromodiphenyl ether to soil. The Technical Guidance Document does give default release figures to soil from production (see Section 3.1.1.1) but information provided by industry suggests that, at the time that production was occurring in the EU, the majority of waste material was disposed of to landfill. No direct release of octabromodiphenyl ether to soil was assumed in the following calculations.

It is also possible that octabromodiphenyl ether may reach the soil compartment either through application of sewage sludge containing it or by dry/wet deposition of the substance from the atmosphere. The Technical Guidance outlines methods to estimate the contribution of these two processes to levels in soil. These two processes are included in the EUSES model and this was used to estimate soil concentrations for octabromodiphenyl ether in the local, regional and continental scenarios. Further details of the model are given in Section 3.1.2.1.3 and Appendix B. The PECs estimated are shown in **Table 3.12**.

Table 3.12 Predicted concentrations of octabromodiphenyl ether in soil

Scenario	Type of soil	Predicted concentration (wet weight basis)	
		1994 data	**1999 data**
PEC$_{local}$ - polymer processing	Grassland, averaged over 180 days	1.40 mg/kg	1.34 mg/kg
	Agricultural soil, averaged over 30 days	3.30 mg/kg	3.25 mg/kg
	Agricultural soil, averaged over 180 days	3.30 mg/kg	3.25 mg/kg
PEC$_{regional}$	Agricultural soil	0.123 mg/kg	0.047 mg/kg
	Natural soil	0.125 mg/kg	0.061 mg/kg
	Industrial soil	8.82 mg/kg	4.26 mg/kg
PEC$_{continental}$	Agricultural soil	0.040 mg/kg	0.018 mg/kg
	Natural soil	0.055 mg/kg	0.027 mg/kg
	Industrial soil	0.944 mg/kg	0.457 mg/kg

The major source of octabromodiphenyl ether on agricultural land in the local scenario is likely to be from spreading of sewage sludge. Thus, it can be concluded that there is the potential for high concentrations of octabromodiphenyl ether to occur in agricultural soil if substantial releases to wastewater treatment plants occur.

The concentration in natural soil was estimated to be around 61-125 μg/kg wet weight in the regional scenario and 27-55 μg/kg wet weight in the continental scenario. Here, atmospheric deposition may be an important route of exposure. The concentrations predicted in industrial soils are dominated by the contribution from emissions of "waste remaining in the environment".

Since octabromodiphenyl ether is a persistent substance, the levels found in soil might be expected to build up with time. The regional and continental concentrations estimated above are "steady state" concentrations, and represent the concentrations 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 octabromodiphenyl ether it is estimated that after 10 years the concentrations predicted represent around 0.4-0.5% of the "steady state" value. This means that higher concentrations would be predicted if longer application periods were considered. Also, although atmospheric deposition only makes a small contribution to the predicted local concentrations in soil, it could, over very long time periods also contribute to a build up in soil (as is seen in the regional modelling).

3.1.3.2 **Measured levels**

No information is available on the measured levels of octabromodiphenyl ether in soil.

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 octabromodiphenyl ether are shown in **Table 3.13**.

Table 3.13 Levels of polybrominated diphenyl ethers in sewage sludge applied to agricultural land

Component	Level (µg/kg dry weight)
Hexabromodiphenyl ether	0-1.21
Heptabromodiphenyl ether	nd-0.46

The Environment Agency (2002) reported the levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether (and 2,2,3,4,4',5'-hexabromodiphenyl ether, 2,2',4,4',5,5'-hexabromodiphenyl ether and 2,2',4,4',5,6'-hexabromodiphenyl ether) in sewage sludge from a treatment plant receiving effluent from a site where octabromodiphenyl ether had been produced in the past (Environment Agency, 2002). Production of the substance (and pentabromodiphenyl ether) at the site ceased in the late 1990s, but octabromodiphenyl ether may currently be imported to the site. It is also possible that there may be other sources of these substances in the area sampled. The concentrations measured were 0.11 mg/kg dry weight for 2,2',3,4,4',5',6-heptabromodiphenyl ether, 1.48 mg/kg dry weight for 2,2,3,4,4',5'-hexabromodiphenyl ether, 1.63 mg/kg dry weight for 2,2',4,4',5,5'-hexabromodiphenyl ether and 1.73 mg/kg dry weight for 2,2',4,4',5,6'-hexabromodiphenyl ether.

Weisser (1992) analysed sewage sludge from ten wastewater treatment plants in Germany. The plants served rural areas, medium sized towns, or large cities, and received differing amounts of industrial wastewater. Octabromodiphenyl ether and nonabromodiphenyl ether (isomers not specified) were only detected in samples from the plants serving large cities, in the range <0.01-0.311 mg/kg dry weight (octabromodiphenyl ethers) and <0.05-0.95 mg/kg dry weight (nonabromodiphenyl ether). A non-identified heptabromodiphenyl ether isomer was found in both rural and city plants, at a mean level of 0.011 mg/kg dry weight in the rural plants and 0.112 mg/kg dry weight in the city plants. In general, samples of digested sludge contained higher levels than raw sludge.

These measured levels are considerably lower than the concentration of 217 mg/kg dry weight predicted for sewage sludge from local releases from polymer processing. The source of the polybrominated diphenyl ethers in the German sewage sludge samples is unknown.

3.1.4   Levels in air

3.1.4.1   Predicted levels

Using the EUSES program, very low levels of octabromodiphenyl ether in air are predicted in all scenarios considered (see Section 3.1.2.1.3 and Appendix B). As well as direct emissions to air, a small fraction (~0.094%) of the emissions to wastewater treatment plants are also estimated by EUSES to be emitted to air. The estimated concentrations are shown in **Table 3.14**.

Table 3.14 Predicted concentrations of octabromodiphenyl ether in air

Scenario	Comment	Predicted concentration	
		1994 data	**1998 data**
PEC_{local}(air) - polymer processing	Concentration during emission episode	$5.2 \cdot 10^{-5}$ mg/m³	$5.2 \cdot 10^{-5}$
	Annual average concentration	$1.5 \cdot 10^{-5}$ mg/m³	$4.3 \cdot 10^{-6}$
$PEC_{regional}$(air)		$2.8 \cdot 10^{-7}$ mg/m³	$1.4 \cdot 10^{-7}$
$PEC_{continental}$(air)		$1.2 \cdot 10^{-7}$ mg/m³	$6.0 \cdot 10^{-8}$

3.1.4.2　　　　　Measured levels

Bergander et al. (1995) analysed air samples from two areas of Sweden for the presence of octabromodiphenyl ether. The areas sampled were Ammarnäs (located on approximately N 65° 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. No octabromodiphenyl ether was found in either the particulate or gas phase samples (the detection limit of the method given was not stated). Indications of the presence of hexabromodiphenyl ether and heptabromodiphenyl ether were found in the particulate phase samples.

No other information is available on the measured levels of octabromodiphenyl ether in air. Information on hexabromodiphenyl ethers (see risk assessment report of pentabromodiphenyl ether (EC, 2000b)) and heptabromodiphenyl ethers (both possible components of commercial octabromodiphenyl ether) is available.

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/m³ and 100 pg/m³ at two sites respectively (DETR, 1999).

The concentration of 2,3,3',4,4',5,6-heptabromodiphenyl ether in air samples from urban (Chicago), rural (Sleeping Bear Dunes on the northeast coast of Lake Michigan and Sturgeon Point on Lake Erie) and remote (Eagle Harbour on Lake Superior) sites in the Great Lakes area (Strandberg et al., 2001). Air samples (both particulates and gas phase) were taken over 24 hours. The average temperature was $20\pm3^{\circ}$C at the time of sampling, and four samples each for the years 1997, 1998 and 1999 were analysed and the mean concentration reported was below the limit of detection of the method used (<0.049-<0.069 pg/m³).

The levels of seven polybrominated diphenyl ether in rain in southern Sweden have been reported (ter Schure and Larsson). The total concentration of polybrominated diphenyl ethers measured in rain was 127 ± 57 pg/l. Bulk deposition samples were used over a 2 week period to determine the deposition rates for 2,2',3,4,4',5',6-heptabromodiphenyl ether (a possible component of commercial octabromodiphenyl ether). These were reported to be 33 pg m^{-2} day^{-1} for the substance in the particulate phase and 131 pg m^{-2} day^{-1} for the substance in the dissolved phase.

Bergman et al. (1997b) looked for the presence of 2,2',3,4,4',5',6-heptabromodiphenyl ether in indoor air where office equipment was used. Particulates in the air were sampled, but no

2,2',3,4,4',5',6-heptabromodiphenyl ether was found in any of the samples (the detection limit of the method is not give).

The levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether in air at another electronic equipment dismantling plant in Sweden were found to be 6.3-87 ng/m^3. The level present in office air was reported to be at most 0.08 ng/m^3 (Sjödin et al., 1999).

3.1.4.3   Comparison of measured and predicted levels

Most of the available information relates to levels of heptabromodiphenyl ether (possible components of commercial octabromodiphenyl ether products) in air and dust at electronic equipment dismantling plants and other locations where human exposure could occur, and so is not directly related to the calculated PECs. This type of information is most relevant to the human health assessment, but it does show that particulate or dust emissions of octabromodiphenyl ether could occur, particularly during the dismantling of electrical equipment. This indicates that the "waste in the environment" considered in this assessment is a possible route by which octabromodiphenyl ether could reach the environment.

3.1.5   Secondary poisoning

3.1.5.1   Predicted concentrations

Concentrations for octabromodiphenyl ether for various parts of the food chain have been calculated using the EUSES model (see Section 3.1.2.1.3 and Appendix B). The results relevant for the assessment of secondary poisoning are shown in **Table 3.15**. The results for the indirect exposure of humans via the environment are shown in Section 4.

Table 3.15 Predicted concentrations for secondary poisoning

Source		Predicted concentration	
		1994 data	**1999 data**
Polymer processing	Concentration in fish	0.18 µg/kg wet weight	0.057 µg/kg wet weight
	Concentration in earthworms	5.57 mg/kg	5.34 mg/kg

In the model, a measured BCF value for fish of 4 was used, but the other necessary (bio)concentration factors for octabromodiphenyl ether have been estimated from the octanol-water partition coefficient. This approach may overestimate the expected concentration of octabromodiphenyl ether in food. This is because octabromodiphenyl ether has a very high octanol - water partition coefficient and as a result many of these bioconcentration factors have been estimated to be very high. It is also not known if all the estimation methods are valid for substances with very high log Kow values.

The available experimental evidence suggests that octabromodiphenyl ether itself does not bioconcentrate and so would not be expected to bioaccumulate and enter into the food chain. However, the commercial product contains small amounts of hexabromodiphenyl ether which has been shown to bioconcentrate in fish (see Section 3.1.1.5.3), and hexabromodiphenyl ether and other components such as heptabromodiphenyl ether have been found to be present in

organisms (see Section 3.1.5.2). Thus it is probable that some components of the commercial product are more bioaccumulative than octabromodiphenyl ether itself. This is considered further in Appendix E and in Section 3.3.

3.1.5.2 Measured levels

The levels of octabromodiphenyl ether in biota samples are shown in **Table 3.16** (United Kingdom) and **Table 3.17** (Other areas).

Table 3.16 Levels of octabromodiphenyl ether in biota from the United Kingdom

Species	Location	Level (µg/kg wet weight)	Reference
Dab (liver)	Off River Tees, UK	325	Law et al., 1996; Allchin et al., 1999
	Off the Wash, UK	18	Law et al., 1996; Allchin et al., 1999
	Bideford Bay, UK	<1	Law et al., 1996; Allchin et al., 1999
	Tees Bay, UK	179	Law et al., 1996; Allchin et al., 1999
Dab (muscle)	Bideford Bay, UK	9.7	Law et al., 1996; Allchin et al., 1999
	Tees Bay, UK	6	Law et al., 1996; Allchin et al., 1999
Whiting (liver)	Bristol Channel, UK	<1	Law et al., 1996; Allchin et al., 1999
Flounder (liver)	Off Lune/Wyre, UK	14	Law et al., 1996; Allchin et al., 1999
	Off River Humber, UK	126	Law et al., 1996; Allchin et al., 1999
	Nith estuary, UK	<1-16 (2 samples)	Law et al., 1996; Allchin et al., 1999
	Bideford Bay, UK	19	Law et al., 1996; Allchin et al., 1999
	Tees Bay, UK	115	Law et al., 1996; Allchin et al., 1999
Flounder (muscle)	Nith estuary, UK	<1 (2 samples)	Law et al., 1996; Allchin et al., 1999
	Bideford Bay, UK	<1	Law et al., 1996; Allchin et al., 1999
	Tees Bay, UK	7	Law et al., 1996; Allchin et al., 1999
Plaice (muscle)	Bideford Bay, UK	3.3	Law et al., 1996; Allchin et al., 1999
	Tees Bay, UK	12	Law et al., 1996; Allchin et al., 1999
Plaice (liver)	Bideford Bay, UK	<1	Law et al., 1996; Allchin et al., 1999
	Tees Bay, UK	41	Law et al., 1996; Allchin et al., 1999
Winkles	River Tweed	<1	Law et al., 1996; Allchin et al., 1999
Mussels	The Wash, UK	16	Law et al., 1996; Allchin et al., 1999

Table 3.17 Levels of octabromodiphenyl ether in biota from the rest of the world

Location	Comments	Level	Reference
Japan, 1987	Detection limit 5 µg/kg	Not detected in 75 samples	Environment Agency Japan, 1991
Japan, 1988	Detection limit 4 µg/kg	Not detected in 144 samples	Environment Agency Japan, 1991

As stated in the introduction to Section 3.1.2.2, the analysis of commercial octabromodiphenyl in biota samples is complicated by the lack of analytical standards for many of the individual components of the mixture. Thus, in many analyses, identification and quantitation is carried out by comparing the chromatographic peaks obtained from the sample with those found in the commercial product. This is a particular problem for octabromodiphenyl ether since it was found in a bioaccumulation experiment (see Section 3.1.1.5.3) that uptake by fish of the lower brominated diphenyl ethers is greater than for the components with a higher degree of bromination. Thus the distribution of congeners found in fish from the environment is unlikely to be the same as that seen in the commercial products used for identification and quantitation. Further, some components of commercial octabromodiphenyl ether (notably hexabromodiphenyl ether) are common to both commercial octabromodiphenyl ether and pentabromodiphenyl ether. This adds further uncertainty to the analysis of octabromodiphenyl ether in biota samples. Thus, until certified reference material is available for most of the components of commercial octabromodiphenyl ether, the results of the analyses should be treated with caution. Although the data show that some components of commercial octabromodiphenyl ether have been detected in biota, the actual magnitude of the measured levels is currently subject to some uncertainty.

Some of the more recent studies have been able to analyse for the presence of individual hexabromodiphenyl ether and heptabromodiphenyl ether isomers. The results for the heptabromodiphenyl ether isomers are reported here as they may be major components of the commercial octabromodiphenyl ether products. The hexabromodiphenyl ether levels are reported in the risk assessment report for pentabromodiphenyl ether (EC, 2000b).

Information on the levels of some heptabromodiphenyl ethers in biota has recently become available. This information is relevant to the assessment as the commercial octabromodiphenyl ether products contain a substantial (~44%: see Section 1.1) amount of heptabromodiphenyl ethers.

Several heptabromodiphenyl ethers have recently been detected in samples of Ontario lake trout and pacific herring (Sergeant et al., 1998). The concentrations present were not given.

Alaee et al. (1999) determined the levels of polybrominated diphenyl ethers in biota from the Canadian environment. The average total 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. Hexa- and heptabromodiphenyl ethers were also detected in some samples.

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, the di-, tri-, hexa- and heptabromodiphenyl ethers were found to account for <10% of the total levels found. The actual levels were only reported in graphical form and so it is not possible to determine the precise concentration of heptabromodiphenyl ether present.

The levels of 2,3,3',4,4',5,6-heptabromodiphenyl ether (and in some cases 2,2',3,4,4',5',6-heptabromodiphenyl ether) in the food chains of the North Sea, Tees estuary, and Western Scheldt have been determined by de Boer et al., 2001. In all 249 samples comprising copepods, prawns, mysid shrimp, *Nereis* sp., whelk, hermit crab, starfish, gudgeon, greater sandeel, herring,

whiting, cod, harbour porpoise, seal, dolphin, common tern egg and cormorant liver were analysed. In all samples, the concentration of the 2,3,3',4,4',5,6-heptabromodiphenyl ether was below the detection limit for the method (the detection limit generally varied between 0.04 and 10 µg/kg lipid, but was up to 100 µg/kg lipid for some species. The 2,2',3,4,4',5',6-heptabromodiphenyl ether isomer was detected in only in 1 sample of cod liver (45 µg/kg lipid), 2 samples of whiting liver (0.2-0.5 µg/kg lipid), 2 samples of harbour seal (2.5-25 µg/kg lipid) and in one sample of dolphin kidney, heart, lung and muscle (13, 27, 38 and 5.2 µg/kg lipid, respectively).

Karasyova et al. (2002) reported the levels of 2,2',3,4,4',5'6-heptabromodiphenyl ether in bream (*Abramis abrama*) and eel (*Anguilla anguilla*) taken from the River Elbe upstream of Dresden in 2001. The detection limit of the method was 0.1-1.3 µg/kg lipid (depending on the lipid content of the sample) and in all 22 samples of bream and five samples of eel were analysed. The heptabromodiphenyl ether was present at a level of up to 0.70 µg/kg lipid in bream and 0.01-0.07 µg/kg lipid in eel. The median concentration found was 0.18 µg/kg lipid in bream and 0.04 µg/kg lipid in eel.

The levels of 2,3,3',4,4',5,6-heptabromodiphenyl ether (and three nonabromodiphenyl ether isomers) have been determined in samples of wild and farmed salmon and salmon feed (Easton et al., 2002). The samples analysed included two salmon feed samples collected in 2000 from Canada, two farmed chinook salmon samples collected in 1999-2000 from Canada, one sample each of wild chinook salmon and chum salmon collected in 2000 from Alaska and two samples of wild chinook salmon collected in 2000 from Canada. 2,3,3',4,4',5,6-heptabromodiphenyl ether was detected at 1.4 ng/kg wet weight in one sample of salmon feed but was below the limit detection (<0.71 ng/kg wet weight) in the remaining samples. No nonabromodiphenyl ether was detected in any sample (detection limit was 1.04 ng/kg wet weight; peaks were detected corresponding to a nonabromodiphenyl ether isomer in one sample of feed and one farmed salmon sample, but the peaks did not meet the quantification criteria of the method used).

Sellström et al. (2001) determined the levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether present in eggs of peregrine falcons (*Falco peregrinus*). The eggs were collected in 1988-1999 from breeding populations from northern Sweden (18 eggs from 18 females), southern Sweden (24 eggs from 17 females) and a captive breeding population from Sweden (10 eggs from 8 females). The heptabromodiphenyl ether was detected in all the samples analysed and the level found in the egg contents was 56-1,300 µg/kg lipid in the wild populations and 6-19 µg/kg lipid in the captive-bred populations. The difference in levels between the captive-bred and wild populations indicates that diet may be an important route of exposure to 2,2',3,4,4',5',6-heptabromodiphenyl ether (the captive birds were fed mainly a diet of chickens).

An octabromodiphenyl ether isomer and 2,2',3,4,4',5',6-heptabromodiphenyl ether have been found to be present in chickens from the United States (Huwe et al., 2001). The chickens analysed were collected either from three locations involved in a dioxin contamination incident, an uncontaminated site or from a grocery. The levels of the octabromodiphenyl ether isomer found in adipose were reported to be not detected-0.12, not detected-0.12 and not detected-0.85 µg/kg lipid in chickens from the dioxin contaminated sites, not detected-0.01 µg/kg lipid in chickens from the uncontaminated site and not detected in chickens from the grocery. The levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether present were 0.03-0.47 µg/kg lipid, 0.01-0.63 µg/kg lipid and 0.13-0.90 µg/kg lipid in chickens from the dioxin contaminated site, 0.05-0.07 µg/kg lipid in chickens from the uncontaminated site and 0.02 µg/kg lipid in chickens from the grocery. The lipid content of the samples was reported to be around 86-96%.

Ryan and Patry (2001) reported the findings from a recent survey of the levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether and 2,3,3',4,4',5,6-heptabromodiphenyl ether in human milk and commercial foods from Canada. The analysis of the substances in these samples was reported to be difficult, and the presence of substances in laboratory blanks made quantification in the samples uncertain. Little or no 2,3,3',4,4',5,6-heptabromodiphenyl ether could be detected in 72 human milk samples from 1992, however 2,2',3,4,4',5',6-heptabromodiphenyl ether was reported to be present at a median level of around 180 ng/kg lipid. In foods, no information on the levels of these substances was provided, however it was reported that the main brominated diphenyl ethers found were 2,2',4,4'-tetrabromodiphenyl ether and 2,2'4,4',5-pentabromodiphenyl ether.

Meironyte, Guvenius and Norén (2001) reported levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether in samples of human milk from Sweden over the years 1998 to 2000. Two pooled samples from each year were analysed (each pooled sample contained milk from 20 mothers) and the levels found were 0.02 μg/kg lipid in 1998, 0.07 μg/kg lipid in 1999 and 0.05 μg/kg lipid in 2000.

The levels of 2,2',3,4,4',5',6-heptabromodiphenyl ether in blood plasma have been measured at <0.025-0.39 μg/kg lipid in hospital workers, <0.02-1.4 μg/kg in computer clerks and 3.1-26 μg/kg in electronic equipment dismantlers (Sjödin et al., 2001). Octa- and nonabromodiphenyl ethers were also found (but not quantified) in plasma samples from electronic equipment dismantlers. Similar levels of 2,2'3,4,4',5',6-heptabromodiphenyl ether of <0.5-1.3 μg/kg lipid, 0.4-0.8 μg/kg lipid, 0.15-4.8 μg/kg lipid and 2.5-12 μg/kg lipid have been reported in the plasma from smelter workers, office workers, computer technicians and electronics dismantlers respectively also from Sweden (Hagmer and Bergman, 2001; Hovander et al., 2001). Similar levels of this isomer in human blood plasma were reported in workers at electronics dismantling plant in Norway (~0.4-0.5 μg/kg lipid), but it was not detected in the plasma from printed circuit board producers or lab personnel (Thomsen et al., 2001a).

These results show that the heptabromodiphenyl ethers appear to be present in a range of biota samples, but only at low levels. This indicates that at least some of the major components of commercial octabromodiphenyl ether have the potential to be taken up by organisms in the environment.

The situation for hexabromodiphenyl ethers is a little more complicated as both commercial pentabromodiphenyl ether and commercial octabromodiphenyl ether products contain hexabromodiphenyl ether isomers and it is not possible to identify the precise source of these substances in organisms in the environment. The available data on levels of hexabromodiphenyl ethers published up to around 2000 are reported in the risk assessment report for pentabromodiphenyl ether (EC, 2000b). These data show that the hexabromodiphenyl ether isomers are found in a wide range of organisms (up to 49 μg/kg lipid in grey seal blubber, 29.2 μg/kg lipid in ringed seal blubber, 370 μg/kg lipid in long-finned pilot whale, 310 μg/kg lipid in steelhead 16.9 μg/kg lipid in salmon, 2.36 μg/kg lipid in sprat, 0.96 μg/kg lipid in herring and 3.74 μg/kg lipid in human adipose). In addition, hexabromodiphenyl ether has also been found in human mothers milk samples. Recently, the results of several new studies reporting levels of hexabromodiphenyl ether in biota have become available. These were generally reported at the Second International Workshop on Brominated Flame Retardants in Stockholm (held on the 14-16 May 2001). The findings of these studies generally confirmed the earlier findings. Thus it was reported that hexabromodiphenyl ethers were present in herring gulls' eggs from the Great Lakes (up to 323 μg/kg wet weight and the levels were thought to have been increasing over the last 19 years with a doubling time of 3.4-5.9 years; Moisey et al., 2001), peregrine falcons' eggs (up to 20,000 μg/kg lipid; Sellström et al., 2001), eggs from birds of prey (levels not given; Herzke et al., 2001), guillemot eggs (mean level ~5 μg/kg lipid; Lundstedt-

Enkel et al., 2001), grey seal (levels not given; Roos et al., 2001), herring (up to 2.2 μg/kg lipid; Nylund et al., 2001), freshwater fish from a sewage treatment plant pond (up to 2,800 μg/kg lipid; Rimkus et al., 2001), salmon and salmon feed from the Alaska and Canada (up to 0.375 μg/kg wet weight in salmon feed, up to 0.277 μg/kg wet weight in farmed salmon and up to 0.010 μg/kg wet weight in wild salmon; Easton et al., 2002), Baltic salmon and pike from Finland (<1 μg/kg lipid; Peltola, 2002), bream and eel from Germany (up to 95.3 μg/kg lipid; Karasyova et al., 2002), human milk samples from Canada (Ryan and Patry, 2001) and Sweden (Lind et al., 2001), human blood plasma from Norway and Sweden (Hagmar and Bergman, 2001; Hovander et al., 2001; Thomsen et al., 2001a), food items from Finland (Strandman et al., 2001) and butter samples from around the world (Jones et al., 2001).

In addition to these studies, the de Boer et al. (2001) study mentioned above also looked for the presence of three hexabromodiphenyl ether isomers in the food chains of the North Sea, Tees estuary and Western Scheldt. Hexabromodiphenyl ethers were found in almost all of the 249 samples analysed and, further, the data indicated that the concentrations present in the marine mammals appeared to be higher than in fish and invertebrates, implying that biomagnification may be occurring the food chain. The maximum levels found (sum of three hexabromodiphenyl ether isomers) in the North Sea food chain were up to 45 μg/kg lipid in starfish, 73.7 μg/kg lipid in hermit crab, 23 μg/kg lipid in whelk, 3.9 μg/kg lipid in shrimp, 8.3 μg/kg lipid in herring liver, 3.2 μg/kg lipid in herring fillet, 1.55 μg/kg lipid in herring mild and eggs, 7.3 μg/kg lipid in cod liver, 3.9 μg/kg lipid in cod filler, 14.1 μg/kg lipid in whiting liver, 4.4 μg/kg lipid in whiting fillet, 1,607 μg/kg lipid in harbour porpoise blubber, 1,560 μg/kg lipid in harbour porpoise liver, 818 μg/kg lipid in harbour seal blubber, 907 μg/kg lipid in harbour seal liver and 1,015 μg/kg lipid in dolphin blubber. In the samples from the Tees estuary the maximum levels found were up to 632 μg/kg lipid in invertebrates, 67 μg/kg lipid in whole sprats, 293 μg/kg lipid in whole whiting, 5.9 μg/kg lipid in flounder liver, 337 μg/kg lipid in porpoise blubber and 1,100 μg/kg lipid in cormorant liver. In the Western Scheldt food chain the maximum levels found were up to 9.3 μg/kg lipid in mysid shrimp, 20 μg/kg lipid in pranus, not detected (<20 μg/kg lipid) in copepods, ~150 μg/kg lipid in gudgeon, ~25 μg/kg lipid in greater sand eel and ~307 μg/kg lipid in cormorant eggs. The levels in whole fish and invertebrates were up to around 1-3 μg/kg on a wet weight basis.

Based on these data, de Boer et al. (2001) estimated biomagnification factors for two hexabromodiphenyl ether isomers (2,2'4,4',5,5'- and 2,2'4,4',5,6'-hexabromodiphenyl ether) for several example food chains. These were displayed graphically in the report. The following approximate values for the biomagnification factors (as read from the graphs) are ~0.6-0.7 for invertebrates to fish, 40-70 for fish to porpoises, 5-10 for fish to seals and 25-40 for invertebrates to seals, all using the North Sea data. Similar high biomagnification factors were estimated using the Western Scheldt data.

3.1.5.3   Comparison of measured and predicted concentrations

The monitoring data indicate that commercial octabromodiphenyl ether is only found in biota at measurable concentrations in industrial areas, particularly where sources of octabromodiphenyl ether are thought to occur. The levels measured are generally of a similar order of magnitude to those predicted in fish. The levels found probably represent the more accumulative, lower brominated congeners present in the commercial formulations.

This is confirmed by the recent monitoring data for some individual components of commercial octabromodiphenyl ether. For example, hexabromodiphenyl ethers have recently been found to occur in many species in the environment, and there is some evidence that the concentration present may increase through the food chain, indicating that biomagnification may be occurring. For heptabromodiphenyl ether, the recent monitoring data indicate that this too is present in some environmental samples at measurable levels, but the occurrence and concentration present is generally lower than found for hexabromodiphenyl ether. There is a general lack of isomer-specific data for octabromodiphenyl ether isomers.

In this respect it is also relevant to consider the available data for decabromodiphenyl ether. These data (see risk assessment report of decabromodiphenyl ether (EC, 2002)) indicate that decabromodiphenyl ether is present in some organisms, particularly those at the top of the food chain, in measurable amounts. This indicates that all components of commercial octabromodiphenyl ether have the potential to be taken up into organisms in the environment. For hexabromodiphenyl ether the available monitoring data are consistent with the substance bioconcentrating in fish and then bioaccumulating in the food chain. However, it is not clear from the available data whether this uptake is occurring via water, food or air for the higher brominated diphenyl ether congeners.

The predicted concentrations in fish for octabromodiphenyl ether itself are consistent with the generally low levels found in fish and so these values will be used in the risk characterisation. However, these values may not take into account sufficiently the more accumulative components of the commercial product and so this will be considered separately in the risk characterisation.

There are no measured data with which to compare the predicted earthworm concentrations. The predicted concentrations will be considered in the risk characterisation, but it is recognised that these may overestimate the actual concentrations present.

The available data on the levels in human breast milk are considered further in the human health risk assessment (Section 4).

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

The interpretation of the toxicity data for commercial octabromodiphenyl ether is not straight forward as the substance is a mixture containing significant amounts of lower brominated diphenyl ethers, notably hexabromodiphenyl ether (the levels of brominated diphenyl ethers with less than six bromines/molecule in current products are now very low and will soon be <0.1% following on from restrictions in the use of pentabromodiphenyl ether). The available data indicate that hexabromodiphenyl ether has a much higher bioconcentration potential than the other components of octabromodiphenyl ether (see Appendix E) and so is likely to have a higher potential to cause adverse effects on organisms in the environment. Wherever possible, the effects of the hexabromodiphenyl ether component of the commercial octabromodiphenyl ether are considered in interpreting the toxicity data. This necessitates the use of data from other polybrominated diphenyl ethers.

3.2.1 Aquatic compartment

3.2.1.1 Toxicity to algae

No data on toxicity to algae are available for commercial octabromodiphenyl ether. It may be possible to estimate this endpoint using the toxicity data available for decabromodiphenyl ether and pentabromodiphenyl ether.

No effects on algal growth were seen with decabromodiphenyl ether at concentrations well in excess of the substance's water solubility (no effects seen at 1 mg/l; see the decabromodiphenyl ether assessment (EC, 2002) for further details).

Given that the main components of commercial octabromodiphenyl ether resemble closely decabromodiphenyl ether in terms of physical properties (log Kow, water solubility; see Appendix E), and it is these properties that are usually considered to be good descriptors for quantitative structure activity relationship (QSAR) analysis of ecotoxicity data, it is likely that octabromodiphenyl ether will also have no effect on algal growth at concentrations below its water solubility. However, consideration also needs to be given to the presence of hexabromodiphenyl ether in the commercial substance.

For pentabromodiphenyl ether, no significant effects were seen in algae exposed over 96 hours to concentrations of up to 26 μg/l of a commercial pentabromodiphenyl ether containing 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether. However, growth inhibition was seen over the first 24 hours, and a 24h-EC_{10} of 2.7-3.3 μg/l was estimated for this end-point, with 10-15% inhibition being seen in at concentrations of 3.3-6.5 μg/l. These effects had disappeared by 48 hours exposure. The results of this study, and significance of the effects seen, are difficult to interpret, as it appears that the test substance was removed from solution (by adsorption onto the algal cells) during the experiment, but it may indicate that the commercial pentabromodiphenyl ether has the potential to cause effects on algae at similar concentrations as seen in long-term studies with *Daphnia magna* (see pentabromodiphenyl ether risk assessment report (EC, 2000b) for further details). The *Daphnia magna* results are discussed further in Section 3.2.1.2.

If it is assumed that the hexabromodiphenyl ether component is of similar toxicity as the commercial pentabromodiphenyl ether formulation (a worst-case assumption) then it is possible

that hexabromodiphenyl ether has the potential to cause effects on algae at similar concentrations as seen in the study with pentabromodiphenyl ether. Again, it should be noted that the significance of the effects seen in the study with commercial pentabromodiphenyl ether is uncertain.

3.2.1.2   Toxicity to invertebrates

A flow-through 21-day reproduction study (OECD 202) has been carried out with *Daphnia magna* (Graves et al., 1997). The study was carried out according to GLP. The octabromodiphenyl ether used in the study was a composite sample from three manufacturers and had the following composition: hexabromodiphenyl ether 5.5%, heptabromodiphenyl ether 42.3%, octabromodiphenyl ether 36.1%, nonabromodiphenyl ether 13.9%, decabromodiphenyl ether 2.1%. Stock solutions of the substance were dissolved in dimethyl formamide and were injected into the diluter mixing chamber of the system such that the solvent concentration was 0.07 ml/l in all tests. A control (no solvent) and solvent control (at a concentration of 0.07 ml/l) were also run. The nominal concentrations of the octabromodiphenyl ether tested were 1.96 µg/l, 0.98 µg/l, 0.49 µg/l, 0.25 µg/l and 0.123 µg/l. The exposure concentrations were verified by measurements (the lowest two concentrations could not be measured but the measured concentrations were 1.7 µg/l, 0.83 µg/l and 0.54 µg/l in the three highest exposures). The concentrations refer to the total commercial product rather than just the octabromodiphenyl ether component (see below). During the test the water hardness was 132-136 mg/l as $CaCO_3$, temperature 20±1°C, dissolved oxygen ~77% saturation and pH 8.2-8.5.

No significant (p >0.05) effects on survival were seen between the exposed and control animals. At the end of the test, the mortality seen in the control and solvent controls was 5% and 0%, respectively. Mortality in the exposed animals was 10%, 0%, 5%, 5% and 5% in the 0.13, 0.25, 0.5, 1.0 and 2.0 µg/l treatments respectively. All surviving adults were normal and healthy. The NOEC for survival was >2.0 µg/l (or >1.7 µg/l based on the measured concentrations).

No significant (p >0.05) effects on reproduction were seen in the exposed animals when compared with controls. Eggs were first observed on day 8 of the test and in general most adults contained eggs in the brood pouch during the reproduction period of the test. No clearly defined dose-response pattern to egg production was observed in the numbers of adults holding eggs in their brood pouch. The adult animals in the control and solvent control groups produced an average of 5.3 and 5.5 live young per reproductive day respectively. The number of live young per reproductive day in the exposed animals was 6.7, 5.2, 5.7, 5.2 and 5.1 in the 0.13, 0.25, 0.5, 1.0 and 2.0 µg/l treatments respectively. No dead or immobile neonates and no aborted eggs were found in any of the treatments. The NOEC for reproduction was >2.0 µg/l (or >1.7 µg/l based on measured concentrations).

The mean length and dry weight of animals in the control and solvent control groups were 4.39 mm, 0.601 mg and 4.42 mm, 0.608 mg, respectively. In the treated animals, the mean lengths were 4.50, 4.50, 4.48, 4.50 and 4.44 mm and the mean dry weights were 0.630, 0.612, 0.609, 0.637 and 0.596 mg in the 0.13, 0.25, 0.50, 1.0 and 2.0 µg/l treatments, respectively. Again, no significant (p >0.05) differences were seen between treated and control animals. The NOEC for growth was >2.0 µg/l (or >1.7 µg/l based on measured concentrations).

The analytical method used in the test consisted of solvent extraction, concentration, followed by analysis by gas chromatography with electron capture detection (GC-ECD). Quantification involved summing the peak areas in the chromatograph corresponding with the hepta-, octa- and

nonabromodiphenyl ether components, using standard solutions of the commercial octabromodiphenyl ether (prepared in diphenyl ether solvent) to construct a calibration curve. 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 allow the following ratios for the peak areas for the hepta- (two components), octa- (two components) and nona- (one component) bromodiphenyl ethers to be estimated: low-concentration calibration standard (prepared in diphenyl ether solvent) hepta:octa:nona 0.57:0.31:0.12; high-level calibration standard (prepared in diphenyl ether solvent) hepta:octa:nona 0.60:0.30:0.10; 0.4 μg/l matrix fortification standard (prepared in same way as test solutions) hepta:octa:nona 0.58:0.29:0.12; 1 μg/l nominal test solution hepta:octa:nona 0.56:0.32:0.12. From these ratios it can be seen that the relative concentrations of the various components of the commercial octabromodiphenyl ether are the same in the standards and the test solution, giving some degree of confidence to the analytical results. No measurements for the hexabromodiphenyl ether component were reported in the test (presumably because the concentration was below the analytical detection limit).

Since octabromodiphenyl ether is a mixture of congeners between hexa- to nonabromodiphenyl ether, some consideration has to be given as to whether the lower brominated components, particularly the hexabromodiphenyl ether, could be more toxic than indicated by the results of the test. In the test, stock solutions of the test substance were prepared by dissolving 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 0.07 ml/l in all cases. 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. Since the hexabromodiphenyl ether component is likely to be the most soluble of all the components in the commercial octabromodiphenyl ether, it is very likely that this component was present in true solution and so the concentration of this component can be estimated from the nominal concentration using the known composition of the commercial substance tested (e.g. 5.5% hexabromodiphenyl ether). Thus the NOEC of >2 μg/l for the commercial compound is equivalent to a NOEC of >0.11 μg/l for the hexabromodiphenyl ether component.

In Appendix E, the water solubility of the hexabromodiphenyl ether component is estimated/extrapolated to be around 4.7 μg/l. Thus it is theoretically possible for the hexabromodiphenyl ether isomers to be present in solution at concentrations higher than those used in this experiment. As part of the 21-day reproduction test carried out for the commercial octabromodiphenyl ether, a range finding 9-day *Daphnia* immobilisation test was carried out using higher nominal concentrations (0.0081, 0.027, 0.09, 0.3 and 1 mg/l) of the commercial octabromodiphenyl ether. Details of the test system used are not reported. Deaths occurred in seven out of the ten exposed *Daphnia* at the 1 mg/l nominal concentration after two to three days but no other mortalities were noted. The number of neonates produced were reported as 32 in the control, 21 in the solvent control, 0 at 0.0081 mg/l, 19 at 0.027 mg/l, 27 at 0.09 mg/l 0 at 0.3 mg/l and 0 at 1.0 mg/l. The significance of these results is unknown. The test concentrations used in this rangefinding test exceed the water solubility of the substance by a considerable amount and thus the mortality seen at 1 mg/l could have been due to a physical effect caused by undissolved test substance. However, it is possible that the effects seen were related to the dissolved chemical. Since the nominal concentration tested was well in excess of the water solubility of the commercial mixture, then each component of the mixture could be present in solution at concentrations close to their individual solubilities. If this is assumed then the effects seen could be due to the most water soluble component of the commercial mixture at a

concentration of around 4.7 µg/l. The results of this analysis should be treated with caution due to the assumptions made, and the fact that the experiment was a rangefinding, rather than definitive, test.

Further information regarding the toxicity of the hexabromodiphenyl ether component to *Daphnia* can be derived from the toxicity results for the commercial pentabromodiphenyl ether (see that assessment for further details of the test). The substance tested had the following composition: 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether and the 48-hour EC_{50} was determined as 14 µg/l and the NOEC was determined as 4.9 µg/l. Similar results were obtained in a 21-day reproduction study using the same test substance, where the NOEC was determined as 5.3 µg/l. If it is assumed that the hexabromodiphenyl ether component is equally as toxic as the commercial formulation (a worst-case assumption) then it is possible that the NOEC for the hexabromodiphenyl ether component would also be around 5 µg/l.

3.2.1.3   Toxicity to fish

An acute toxicity test using adult orange-red killifish (*Oryzias latipes*) has been carried out using octabromodiphenyl ether. The octabromodiphenyl ether tested was a mixture of congeners with between six and ten bromine atoms/molecule, with hepta, octa and nonabromodiphenyl ethers accounting for around 86% of the total. The fish used had an average body weight of 0.32 g and a dispersing agent (polyoxyethylene hydrogenated castor oil) was used to help maintain octabromodiphenyl ether in solution. The 48-hour LC_{50} for octabromodiphenyl ether was determined as >500 mg/l at 25°C. At this concentration, the concentration of the dispersing agent was around 20 g/l (CITI, 1992).

In this test, as the concentration of the substance tested was very high, it is likely that the concentration of the individual components of the mixture were present in solution at around their individual solubility limits. As no effects were seen it can be concluded that none of the components of commercial octabromodiphenyl ether are likely to cause toxic effects to fish in acute exposures. Further evidence for this comes from the fact that no toxic effects were seen with commercial pentabromodiphenyl ether (containing around 11.7% of a hexabromodiphenyl ether) at concentrations up to 500 mg/l over 48 hours with *Oryzias latipes* or concentrations up to 21 µg/l over 96 hours with *Oncorhynchus mykiss* (see the pentabromodiphenyl ether assessment for further details).

Further information regarding the toxicity of the hexabromodiphenyl ether component to fish can be derived from the results of a recent fish early life stage test with *Oncorhynchus mykiss* that has been carried out with a commercial pentabromodiphenyl ether (see that assessment for further details of the test). The substance tested had the following composition: 0.23% tribromodiphenyl ether, 36.02% tetrabromodiphenyl ether, 55.1% pentabromodiphenyl ether and 8.58% hexabromodiphenyl ether and the 87-day NOEC from the study was determined as 8.9 µg/l. Since the water solubility of hexabromodiphenyl ether is thought to be around 4.7 µg/l it is unlikely that hexabromodiphenyl ether would be able to cause effects on fish at concentrations up to its water solubility (this assumes that the hexabromodiphenyl ether component would be equally as toxic as the commercial formulation tested).

3.2.1.4 QSAR data

The high octanol-water partition coefficient of the commercial octabromodiphenyl ether (log Kow = 6.29) means that it is not ideally suited for QSAR predictions (generally only valid for substances with log Kow between -1 and 6). Aquatic toxicity predictions have been obtained using the equations given for non-polar narcosis in Appendix II of Chapter 4 in the Technical Guidance Document. The results are shown below.

$$96\text{h-LC}_{50} \text{ for fish} = 1.8 \cdot 10^{-7} \text{ mol/l} = 147 \text{ µg/l}$$
$$28\text{d-NOEC for fish} = 1.1 \cdot 10^{-8} \text{ mol/l} = 8.8 \text{ µg/l}$$
$$48\text{h-EC}_{50} \text{ for } Daphnia = 5.1 \cdot 10^{-8} \text{ mol/l} = 40.6 \text{ µg/l}$$
$$16\text{d-NOEC for } Daphnia = 3.5 \cdot 10^{-9} \text{ mol/l} = 2.8 \text{ µg/l}$$
$$72\text{-}96\text{h-EC}_{50} \text{ for algae} = 3.0 \cdot 10^{-8} \text{ mol/l} = 24.2 \text{ µg/l}$$

The predicted NOECs and L(E)C$_{50}$s are all greater than the water solubility of octabromodiphenyl ether. The predicted NOEC of 2.8 µg/l for *Daphnia* does not conflict with the experimental NOEC of >2 µg/l seen in a 21-day study.

3.2.1.5 Toxicity to sediment organisms

Prolonged sediment toxicity tests using octabromodiphenyl ether have been carried out with the oligochaete *Lumbriculus variegatus* using a flow-through test system with sediments of either 2.4% organic carbon content (Krueger et al., 2001a) or 5.9% organic carbon content (Krueger et al., 2001b). The test protocol was based on the ASTM E 1706-95b Guideline and US EPA Series 850 Ecological Effects Test Guidelines (OPPTS No. 850.1736).

The sediment used in the test was an artificial sediment consisting of 0.01% humic acid, 0.5% dolomite and either 5% alpha cellulose, 14% kaolin clay and 80% industrial quartz sand (for the 2.4% organic carbon content sediment) or 16% alpha cellulose, 10% kaolin clay and 74% industrial quartz sand (for the 5.9% organic carbon content sediment). The alpha cellulose acted as the source of organic matter in the sediment.

The test substance was supplied from a current manufacturer and had a bromine content of 78.6%. The test substance was weighed directly into the dry sediment. The sediment/test substance mixture was then mixed for 24 hours. After mixing, 100 ml of the spiked sediment was placed in 300 ml glass beakers and placed into diluter tanks and overlying water (approximated 100-150 ml of moderately hard (130 mg/l as CaCO$_3$) well water that was filtered to 0.45 µm to remove microorganisms) was allowed to flow through the test system. The system was allowed to equilibrate for approximately 48 hours prior to addition of the test organisms. The flow-rate through the system provided approximately two volume additions of water/day and the representative depth of water in the tanks was 6.4-7.8 cm. The total exposure period was 28 days.

The nominal concentrations tested in the studies were 94, 188, 375, 750 and 1,500 mg/kg dry weight, plus a control group. Each treatment and control group was replicated eight times with ten oligochaetes/replicate. Additional replicates were also run in each treatment and control group for analytical sampling of water and sediment.

During the tests the temperature was maintained at 23±2°C and the pH was in the range 7.6 to 8.4 in the test with the 2.4% organic carbon sediment and 7.5 to 8.3 in the test with the 5.9% organic carbon sediment. The dissolved oxygen concentration fell below 60% of saturation on

day 10 of the test with the 2.4% organic carbon sediment (the minimum dissolved oxygen concentration reached was 3.8 mg/l or 45% of saturation in treatment). At all other times in the test with the 2.4% organic carbon content sediment, and at all sampling times in the test with the 5.9% organic carbon sediment, the dissolved oxygen concentration was >60% saturation.

The organisms were fed salmon starter during the tests. A 20 mg aliquot of food was added to each test compartment every three days during the tests. The food was not spiked with octabromodiphenyl ether. The revised Technical Guidance Document (EC, 2003) indicates that for highly adsorptive substances such as octabromodiphenyl ether, food could be an important exposure pathway in this type of sediment toxicity test, and recommends that the test method used should try to ensure that exposure via this route cannot be avoided in the test. In this case, as octabromodiphenyl ether was not present in food, it is possible that the results of the test could underestimate the actual toxicity, although the significance of this route of exposure for octabromodiphenyl ether is unknown.

The endpoints investigated in the studies were survival/reproduction (as measured by the total number of organisms present which is a combination of parent survival and reproduction) and growth (as determined by dry weight of organism).

In the experiment with the 2.4% organic carbon sediment, all replicates appeared normal, with no signs of mortality or abnormal behaviour being seen in any treatment or control group. The mean number of worms present at test termination and the average dry weight/worm at the end of the study is shown in **Table 3.18**. At the end of the test, except for one replicate in the 188 mg/kg dry wt. treatment and two replicates in the 750 mg/kg dry wt. treatment, there was an increase in the number of worms present, indicating that reproduction had occurred. No statistically significant (p=0.05) differences were found between the mean number of worms present in the treatment groups when compared with the control groups. For the mean dry weight/worm, statistically significant differences were found between all treatment groups and the control group. The report indicated that this reduction in the individual worm weights was primarily the result of fewer worms, each with higher weights, being present in the control group than in the treatment groups. The average biomass/replicate was also given in the test report. These were 27.7 mg for the control group, and 24.9 mg, 27.9 mg, 25.0 mg, 24.4 mg and 24.1 mg for the 94, 188, 375, 750 and 1,500 mg/kg dry wt. treatments respectively. The report indicated that that these data showed that although the mean weight/worm present in the treatment groups was significantly reduced compared with the control group, the total biomass present was similar to the control group. Thus the paper concluded that the reduction in the mean dry weight/worm was not treatment related. Therefore the overall NOEC from this study was reported as >1,500 mg/kg dry weight based on the nominal concentration.

In the test with the 5.9% organic carbon sediment no signs of abnormal behaviour or mortality were seen during the test. The mean number of worms present at test termination and the average dry weight/worm at the end of the study is shown in **Table 3.18**. With the exception of one replicate in the 188 mg/kg treatment group, there was an increase in the number of worms in all treatment and control replicates. The mean number of worms present in the treatment groups were not statistically significantly different from the control group (p=0.05) at any treatment level. No statistically significant effects were seen on the mean dry weight/worm between any treatment group and the control group. Therefore the overall NOEC from this study was reported as ≥1,500 mg/kg dry weight based on the nominal concentration.

Table 3.18 Results of toxicity test with *Lumbriculus variegatus* in sediment

Treatment (mg/kg dry weight)	2.4% Organic carbon sediment		5.9% Organic carbon sediment	
	Mean number of worms/replicate	Mean dry weight/worm (mg)	Mean number of worms/replicate	Mean dry weight/worm (mg)
Control	11.6	2.38	13.4	1.09
94	14.8	1.69 *	16.4	1.02
188	14.4	1.97 *	12.6	1.18
375	13.1	1.94 *	14.3	1.07
750	11.8	2.08 *	16.6	1.04
1,500	12.8	1.91 *	13.3	1.29

* Statistically significant difference from control group (p=0.05)

During the studies, the concentration of octabromodiphenyl ether present in the sediment, overlying water and pore water phases of the test medium were determined analytically. These results are shown in **Table 3.19**. These show that the concentration of octabromodiphenyl ether in the sediment phase remained relatively constant throughout the test. The high concentration of octabromodiphenyl ether in the pore water probably reflects the fact that sediment-bound substance may also have been analysed in this fraction, along with octabromodiphenyl ether in the dissolved phase.

Based on the analytical results, the NOECs from these studies based on measured concentrations are ≥1,340 mg/kg dry weight for the 2.4% organic carbon sediment and ≥1,272 mg/kg dry weight for the 5.9% organic carbon sediment.

The amount of hexabromodiphenyl ether component present in the commercial octabromodiphenyl ether tested was not given. If it is assumed that the test substance contained 5.5% hexabromodiphenyl ether (typical of current products) then the estimated NOECs for the hexabromodiphenyl ether component alone based on these results would be ≥74 mg/kg dry weight for the 2.4% organic carbon content sediment and ≥70 mg/kg dry weight for the 5.9% organic carbon content sediment.

Table 3.19 Measured concentrations during toxicity test with *Lumbriculus variegatus*

Treatment - nominal sediment concentration (mg/kg dry wt.)	Sampling time	2.4% Organic carbon sediment			5.9% Organic carbon sediment		
		Dry sediment (mg/kg)	Overlying water (µg/l)	Pore water (µg/l)	Dry sediment (mg/kg)	Overlying water (µg/l)	Pore water (µg/l)
Control	Day 0	<0.354	<1.20	<2.86	<12.5	<1.20	<2.61 [a]
	Day 7	<0.354	<1.20	<3.43	<12.5	<1.20	<3.75 [a]
	Day 28	<0.354	<1.20	<4.80	<12.5	<1.20	<4.62 [a]
94	Day 0	72.1-86.9	<1.20	917	76.3-95.1	<1.20	0.545 [a]
	Day 7	65.2-72.9	<1.20	163	82.6-118	<1.20	0.442 [a]
	Day 28	68.8-94.5	<1.20	368	79.6-92.3	<1.20	0.805 [a]
	Mean	76.7	<1.20	306	90.7	<1.20	0.597 [a]
750	Day 0	735-988	1.69-1.84	2,022	564-615	<1.20	2.45 [a]
	Day 7	620-651	<1.20	2,570	740-934	1.56-1.98	2.44 [a]
	Day 28	758-777	1.14-1.18	3,720	749-849	<1.20	6.45 [a]
	Mean	755	1.47	676	742	1.77	3.78 [a]
1,500	Day 0	1,426-1,429	2.17-28.2	5,596	1,195-1,220	<1.20-1.89	7.85 [a]
	Day 7	1,166-1,347	<1.20-1.80	12.8 [a]	1,200-1,380	<1.20-7.45	9.73 [a]
	Day 28	1,334-1,335	0.80-1.51	5.32 [a]	1,298-1,337	<1.20-24.2	7.56 [a]
	Mean	1,340	6.90	1,871	1,272	11.2	8.38

a)   In the test report these values are given as both mg/l and µg/l at various places

3.2.1.6   Toxicity to microorganisms

An activated sludge respiration inhibition (OECD 209) test has been carried out with a commercial octabromodiphenyl ether product (Schaefer and Siddiqui, 2001). The substance was tested in triplicate at a concentration of 15 mg/l. The inoculum used in the test was activated sludge from a wastewater treatment plant that received predominantly domestic waste. The test was carried out at 20-21°C and the respiration rate of the activated sludge over three hours was determined. Two controls and a positive control (3,5-dichlorophenol at concentrations of 5, 15 and 50 mg/l) were also run. The respiration rates in the two controls were 48.8 and 51.4 mg O$_2$/l/hour (mean value was 50.1 mg O$_2$/l/hour). The respiration rates in the octabromodiphenyl ether treatments were 5.27, 50.9 and 49.7 mg O$_2$/l/hour (mean value 51.1 mg O$_2$/l/hour) and so no inhibition of respiration was seen at the concentration tested. The EC$_{50}$ for the positive control was determined as 11.3 mg/l, which is within the normal range of 5 to 30 mg/l for this test. The NOEC for octabromodiphenyl ether from this test is therefore ≥15 mg/l.

3.2.1.7   Predicted no effect concentration (PNEC) for the surface water

3.2.1.7.1   Commercial octabromodiphenyl ether

The available toxicity data for octabromodiphenyl ether show that no acute effects in fish or longer-term effects in *Daphnia* would be expected to occur at concentrations of octabromodiphenyl ether up to its solubility limit. QSAR predictions are also consistent with this. A tentative $PNEC_{water}$ can be derived from the measured NOEC for *Daphnia* of >2 µg/l. Applying an assessment factor of 10 to this value gives a $PNEC_{water}$ of >0.2 µg/l (i.e. octabromodiphenyl ether is not expected to cause adverse effects on aquatic organisms at concentrations up to its solubility limit).

There is considerable uncertainty about the derived PNEC for water. This is because no toxic effects were seen at concentrations up to the water solubility of the substance in the test medium. Thus for water it seems sensible to assume that no adverse effects on aquatic organisms are likely to occur at concentrations up to the substance's water solubility.

3.2.1.7.2   Hexabromodiphenyl ether component

Analysis of all currently available data indicates that the hexabromodiphenyl ether congener may cause toxic effects to daphnia (and also possibly algae) at concentrations around its water solubility. Thus, the hexabromodiphenyl ether component of the commercial octabromodiphenyl ether needs to be considered in the risk assessment.

Based on the available experimental data, the lowest NOEC in long-term tests expected for hexabromodiphenyl ether is around 5 µg/l, based on the experiments with commercial pentabromodiphenyl ether. A long-term NOEC of around >0.11 µg/l or greater for hexabromodiphenyl ether has been estimated for *Daphnia* reproduction, based on the results of a test with commercial octabromodiphenyl ether.

As a worst-case approach, the $PNEC_{water}$ for the hexabromodiphenyl ether component can be assumed to be the same as that derived for pentabromodiphenyl ether (see pentabromodiphenyl ether assessment (EC, 2000b)). Using an assessment factor of 10 on the long-term NOEC for pentabromodiphenyl ether gives a PNEC of 0.53 µg/l for hexabromodiphenyl ether (this assumes that the toxicity of hexabromodiphenyl ether is the same as that of the commercial pentabromodiphenyl ether formulation).

3.2.1.8   Predicted no effect concentration (PNEC) for microorganisms

3.2.1.8.1   Commercial octabromodiphenyl ether

For microorganisms, a NOEC of ≥15 mg/l has been determined for octabromodiphenyl ether in an activated sludge respiration inhibition test. According to the Technical Guidance Document, an assessment factor of 10 is appropriate for this type of result. Thus the $PNEC_{microorganism}$ is ≥1.5 mg/l for octabromodiphenyl ether.

3.2.1.8.2   Hexabromodiphenyl ether component

It is not necessary to estimate a $PNEC_{microorganisms}$ for the hexabromodiphenyl ether component, as the sewage treatment plant will effectively be exposed to the commercial product before any differences in distribution/accumulation of the individual components of the product can be realised. Thus, the $PNEC_{microorganisms}$ derived for the commercial octabromodiphenyl ether should protect wastewater treatment plants from all components of the product.

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

3.2.1.9.1   Commercial octabromodiphenyl ether

Octabromodiphenyl ether has been tested with *Lumbriculus variegatus* in two different sediments. No effects were seen in these studies and the lowest NOEC from these studies was $\geq 1{,}272$ mg/kg dry weight. Studies on three sediment species with the substance pentabromodiphenyl ether (see the published EC risk assessment report, (EC, 2000b)) suggest that other available test species are unlikely to be more sensitive to octabromodiphenyl ether than *Lumbriculus*. An assessment factor of 10 is therefore appropriate to derive the PNEC from the lowest NOEC from the two different sediments used. Therefore the $PNEC_{sed}$ is ≥ 127 mg/kg dry weight. Expressed on a wet sediment basis (using the default sediment water contents from the Technical Guidance Document) the $PNEC_{sed}$ is ≥ 49 mg/kg wet weight.

An alternative $PNEC_{sed}$ can be estimated using the equilibrium partitioning approach. A $PNEC_{sed}$ of ≥ 5.93 mg/kg wet weight can be estimated assuming a value for $K_{susp-water}$ of 34,076 m^3/m^3 (see Section 3.1.1.5.2). This value is consistent with the $PNEC_{sed}$ of ≥ 49 mg/kg wet weight based on the sediment toxicity tests and this latter value will be used in the risk characterisation.

3.2.1.9.2   Hexabromodiphenyl ether component

The NOEC estimated for the hexabromodiphenyl ether component in the commercial octabromodiphenyl ether product is ≥ 70 mg/kg dry weight. Using an assessment factor of 10 as above this leads to a $PNEC_{sed}$ of ≥ 7.0 mg/kg dry weight or ≥ 2.7 mg/kg wet weight.

A $PNEC_{sed}$ for hexabromodiphenyl ether can also be estimated using the equilibrium partitioning method. An organic carbon-water partitioning coefficient of $1.06 \cdot 10^6$ l/kg has been estimated for hexabromodiphenyl ether (see Appendix E), which gives a value for $K_{susp-water}$ of 26,506 m^3/m^3. Thus the $PNEC_{sed} = 2.54$ mg/kg wet weight.

The $PNEC_{sed}$ of ≥ 2.7 mg/kg wet weight will be used in the risk characterisation as it is derived from actual sediment toxicity data and is based on the probable amount of hexabromodiphenyl ether present in the test.

3.2.2 Terrestrial compartment

3.2.2.1 Toxicity to plants

The toxicity of octabromodiphenyl ether to six species of plants has been determined using OECD Guideline 208 (the protocol is based on the 1998 proposal for revision of this test guideline) (Porch and Krueger, 2001). The soil used in the test was an artificial sandy loam 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 substance used in the test was a commercial sample from a manufacturer and was reported to have a bromine content of 78.6%.

The test soils were prepared by mixing a known weight of the test substance in a sub-sample of 1 kg of the soil overnight. 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, three sub-samples of the test soil were collected for analysis to confirm the initial concentration of the substance in 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*) and ryegrass (*Lolium perenne*); dicots; cucumber (*Cucumis sativa*), soybean (*Glycine max*) and tomato (*Lycopersicon esculentum*). For each species a control group and five treatment groups were run. Each group consisted of four replicate pots each containing ten seeds (giving 40 seeds per control of treatment group). The nominal concentrations used were 94, 188, 375, 750 and 1,500 mg/kg dry soil. Analysis by HPLC with UV detection gave the mean measured concentrations in these treatments as 83.4, 157, 326, 664 and 1,190 mg/kg dry soil respectively. The results from the analysis indicated that the test soils were homogeneous. During the 21-day test, weekly observations of emergence (number of emerged seedlings per pot) were made. These results are shown in **Table 3.20**.

Table 3.20 Effects of octabromodiphenyl ether on seedling emergence, survival and growth

Plant	Endpoint		Nominal treatment level (mg/kg dry wt)					
			Control	94	188	375	750	1,500
Corn	Number of emerged seedlings/ replicate	day 7	9.00	9.00	9.75	10.0	9.25	9.75
		day 14	9.00	9.00	9.75	10.0	9.25	10.0
		day 21	9.00	9.00	9.75	10.0	9.25	10.0
	Number of surviving seedlings/replicate		9.00	8.50	9.50	9.75	9.25	10.0
	Mean seedling dry wt		0.716 g	0.736 g	0.790 g	0.644 g	0.752 g	0.703 g
	Seedling height		59.6 cm	57.2 cm	59.9 cm	53.9 cm	61.1 cm	59.1 cm

Table 3.20 continued overleaf

Table 3.20 continued Effects of octabromodiphenyl ether on seedling emergence, survival and growth

Plant	Endpoint		Nominal treatment level (mg/kg dry wt)					
			Control	94	188	375	750	1,500
Cucumber	Number of emerged seedlings/ replicate	day 7	10.0	10.0	9.75	10.0	10.0	10.0
		day 14	10.0	10.0	9.75	10.0	10.0	10.0
		day 21	10.0	10.0	9.75	10.0	10.0	10.0
	Number of surviving seedlings/replicate		10.0	10.0	9.75	10.0	10.0	10.0
	Mean seedling dry wt		0.429 g	0.396 g	0.432 g	0.376 g	0.377 g	0.414 g
	Seedling height		16.6 cm	15.9 cm	17.2 cm	15.1 cm	15.1 cm	17.2 cm
Onion	Number of emerged seedlings/ replicate	day 7	9.00	8.50	9.25	8.50	9.00	9.75
		day 14	8.75	8.50	9.25	8.50	9.25	9.75
		day 21	8.75	8.75	9.25	8.75	9.50	9.75
	Number of surviving seedlings/replicate		6.75	7.75	8.25	8.75	8.75	9.25
	Mean seedling dry wt		5.6 mg	8.4 mg	7.3 mg	8.1 mg	7.6 mg	4.0 mg
	Seedling height		5.6 cm	7.9 cm	7.2 cm	8.1 cm	7.1 cm	4.4 cm
Ryegrass	Number of emerged seedlings/ replicate	day 7	9.25	9.25	9.50	9.50	9.00	9.75
		day 14	9.25	9.25	9.75	9.75	9.25	9.75
		day 21	9.25	9.50	9.75	9.75	9.50	9.75
	Number of surviving seedlings/replicate		9.25	9.50	9.75	9.75	9.50	9.75
	Mean seedling dry wt		0.022 g	0.019 g	0.022 g	0.020 g	0.019 g	0.024 g
	Seedling height		15.4 cm	15.3 cm	15.8 cm	15.4 cm	16.0 cm	16.1 cm
Soybean	Number of emerged seedlings/ replicate	day 7	6.75	7.25	6.75	7.25	6.75	8.00
		day 14	7.00	8.25	7.50	7.25	8.00	8.00
		day 21	7.50	8.50	7.75	7.25	8.00	8.00
	Number of surviving seedlings/replicate		7.50	8.50	7.75	7.25	8.00	7.75
	Mean seedling dry wt		0.592 g	0.673 g	0.682 g	0.686 g	0.604 g	0.644 g
	Seedling height		22.7 cm	21.9 cm	22.6 cm	24.0 cm	23.8 cm	23.7 cm
Tomato	Number of emerged seedlings/ replicate	day 7	7.25	6.50	9.50	7.75	8.50	7.25
		day 14	8.25	8.00	9.75	8.00	9.00	8.75
		day 21	8.25	8.25	9.75	8.00	9.00	8.75
	Number of surviving seedlings/replicate		8.25	7.75	9.75	8.00	9.00	8.50
	Mean seedling dry wt		0.038 g	0.039 g	0.054 g	0.057 g	0.054 g	0.028 g
	Seedling height		5.5 cm	5.1 cm	6.9 cm	6.8 cm	6.1 cm	4.7 cm

*   Response statistically significantly different from control group (p=0.05)

In addition, a qualitative assessment of the condition of each seedling was made (i.e. presence or absence of signs of phytotoxicity such as colour changes, necrosis, leaf wrinkling, chlorosis, 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 the mean shoot dry weight. The growth data are also shown in **Table 3.20**.

The visual observations carried out during the test revealed no signs of treatment-related phytoxicity in any species and any treatment level. For all the species tested, no statistically significant differences (p=0.05) between any of the treatment groups and the control groups were seen in seedling emergence, seedling survival or growth (height or dry weight).

Overall, the NOEC from these studies was given as ≥1,500 mg/kg dry soil based on nominal values or ≥1,190 mg/kg dry soil based on the mean measured concentration in soil at the start of the test.

The amount of hexabromodiphenyl ether present in the commercial octabromodiphenyl ether tested was not given. If it is assumed that the test substance contained 5.5% hexabromodiphenyl ether (typical of current products) then the estimated NOEC for the hexabromodiphenyl ether component based on these results is ≥65.5 mg/kg dry weight.

3.2.2.2 Toxicity to earthworms

A 56-day earthworm reproduction study has been carried out with octabromodiphenyl ether. However the reproduction rate found in the control group was below that required in the test guideline (the mean number of juveniles/replicate (of ten adults) was 0.5 compared with 30 required in the test guideline. Consequently the test was repeated (ABC, 2001). The repeat test was carried out according to the proposed OECD 207 test guideline "Earthworm Reproduction Test (*Eisenia fetida/andrei*)". The test used an artificial soil made by mixing 70% silica sand, 20% koalin clay and 10% sphagnum peat, and the resulting soil had an organic carbon content of 4.7%. The pH of the artificial soil was adjusted to 6.0±0.5. The water holding capacity of the soil was determined to be 66.4 ml/100 g and the percentage water at 60% of the water holding capacity was calculated to be 26% on a dry weight soil basis. The homogeneity of the samples was checked by measuring the concentration in samples from the top, middle and bottom of the soils after mixing/hydration of the highest and lowest exposure concentrations. The concentrations in the homogeneity samples were 101, 108 and 122% of the nominal values in the low-dose soil and 96.7, 98.1 and 108% of the nominal values in the high dose soil, indicating that the soils were well mixed.

The organisms used in the test were *Eisenia fetida*. The organisms were at least four months old and had developed clitellum. The weight of the worms was in the range 300.6 to 435.4 mg/worm at start of the test, with the mean initial weight being 316.9 mg/worm in the control population and 318.1-360.8 mg/worm in the treatment groups. Eight replicate test chambers were used for the control population and four replicate test chambers were used for each treatment group. Each replicate contained ten worms, giving a total of 80 worms in the control group and 40 worms in each treatment group. The nominal concentrations of octabromodiphenyl ether used in the test were 94, 188, 375, 750 and 1,500 mg/kg dry weight. The test soils were prepared by adding pulverised octabromodiphenyl ether directly dry soil and mixing for at least 24 hours. The soils were then hydrated to ~60% of their water holding capacity and then mixed to a uniform consistency. Approximately 630 g of wet soil were used in each replicate. The concentration of octabromodiphenyl ether present in the soil was measured at day 0, day 28 and day 56 of the test.

The mean concentrations found were 84.9, 166, 361, 698 and 1,470 mg/kg dry weight, which were very close to the nominal values.

The exposures were initiated by adding the worms directly to the surface of the spiked soil. The burrowing behaviour was monitored over the first hour after addition of the worms, after which the soils were covered with lids and maintained at $20\pm2^{\circ}C$. The worms were fed a diet of invertebrate slurry (approximately 5-6 ml) at least weekly during the first 28 days of the study. Around 2-5 ml of potable water was also added along with the diet. During the final 28 days of the study, 3 ml of invertebrate diet slurry and 2-5 ml potable water were added at least twice each week. Neither the diet nor the potable water was contaminated with octabromodiphenyl ether. The water content of the soil was around 25.3-27.4% on a dry weight basis at the start of the test and was 36.4-45.3% on a dry weight basis at the end of the test.

After 28 days exposure, the adult worms were removed from the soil and the number of live and dead worms was determined. The soil was then replaced in the test chambers and incubated for a further 28 days to allow any cocoons to hatch. The number of juvenile worms was determined at the end of the second 28-day period.

No abnormal burrowing or avoidance behaviour was seen in the first 60 minutes of the test. After the first 28 days of exposure the mortality of adult worms in the control was 3%. The adult mortality in the treatment groups was in the range 0 to 5% and was not statistically significantly different (p=0.05) from the control population. All live worms were normal in appearance. The control worms were found to increase in weight by an average of 2.921 g/replicate (or 92% of the total replicate mass) during the first 28 days of the study. The worms in the treatment groups all increased in weight by 3.174-3.921 g/replicate (or 95-119% of the replicate animal mass) over the same period, which is similar to, or greater than, that found in the control population.

The average number of young worms in the control was 186 juveniles/replicate at the end of the study. The coefficient of variation in the control data was 21% which is within the figure of 30% specified in the protocol. The reproductive output in all treatment groups was 185-225 juveniles/replicate, which is similar to, or higher than, that found in the control population.

Overall, no significant adverse effects on survival or reproduction were seen in this study and so the NOEC is $\geq$ 1,470 mg/kg dry weight.

The amount of hexabromodiphenyl ether component present in the commercial product tested is unknown. If it is assumed that the test substance contained 5.5% hexabromodiphenyl ether (typical of current products), then the estimated NOEC for the hexabromodiphenyl ether component based on these results is $\geq$ 81 mg/kg dry weight.

3.2.2.3   Derivation of PNEC

3.2.2.3.1   Commercial octabromodiphenyl ether

Toxicity data are available for plants and for earthworms. No effects were seen on plants at concentrations up to 1,190 mg/kg dry weight. The NOEC from the earthworm study is $\geq$1,470 mg/kg dry weight.

Based on the NOEC of $\geq$ 1,190 mg/kg dry weight and an assessment factor of 50 (NOECs are available for two species) the PNEC$_{soil}$ can be estimated as $\geq$23.8 mg/kg dry weight. This is

equivalent to a $PNEC_{soil}$ of $\geq$ 20.9 mg/kg wet weight using the default water content given in the TGD.

According to the TGD a PNEC for the terrestrial compartment can also be estimated using the equilibrium partitioning method. Using a value of $K_{soil-water}$ of 40,892 m^3/m^3 (see Section 3.1.1.5.2) gives a value for $PNEC_{soil}$ of $\geq$4.81 mg/kg wet weight.

As is the case with the PNEC for sediment, there is a large uncertainty in this value, but it is consistent with the $PNEC_{soil}$ of $\geq$20.9 mg/kg wet weight estimated based on the available soil toxicity data. The value of $\geq$20.9 mg/kg wet weight will be used in the risk characterisation.

3.2.2.3.2   Hexabromodiphenyl ether component

The NOEC estimated for the hexabromodiphenyl ether component in the commercial octabromodiphenyl ether product is $\geq$65.5 mg/kg dry weight based on the results of the plant test. Using an assessment factor of 50 as before this leads to a $PNEC_{soil}$ of $\geq$1.3 mg/kg dry weight or $\geq$1.2 mg/kg wet weight.

A $PNEC_{sed}$ for hexabromodiphenyl ether can also be estimated using the equilibrium partitioning method. An organic carbon-water partitioning coefficient of $1.06 \cdot 10^6$ l/kg has been estimated for hexabromodiphenyl ether (see Appendix E), which gives a value for $K_{soil-water}$ of 31,808 m^3/m^3. Thus the $PNEC_{soil}$ = 9.9 mg/kg wet weight.

The $PNEC_{soil}$ of $\geq$1.2 mg/kg wet weight, based on the results of the soil toxicity tests will be considered in the risk characterisation.

3.2.3   Atmosphere

Very low concentrations of octabromodiphenyl ether 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, octabromodiphenyl ether can be considered to present a negligible risk of adding to effects such as global warming, ozone depletion in the stratosphere and acidification.

3.2.4   Secondary poisoning

The toxicity of octabromodiphenyl ether to mammalian systems has been reviewed in Section 4 as part of the human health assessment. It has been shown to produce developmental effects in rats and slight fetotoxic effects in rabbits via oral exposure, and effects on female fertility in rats via inhalation exposure. The lowest reported oral NOAEL was 2 mg/kg bw/day for fetotoxic effects in rabbits (see Section 4). Using the conversion factors given in Appendix VII of the Technical Guidance Document (rabbit body weight = 2,000 g; daily food intake = 60 g) a dose of 2 mg/kg bw/day in rabbits is equivalent to a concentration in food of 66.6 mg/kg food.

According to the Technical Guidance Document, an assessment factor of 10 can be applied to a NOAEL for reproductive effects, giving a PNEC for secondary poisoning of 6.7 mg/kg food for octabromodiphenyl ether.

Of more concern with regard to secondary poisoning, and also direct toxic effects, is the presence of lower brominated diphenyl ethers in the commercial products. It is known that some

lower brominated diphenyl ethers e.g. tetra- and pentabromodiphenyl ether and hexabromodiphenyl ether are potentially much more bioaccumulative than octabromodiphenyl ether and so may be of concern with regard to secondary poisoning. As commercial octabromodiphenyl ether contains a significant fraction of hexabromodiphenyl ether, this needs to be addressed in the secondary poisoning assessment. As a worst-case approach, it will be assumed that the effects seen in the mammalian toxicity tests are due entirely to the hexabromodiphenyl ether component. The material tested in the rabbit study contained 8.6% hexabromodiphenyl ether and so a PNEC of 6.7 mg/kg food based on the commercial formulation is equivalent to a PNEC of 0.58 mg/kg food based on the hexabromodiphenyl ether component being responsible for the effects.

Another approach to estimating the PNEC for the hexabromodiphenyl ether would be to assume that it is of similar toxicity to the commercial pentabromodiphenyl ether formulation. The PNEC derived for commercial pentabromodiphenyl ether was 1 mg/kg food (see the pentabromodiphenyl ether assessment (EC, 2000b)), which is similar to the value of 0.58 mg/kg food estimated above. The 0.58 mg/kg value will be used here in the risk characterisation.

Some recent studies (e.g. Meerts et al., 2001) carried out with various possible components of the commercial octabromodiphenyl ether showed that 2,2',3,4,4',5'-hexabromodiphenyl ether, 2,2',4,4',5,5'-hexabromodiphenyl ether, 2,3,4,4',5,6-hexabromodiphenyl ether and 2,3,3',4,4',5,6-heptabromodiphenyl ether, did not show estrogenic activity when tested in the ER-CALUX assay, but antiestrogenic activity was found with the 2,2',4,4',5,5'- and 2,3,4,4',5,6-hexabromodiphenyl ethers and 2,3,3',4,4',5,6-heptabromodiphenyl ether. The human health risk assessment (Section 4) considers the possible endocrine disruptor potential of commercial octabromodiphenyl ether and indicates that further information is needed on this endpoint before firm conclusions can be drawn on this issue.

It has also been shown recently (Viberg et al., 2001), that neonatal exposure to 2,2',4,4',5,5'-hexabromodiphenyl ether at doses of 0.45 to 9 mg/kg body weight can cause irreversible behavioural disturbances (as determined by disruption of habituation) in adult mice. The toxicological significance of these findings is unclear. Using the conversion factors given in the Technical Guidance Document a single dose of 0.45-9 mg/kg body weight is equivalent to a single dose of 3.7-75 mg/kg food. As effects were seen at all concentrations tested, and the environmental significance of these findings (in terms of population survival) is unclear it is not possible to derive a PNEC for this endpoint. However, these findings are considered in a qualitative fashion in the risk characterisation for secondary poisoning.

Another possible source of lower brominated diphenyl ethers is as a result of photolysis/degradation reactions of octabromodiphenyl ether. It is likely that octabromodiphenyl ether (or some of the components within the commercial product) will undergo degradation by photolysis in the environment. The available evidence indicates that more toxic and accumulative lower brominated congeners, if formed, would only be minor products of these reactions, but there is some uncertainty over the actual significance of this process in the environment. In addition, it is possible that octabromodiphenyl ether could also undergo slow degradation under anaerobic conditions, although again there is uncertainty over the extent of this reaction in the environment. Further uncertainty arises as not all the products from these possible reactions are known. This is considered further in the risk characterisation Section.

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), metal recycling (if the metal is contaminated with plastic containing octabromodiphenyl ether; this

appears to be unlikely as the main use of plastic containing octabromobiphenyl ether is computer/business machine housings), or accidental fires) involving articles containing octabromodiphenyl ether. The available information is discussed in Appendix A and Section 2.4.

3.3   RISK CHARACTERISATION

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 to some extent the possible amount of octabromodiphenyl ether present in finished articles in the EU (allowance is made for the fact that plastic products and masterbatch maybe imported into (or exported from) the EU, although the actual amounts involved are unknown)). At the regional level, releases to the environment are predicted to be dominated by volatilisation losses from plastic articles over their service life, and also release from articles of polymer particulates containing octabromodiphenyl ether over their lifetime and at disposal.

For the risk characterisation, both the total concentrations of octabromodiphenyl ether and the concentrations of the hexabromodiphenyl ether component in the commercial product are considered (the level of pentabromodiphenyl ether component in current products will be <0.1% as a result on controls placed on the marketing and use of polybrominated diphenyl ethers; these levels are not thought to present a risk to the environment (Crookes, 2001)). The PECs for octabromodiphenyl ether are derived in Section 3.1 of this report. The PECs for the hexabromodiphenyl ether have been derived in a similar way by considering the releases of this specific component of the commercial mixture and modelling the environmental behaviour using EUSES. Details of the physico-chemical properties used and modelling results are shown in Appendix E.

Another area of potential 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), metal recycling or accidental fires) (discussed in Section 2.4 and Appendix A). Overall it can be concluded that octabromodiphenyl ether, as a source of bromine, can contribute to the formation of halogenated dibenzo-*p*-dioxins and dibenzofurans generated during such processes. It is not possible from the available data (and it is beyond the scope of the risk assessment) to quantify the actual contribution that octabromodiphenyl ether makes to the total "toxic" products (fires etc. can generate products other than halogenated dibenzo-*p*-dioxins and dibenzofurans that are considered toxic (e.g. polycyclic aromatic compounds)). Formation of halogenated dibenzo-*p*-dioxins and dibenzofurans in some of these processes is well known and emission control technology is available for incinerators and metal recycling facilities that can reduce emissions to acceptable levels. Although incineration or metal recycling could take place at installations without suitable emission reduction equipment, it should be noted that in most situations octabromodiphenyl ether is unlikely to be the only source of halogenated dioxins/furans. Emission control technology cannot be applied to landfill or other accidental fires. Recycling of plastics containing the substance does not appear to contribute to brominated dibenzo-*p*-dioxin or furan formation.

3.3.1   Aquatic compartment (including sediment)

3.3.1.1   Water

A $PNEC_{water}$ of >0.2 µg/l has been estimated for commercial octabromodiphenyl ether. This is similar to the upper limit for the measured water solubility of octabromodiphenyl ether (solubility ~0.5 µg/l). The predicted environmental concentrations and the resulting PEC/PNEC ratios are shown in **Table 3.21**.

Table 3.21 PEC/PNEC ratios for surface water

Scenario	PEC (µg/l)		PEC/PNEC ratio	
	1994 data	**1999 data**	**1994 data**	**1999 data**
Polymer processing (local)	0.27	0.27	<1.35	<1.35
Regional scale	0.0075	0.0036	<0.038	<0.018

The PEC estimated at the local scale is close to the water solubility of octabromodiphenyl ether. Given the nature of the substance, any releases to water are likely to be associated with the sediment/solid phase and so the assessment of effects on sediment is much more relevant for this substance. From the PEC/PNEC ratios, it can be concluded that the risk to surface water from octabromodiphenyl ether itself is low.

In the assessment of the commercial octabromodiphenyl ether it is also important to consider the presence of potentially more toxic impurities such as hexabromodiphenyl ether. A PNEC for water (0.53 µg/l) has been derived for this component and is compared with the predicted environmental concentrations of that component from the use of octabromodiphenyl ether in **Table 3.22** (see Appendix E for further details).

The PEC/PNEC ratios obtained for surface water for the hexabromodiphenyl ether component confirm the conclusion of low risk based on octabromodiphenyl ether itself.

Table 3.22 PEC/PNEC ratios specific for the hexabromodiphenyl ether component for surface water

Scenario	PEC (hexabromodiphenyl ether, µg/l)		PEC/PNEC ratio	
	1994 data	**1999 data**	**1994 data**	**1999 data**
Polymer processing (local)	0.017 [a] 0.019 [b]	0.018 [b]	0.032 0.033	0.032
Regional scale	$1.5 \cdot 10^{-4}$ [a] $1.6 \cdot 10^{-3}$ [b]	$1.1 \cdot 10^{-3}$	$2.8 \cdot 10^{-4}$ 0.0030	0.0019

a)   Calculation without contribution from "waste remaining in the environment" from Appendix E
b)   Calculation including contribution from "waste remaining in the environment"

3.3.1.2   Sediment

For sediment, a $PNEC_{sed}$ of >49 mg/kg wet weight was determined for commercial octabromodiphenyl ether based on the results of sediment toxicity tests. The estimated PECs and the PEC/PNEC ratios for the sediment compartment are shown in **Table 3.23**.

Table 3.23 PEC/PNEC ratios for sediment

Scenario	PEC		PEC/PNEC ratio	
	1994 data	1999 data	1994 data	1999 data
Polymer processing	8.0 mg/kg wet wt.	8.0 mg/kg wet wt.	<0.16	<0.16
Regional scale	0.39 mg/kg wet wt.	0.19 mg/kg wet wt.	<0.008	<0.004
Measured data - highest value	3.0 mg/kg dry wt. (~1.14 mg/kg wet wt.[a])		<0.023	
Measured data - industrial areas (regional scale)	0.02-0.2 mg/kg dry wt. (~0.008-0.076 mg/kg wet wt.[a])		<1.6 · 10⁻⁴-<0.002	

a)   Assumes the sediment is approximately 62% water by weight

A PNEC for sediment (>2.7 mg/kg wet weight) has been derived for the hexabromodiphenyl ether component, and this is compared in **Table 3.24** with the predicted environmental concentrations of that component from the use of octabromodiphenyl ether (see Appendix E for further details).

Table 3.24 PEC/PNEC ratios specific for the hexabromodiphenyl ether component for sediment

Scenario	PEC (mg/kg wet wt.)		PEC/PNEC ratio	
	1994 data	1999 data	1994 data	1999 data
Polymer processing	0.40 [a] 0.43 [b]	0.42 [b]	<0.15 <0.16	<0.16
Regional scale	0.0062 [a] 0.063 [b]	0.046 [b]	<0.0023H <0.023	<0.017

a)   Calculation without contribution from "waste remaining in the environment" from Appendix E
b)   Calculation including contribution from "waste remaining in the environment"

Based on the upper limits for the PEC/PNEC ratios for octabromodiphenyl ether, and the PEC/PNEC ratios for the hexabromodiphenyl ether component, the risk to the sediment compartment from local and regional sources appears to be low.

In addition, the possibility of components of octabromodiphenyl ether degrading in the environment to give more toxic brominated diphenyl ethers needs to be considered further. The available evidence indicates that the lower brominated diphenyl ethers, if formed, are likely to be only minor products, but there is some uncertainty over the actual significance of the process in the environment, and it is currently not possible to quantify the actual risk from these processes. This is considered further in the risk characterisation for secondary poisoning (Section 3.3.4).

3.3.1.3   Sewage treatment processes

The PNEC$_{microorganisms}$ for octabromodiphenyl ether is ≥ 1.5 mg/l. The predicted concentrations of octabromodiphenyl ether in the effluent to wastewater treatment plants are 0.008 mg/l for use in polymers and 1.27 and 0.21 for the worst-case calculation for a hypothetical production site. Thus, the risk to wastewater treatment plants from octabromodiphenyl ether is low.

3.3.1.4   Summary

The results for the aquatic compartment are summarised below.

Result

Conclusion (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 assessment for surface water, sediment and wastewater treatment plants from local and regional sources of octabromodiphenyl ether.

3.3.2   Terrestrial compartment

A $PNEC_{soil}$ of $\geq$20.9 mg/kg wet weight has been derived for octabromodiphenyl ether based on the available results of toxicity tests on soil organisms. The estimated PECs and the PEC/PNEC ratios for the agricultural soil compartment (averaged over 30 days) and the regional industrial/urban soil compartment are shown in **Table 3.25**. The concentrations predicted at the local level assume 10 years continuous application of sewage sludge. However, since octabromodiphenyl ether is a persistent substance, concentrations could build up in soil over longer periods. The percentage of the steady-state concentration estimated after 10 years continuous application is around 0.4-0.5%.

Table 3.25 PEC/PNEC ratios for soil

Scenario	Soil type	PEC (mg/kg wet wt.)		PEC/PNEC ratio	
		1994 data	1999 data	1994 data	1999 data
Polymer processing	Agricultural	3.30	3.25	$\leq$0.16	$\leq$0.16
Regional scale	Agricultural	0.123	0.047	$\leq$0.006	$\leq$0.002
Regional scale	Natural	0.125	0.061	$\leq$0.006	$\leq$0.003
Regional scale	Industrial/urban	8.82	4.26	$\leq$0.42	0.20

In the assessment of the commercial octabromodiphenyl ether it is also important to consider the presence of potentially more toxic impurities such as hexabromodiphenyl ether. A PNEC for soil of $\geq$1.2 mg/kg wet weight has been derived for this component and this is compared below in **Table 3.26** with the predicted environmental concentrations in agricultural soil and industrial/urban soil of that component from the use of octabromodiphenyl ether (see Appendix E for further details).

Table 3.26 PEC/PNEC ratios specific for the hexabromodiphenyl ether component for soil

Scenario	PEC (hexabromodiphenyl ether, mg/kg wet wt.)		PEC/PNEC ratio	
	1994 data	**1999 data**	**1994 data**	**1999 data**
Polymer processing (local) - agricultural soil	0.19 [a) b)]	0.19 [b)]	≤0.16	≤0.16
Regional scale - agricultural soil	0.013 [a) b)]	0.011 [b)]	≤0.011	
Regional scale - industrial/urban soil	0.014 [a)] 1.11 [b)]	0.79 [b)]	≤0.012 ≤0.93	≤0.66

a) Calculation without contribution from "waste remaining in the environment" from Appendix E
b) Calculation including contribution from "waste remaining in the environment"

From the estimated PEC/PNEC ratios the risk to the terrestrial compartment from both the commercial octabromodiphenyl ether and the hexabromodiphenyl ether component is low.

It should be noted that for industrial soil in particular, a very conservative approach has been used in the estimation of releases to this compartment, mainly in the form of "waste remaining in the environment" (see Section 3.1.1.2.4). The approach taken may overestimate the actual concentrations, and hence risk, in this type of soil. Despite this, the resulting PEC/PNEC ratio is <1 and so, in this case, the nature of the approach taken provides added reassurance that the risk from this source is low.

Result

Conclusion (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.

The assessment indicates no risk for the terrestrial compartment.

3.3.3   Atmosphere

Neither biotic nor abiotic effects are considered likely because of the limited release and low volatility of octabromodiphenyl ether. The predicted atmospheric concentrations of octabromodiphenyl ether are all very low (<0.1 $\mu g/m^3$).

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. Nevertheless, the possible long-term increase in levels as a result of releases from waste sites might need to be considered further in any future revision of this risk assessment report.

Result

Conclusion (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.

3.3.4   Secondary poisoning

The available information indicates that all components of the commercial octabromodiphenyl ether products can be taken up by organisms in the environment. The concentrations of the various possible components found in organisms appear to decrease with increasing degree of bromination, although the available database for some of the higher brominated components (for example octabromodiphenyl ether isomers) is much smaller than for some other lower brominated components (for example hexabromodiphenyl ether isomers).

A PNEC for secondary poisoning of 6.7 mg/kg food has been derived for octabromodiphenyl ether. The predicted concentrations in fish and the PEC/PNEC ratios are shown in **Table 3.27**.

Table 3.27 Predicted concentrations for secondary poisoning

Scenario	PEC (µg/kg wet wt.)		PEC/PNEC	
	1994 data	1999 data	1994 data	1999 data
Fish-based food chain				
Polymer processing	0.18	0.057	$2.7 \cdot 10^{-5}$	$8.5 \cdot 10^{-6}$
Measured data - highest value	325		0.048	
Earthworm-based food chain				
Polymer processing	5,570	5,340	0.83	0.80

In the assessment of the commercial octabromodiphenyl ether it is also important to consider the presence of potentially more toxic impurities such as hexabromodiphenyl ether. A PNEC for secondary poisoning of 0.58 mg/kg wet weight has been derived for this component and this is compared below in **Table 3.28** with the predicted environmental concentrations of that component from the use of octabromodiphenyl ether (see Appendix E for further details).

Table 3.28 PEC/PNEC ratios specific for the hexabromodiphenyl ether component for secondary poisoning

Scenario	PEC (µg/kg wet wt.)		PEC/PNEC ratio	
	1994 data	1999 data	1994 data	1999 data
Fish-based food chain				
Polymer processing	8.6 [a] 13.0 [b]	6.1 [a]	0.015 [a] 0.022	0.011
Measured data - general background	up to around 1-3		0.0017-0.005	
Measured data - close to wastewater treatment plant	up to ~16.8		0.029	
Earthworm-based food chain				
Polymer processing	690 [a] 687 [b]	673 [b]	1.2 [a] 1.2 [b]	1.2 [b]

a)   Calculation without contribution from "waste remaining in the environment" from Appendix E
b)   Calculation including contribution from "waste remaining in the environment"
c)   The measured value was 2,800 µg/kg lipid - the actual lipid content of the fish was 0.6% - this has been used to estimate the wet weight concentration

The information available indicates that octabromodiphenyl ether has a low potential for bioconcentration and bioaccumulation. The PEC/PNEC ratios for secondary poisoning are all <1. Higher concentrations of octabromodiphenyl ether have been estimated in earthworms (5.57 mg/kg wet wt.) than in fish but it is thought that the estimation methods used may not be applicable for this substance. Even so, the PEC/PNEC ratio for earthworms is still <1. Therefore, it can be concluded that the risk of secondary poisoning by octabromodiphenyl ether is of low concern using the conventional PEC/PNEC approach.

A possible concern with regard to secondary poisoning is the presence of lower brominated diphenyl ethers in the commercial products. The screening assessment carried out above for the hexabromodiphenyl ether component indicates that the PEC/PNEC ratio is <1 in fish. Again higher concentrations were predicted in earthworms (0.69-0.70 mg/kg wet wt.; see Appendix E) and indicate that the PEC/PNEC ratio could be just greater than 1 when the earthworm scenario is considered. Again, it is not known if the estimation methods used are applicable to this substance, particularly as the bioaccumulation potential for the polybrominated diphenyl ethers as a whole appears to reach a peak at compounds with around 4-5 bromine atoms/molecule, and then falls off markedly with increasing bromination (this is not accounted for in the current earthworm estimation method). The producers of octabromodiphenyl ether have all signed up to a Voluntary Industry Commitment to look at ways of minimising the levels of the lower brominated congeners present in the commercial octabromodiphenyl ether and this result confirms the need for such a commitment.

The assessment for hexabromodiphenyl ether assumes that it is present at around 5.5% in the current commercial octabromodiphenyl ether products and that both commercial octabromodiphenyl ether products and commercial pentabromodiphenyl ether products can contribute to the regional concentration of hexabromodiphenyl ether (see Appendix E). Two issues need to be considered in this respect. Firstly, the regional contribution from commercial pentabromodiphenyl ether products is likely to reduce significantly in the near future as a result of controls on the marketing and use of that substance. This means that the measured concentrations in biota in the environment would also be expected to decrease in line with the reduced emissions from this source. Secondly, the concentration of hexabromodiphenyl ether impurities in some commercial octabromodiphenyl ether products has been given as up to 12% in the past (see Section 2). At this level in the commercial product, the estimated PECs would be approximately 2 times those currently estimated for the hexabromodiphenyl ether component. These would still not indicate a risk via the fish food chain but would by the earthworm food chain.

However, despite the uncertainties in the assessment for the hexabromodiphenyl ether component it has to be concluded that high levels of hexabromodiphenyl ether component in commercial octabromodiphenyl ether products could lead to a concern for secondary poisoning via the earthworm route. This is supported by the fact that hexabromodiphenyl ether appears to be widespread in biota in the environment, and there is some circumstantial evidence from monitoring data that the concentrations found in organisms may increase through the food chain (concentrations in excess of 1 mg/kg lipid have been measured in some marine mammals). Therefore, based on these findings, there is a need to reduce the risk from the hexabromodiphenyl ether component present in the commercial octabromodiphenyl ether product.

Additional uncertainties

The current approach to risk assessment implies that there is no risk of secondary poisoning (with the exception of the hexabromodiphenyl ether component), and the PEC/PNEC ratios are

much less than 1 for the commercial octabromodiphenyl ether product itself. Although it appears to be persistent in the environment, the commercial substance is considered to have a low bioaccumulation potential based on the available laboratory data. It also shows no toxicity towards aquatic organisms up to the limit of water solubility, and effects in other organisms are only observed at relatively high concentrations, based on standard laboratory tests.

Nevertheless, the most recent analytical monitoring surveys indicate that, as well as hexabromodiphenyl ethers, hepta- and octabromodiphenyl ethers (the major components of commercial octabromodiphenyl ether) are present at (relatively) low concentrations in fish, marine mammals and predatory birds' eggs (those of bird-eating Peregrine Falcons and fish-eating Common Terns). A similar occurrence of decabromodiphenyl ether in some higher mammals and birds' eggs has also been reported (see risk assessment report for decabromodiphenyl ether (EC, 2002)) and these findings appear to contradict the conventional wisdom that molecules such as decabromodiphenyl ether and to a lesser extent octa- and heptabromodiphenyl ether are too large to pass through biological membranes and should not accumulate in organisms. The finding of these higher brominated diphenyl ether congeners in some higher mammals and birds' eggs indicates that uptake can occur (the route of this uptake, i.e. whether by food, air or water, is currently uncertain). The levels of these higher congeners found in fish, etc., are below those that are predicted to cause effects on fish-eating species using the PEC/PNEC approach. However, the sample sizes are small, and the trend in these levels is unknown. It is also possible that higher concentrations could be found in other organisms. In addition, the available data indicate that some components of the commercial octabromodiphenyl ether products (e.g. hexabromodiphenyl ether congeners) are more bioaccumulative than octabromodiphenyl ether itself and have been found to be widespread in biota in the environment.

It is not possible to assess the effects of the concentrations of these higher brominated components of the commercial product present in, for example, birds' eggs using the current approaches. The mere presence of a chemical in biota is not necessarily a cause for concern, and there is no evidence at this point in time of biomagnification taking place or actual environmental harm arising from this substance at these levels. However, there is some evidence from recent non-standard behavioural tests on mice that neonatal exposure to some of the components of commercial octabromodiphenyl ether (2,2',4,4',5,5'- hexabromodiphenyl ether) at doses of 0.45 to 9 mg/kg body weight may cause irreversible behavioural disturbances (as determined by disruption of habituation) in adult mice. The toxicological significance of these findings (in terms of population survival) is unclear, and so it is not currently possible to derive a PNEC for the hexabromodiphenyl ether congener based on these endpoints. However, this dose range is below those at which no effects were observed in standard mammalian toxicity tests (such effects have been seen for hexabromodiphenyl ether and decabromodiphenyl ether and so it is likely that other components of the commercial octabromodiphenyl ether product may cause such effects). In addition, it has recently been shown that some components of commercial octabromodiphenyl ether   (2,2',4,4',5,5'- and 2,3,4,4',5,6-hexabromodiphenyl ethers and 2,3,3',4,4',5,6-heptabromodiphenyl ether) show antiestrogenic activity.

In general, a NOAEL has not been established for these types of effects with polybrominated diphenyl ethers. Even if these studies represent a reproducible effect, the interpretation of such an effect in the context of this assessment is unclear, especially in terms of assessment factors and comparison with actual tissue levels (rather than dose). However, they do imply that the standard toxicity tests might not have picked out subtle effects of octabromodiphenyl ether that could be significant at sensitive life stages. This raises some concern about the presence of the substance in birds' eggs. This substance is persistent and so it is also possible that slow uptake

may be occurring over extended timescales, so that levels in biota may increase with time. It is therefore possible that the current PEC/PNEC approach for secondary poisoning may not be appropriate for octabromodiphenyl ether in terms of both the PEC and the PNEC, and could underestimate the risk. This issue needs further investigation.

A second aspect of concern is that although the substance is persistent, there is evidence that it can degrade under some conditions. For example, photolysis on solid surfaces has been demonstrated for deca- and tetrabromodiphenyl ether under laboratory conditions, and so octabromodiphenyl ether can be expected to behave similarly. Lower brominated diphenyl ether congeners have been identified among the degradation products from these studies (some products remain unidentified). Limited anaerobic degradation of lower congeners has also been demonstrated in the laboratory. The overall environmental degradation rate has not been determined and the environmental significance of any degradation pathway remains uncertain. There is currently no evidence that significant degradation to lower brominated diphenyl ether congeners is actually occurring in the environment (although it is difficult to state definitively that there is no degradation, since monitoring studies may simply reflect levels of commercial congeners on the market, and this might mask low levels of formation due to degradation). This point is considered further in Appendix F. Since some of the products may be more bioaccumulative and toxic than the parent compound, any significant formation would be a cause for concern. The current database is inconclusive on this point, and further work might be needed.

Result

Two conclusions must be drawn for the secondary poisoning assessment:

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

This conclusion applies to the risk of secondary poisoning from all sources of octabromodiphenyl ether. Four possible areas for further work are as follows:

a)   A more widespread monitoring project to determine whether the finding in top predators (including birds' eggs) is a widespread or localised phenomenon, and trends (if possible). Assuming sufficient and appropriate sample material already exists, this work could be done relatively quickly. It should, however, be noted that there are likely to be difficulties in the interpretation of results from older samples. If the substance is not found, it could be argued that insufficient time had elapsed for levels to build up (either in organisms or in the environment); conversely, if it is detected it could be argued that this reflects older use patterns and levels. If existing sample material were not available, a sampling programme would be necessary, which would require authorised collection of an appropriate number of samples from a suitable variety of species and geographical area during 2002, and this might require licensing from appropriate authorities.

b)   Further toxicity testing. The existence of a mammalian toxicity data set means that testing could be considered on birds (e.g. an avian reproduction test (OECD 206), with appropriate tissue analysis). The exposure period required to achieve tissue levels comparable to or higher than those seen in the wild in unknown, but could be very long. Alternatively, a study that administers the substance by injection of eggs could be done to determine whether adverse developmental effects are detectable. This is not a standard test, and the results of such a study could be difficult to interpret and may not be relevant. In addition, such an exposure route could not be related to levels in the environment/diet, although the exposure levels might be compared to the measured levels in eggs - this route is not typically considered in risk assessments. Overall, the benefit of further vertebrate testing is open to

question due to expected difficulties in achieving sufficiently high exposures. This leaves the toxicity issue with some unresolved uncertainty.

c)   An investigation of the rate of formation of degradation products under environmentally relevant conditions over a suitably prolonged time period (e.g. years) - for example, an extended monitoring programme to determine trends in degradation product levels in various environmental compartments. This could be coupled with analysis of the parent compound to detect whether it is building up in the environment or has achieved equilibrium. It should be noted that the interpretation of the levels of degradation products is likely to be confounded by changes in the use pattern of the lower congeners - commercial pentabromodiphenyl ether is being removed from the market, and the use of commercial octabromodiphenyl ether itself appears to be declining. It therefore seems likely that only the parent compound levels may be easy to interpret, provided the inputs into the environment are well understood - however, these come in large part from articles, so this may also be a problem. A controlled field study (or studies) might be the way forward, with controlled continuous input of the substance and regular monitoring of other components - the extent to which such a study could be considered representative could be challenged, and the time needed to produce meaningful results is uncertain.

d)   Further toxicological work on the non-diphenyl ether degradation products, to determine if they pose a hazard or risk. Some of these products remain unidentified and/or are not commercially produced, so this could be difficult and time consuming. It might be possible to use structure-activity relationships to some extent.

There is a high level of uncertainty associated with the suitability of the current risk assessment approach for secondary poisoning and the debromination issue. The combination of uncertainties raises a concern about the possibility of long-term environmental effects that cannot easily be predicted. There is insufficient confidence in the PEC and PNEC estimates to reach either conclusion (ii) or (iii) for this endpoint. In order to be able to reduce the uncertainties to an acceptable level, further research could be attempted. It is noted, however, that much of the information required above would take some considerable time to be generated or gathered, and might not be sufficiently comprehensive to remove all uncertainty. There is evidence that octabromodiphenyl ether is highly persistent, and of particular note, most of the major components of the commercial product have been detected, albeit at relatively low levels and from a limited sample, in predatory birds' eggs and marine mammals. The trend in these levels is unknown. It is not possible to say whether or not on a scientific basis there is a current or future risk to the environment. However, given the persistent nature of the substance, it would be of concern if, once the further information had been gathered, the analysis indicated a risk to predators, since it could then be difficult to reduce exposure.

In summary, although it is concluded that further information should be gathered in order to refine the risk assessment, in light of:

·   the persistence of the substance,
·   the time it would take to gather the information and
·   the fact that there is no guarantee that the studies would provide unequivocal answers,

consideration should be given at a policy level of the need to investigate risk management options now in the absence of adequate scientific knowledge.

[N.B. A number of technical experts from EU member states consider that this uncertainty is sufficient to warrant risk reduction measures directly (conclusion (iii)) based on the information currently provided in this assessment.]

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

This applies to the assessment of secondary poisoning via the earthworm route for the hexabromodiphenyl ether component in the commercial octabromodiphenyl ether product from the use in polymer applications. The PEC/PNEC ratio for this endpoint indicates a possible risk.

4 HUMAN HEALTH

4.1 HUMAN HEALTH (TOXICITY)

4.1.1 Exposure assessment

4.1.1.1 General discussion

OBDPO is a solid with a very low vapour pressure ($6.6 \cdot 10^{-6}$ Pa at 21°C) and a calculated saturated vapour concentration (SVC) of 30 μg/m^3 at 21°C. Therefore exposure to the vapour will not exceed 30 μg/m^3 at ambient temperature (in reality it will be far below this value) and inhalation of dust and skin contact are the predominant routes of exposure.

When OBDPO is heated the vapour pressure will rise with a concomitant increase in the SVC. Increases in temperature may lead to some increase in volatilisation and the vapour will quickly condense to form a mist. Therefore the release of OBDPO on heating may also be a potential source of inhalation exposure.

During processing at high temperatures, fumes of breakdown products (polybrominated dibenzodioxins and dibenzofurans) may also be emitted. Occupational exposure to dioxins and furans is tentatively assessed elsewhere in this report (see Appendix D).

Oral exposure is not considered to be a significant route of exposure under normal working practices.

According to the data provided by one producer, the particle size distribution of the commercial product may be of concern (about 45% (in volume) of the particles have a diameter < 10 μm and 15 % (in volume) of the particles have a diameter < 5 μm) and will generate respirable dust. Another producer supplies a flaked material with a particle size range from 177-840 μm; in this case, exposure is likely to be significantly reduced.

4.1.1.2 Occupational exposure

No specific occupational limit value has been proposed for OBDPO by professional agencies (i.e. ACGIH) or governmental agencies. The manufacturer Great Lakes Chemical Corporation has established a recommended workplace exposure limit for internal and customer use of 0.14 mg/m^3.

Occupational exposure may occur during manufacture, industrial processing in the plastic industry, equipment manufacture and end uses of flame retarded products. The figure below illustrates the progress of flame retardants.

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                          ┌─────────────────────┐
                          │    Manufacturer      │
                          └─────────────────────┘
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(flowchart)

Manufacturer → Master Batchers, Compounders, Self-compounders (compounders and moulders)

Master Batchers → Compounders

Compounders → Moulders → Equipment manufacturers

Self-compounders (compounders and moulders) → Equipment manufacturers
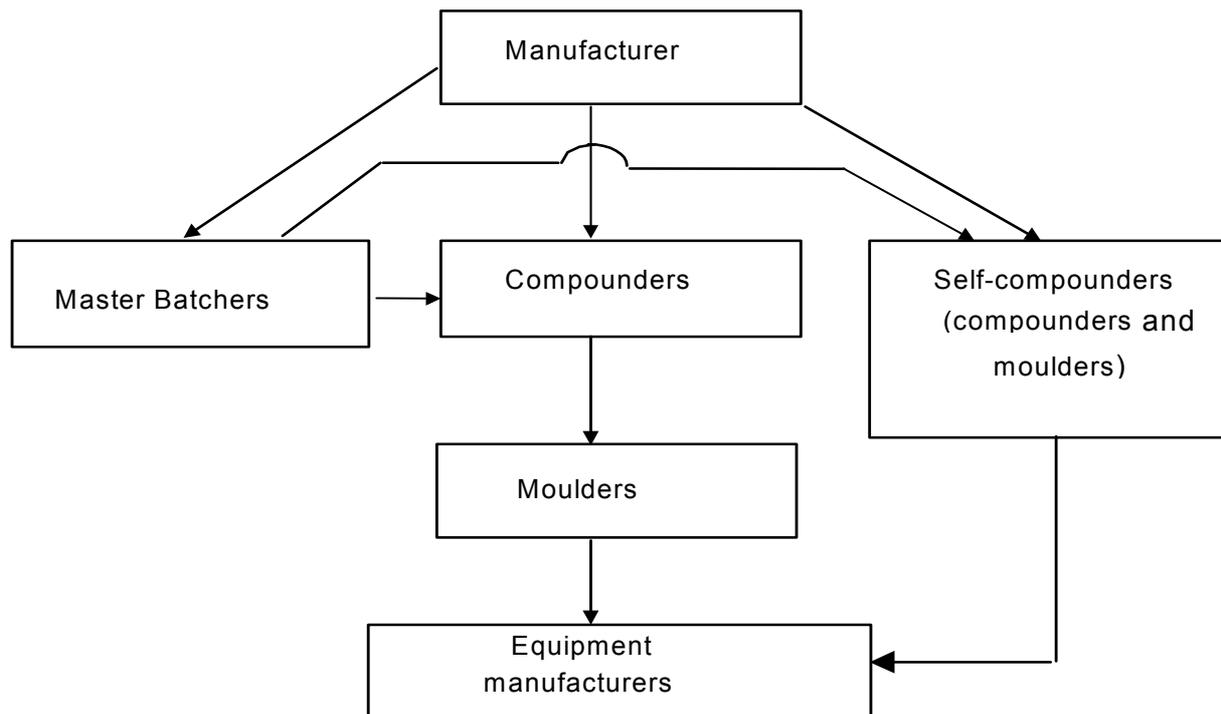
4.1.1.2.1   Manufacture

OBDPO was manufactured in only two plants in Europe until 1999. OBDPO is produced outside the EU in a closed system. Highest inhalation and dermal exposures are likely to occur during bagging, check weighing and activities such as material sampling and maintenance. Dust exposure generally only occurs during bagging and weighing as during the rest of the process the substance is contained in the processing solvents. Extraction ventilation and personal protective equipment are employed to reduce exposure.

Air measuring data supplied by one company give exposures to total inhalable dust (which is assumed to be all OBDPO as no other materials are present) ranging from 2 to 7 mg/m^3: 2 samples were taken during bagging (6 and 7 mg/m^3) and 2 samples during check weighing (2.2 and 4.4 mg/m^3) with a sampling flow rate of 1.5 l/min. These values apply to the actual task and not to a 8-hour shift exposure (HSE source, 1995). The low sampling flow rate may have resulted in underestimates of exposure, although the result may have been significant due to the large proportion of respirable dust in OBDPO. Clearly, four sample results are insufficient to establish with confidence the level of exposure during manufacture.

To further determine the exposure, the EASE model was used, dry manipulation and the presence of local exhaust ventilation (LEV), this predicts dust exposure in the range of 2-5 mg/m^3 (8-hour TWA), which is in agreement with the above measured values.

Consequently, a full-shift exposure of 5 mg/m^3 will be used to describe a reasonable worst-case scenario during manufacture, (with the highest exposure level during bagging), even though it is likely to be lower, as these tasks will rarely take 8 hours and will be intermittent.

In the case of skin exposure, assuming a non dispersive use and an intermittent contact, the EASE model predicts that the exposure to a dusty substance will be in the range of 0.1-1 mg/cm^2/day. An exposure of 1 mg/cm^2/day will be used as a reasonable worst case. However, in practice dermal exposure will be considerably reduced by the use of personal protective equipment.

4.1.1.2.2   **Plastic industry**

Following manufacture, the first step in the use of flame retardant is the production of flame retarded pellets by specialized compounders. OBDPO is incorporated to a polymer (mainly ABS) in conjunction with a synergist (antimony trioxide) and other additives. The pellet formulation is about 70% polymer and 30% flame retardant/synergist. The ratio of flame retardant to synergist is generally 3:1.

The pellets produced by compounders are then supplied to plastic injection moulders who produce semi-finished parts which are used in the end by the manufacturers of the final articles. Following manufacture, industry also reported that some companies (master batchers) might produce pre-formulated mixes of ingredients (flame retardant, synergist and pigment) that are then supplied to compounders. However this will not change the type of exposure. Therefore the use of OBDPO in plastic industry can be split in two areas which are described below:

- compounders and master batchers;
- moulders.

The number of exposed workers is not known, however it is likely to be several thousands.

Compounders and master batchers

Compounding is a batch process using a mixer, a compounding mill and an extruder. The typical temperature in the extruder is average 200°C and does not exceed 300°C.

Dust exposure is likely to be intermittent and may occur when OBDPO bags are emptied in the mixer. The use of antimony trioxide in association with OBDPO should impose strict processing procedures with high standard dust control. However occupational hygiene practice may change significantly from one company to another.

In a recent survey performed in the USA and submitted to CMA (BFRIP), 276 customers were contacted by mail and the findings were that most of them do not routinely collect exposure to brominated flame retardants. Seven companies reported total dust sample results, most of the air sampling was conducted during DBDPO handling. The personal total dust samples (n=52) averaged 1.67 mg/m^3 and ranged from less than 0.12 to 15.4 mg/m^3. Interpretation of this results is limited due to the lack of information on sample duration and the authors of the report conclude that these data are of limited utility for risk assessment (P. Breysse and J. Kacergis, May 2000).

No other measured data are available either for OBDPO or for other brominated flame retardants.

Assuming dry manipulation, the EASE model predicts dust exposure in the range of 2-5 mg/m^3 in the presence of LEV and in the range of 5-20 mg/m^3 without LEV. These values are full-shift exposure levels. As the task (bag emptying) typically takes 1 to 3 hours a day and do not occur every working day (batch process which may use many other flame retardants), levels at the bottom of the given ranges are more likely to occur. Consequently, during bag emptying, an inhalation exposure of 5 mg/m^3, full shift, will be assumed.

In the case of skin exposure, assuming a non dispersive use and an intermittent contact, the EASE model predicts that the exposure to a dusty substance will be in the range of 0.1-1 mg/cm^2/day. An exposure of 1 mg/cm^2/day will be used as a reasonable worst case. In practice, dermal exposure will be reduced for the same reasons as mentioned above (duration and frequency of the task) and by the use of personal protective equipment.

Release of OBDPO fumes during extrusion may be a source of exposure. A quantitative estimation of the level of exposure is problematic because a lot of uncertainties remain about the mist formation process and there is no suitable model to predict it. However, the low vapour pressure of the substance will minimise emission. Furthermore it is likely that extraction ventilation will be used to control the generation of fume due to the presence of irritant and noxious degradation products encountered when heating plastics and exposure to the mist is thought to be extremely low.

After extrusion the flame retardant is incorporated in the polymer matrix. In addition, the polymer is in a non-dusty pellet form. The potential for further exposure is likely to be negligible.

Moulders

Inhalation and dermal exposure is expected to be low because of incorporation of the substance in the polymer matrix. The generation of dust during handling of pellets is likely to be negligible.

Temperatures used by injection moulders are generally similar to those used for extrusion. Release of OBDPO fumes during injection may be a source of exposure but the low vapour pressure of the substance and the presence of extraction ventilation will minimise exposure.

Equipment manufacture

Workers will handle plastic parts and not powder or even pellets. Exposure is expected to be low because of enclosure of the substance in the polymer matrix. In case of heating of the flame retarded plastic, release of fumes is unlikely to be a significant source of exposure (of the same order as during moulding).

End uses of the flame retarded products

The fire retardant is physically bound within the polymer matrix, however it is not chemically bound and could theoretically migrate. Therefore release of OBDPO to atmosphere from plastic products (office equipment, computer) may be a potential way of exposure but the very low vapour pressure and high molecular weight of the polybromodiphenyl oxides lead to negligible migration.

An investigation was conducted to determine the emission of PBDPO from plastics in two TV sets, two computer monitors and three printers under conditions of use. Each appliance was placed in a test chamber of 1.17 m^3 for three days, pure air was continuously drawn through the chambers at a rate of $1.5 \text{ m}^3/\text{h}$ and the emitted compounds were adsorbed on a sampler for subsequent extraction and determination of PBDPOs with 4 or more bromine. PBDPOs were found to vary between 0.4 and 889 ng/appliance (Ball et al., 1991).

Determination of PBDPOs in air and in dust was made in offices having a large number of TV or computer monitors in operation: the police traffic control of Hamburg and three rooms of a television company. Concentration in air was 97 pg/m^3. Indoor dust sampling contained PBDPO at high ppb levels (Ball et al., 1992).

Quantitative measurements of PBDPOs in ambient air at a plant for dismantling electronics show concentrations of 2,2',3,4,4',5',6 HpBDPO in the range of 6.3-87 ng/m^3. In this plant, the work includes manual dismantling of electronic goods such as personal computers, television sets and radio. Plastic goods were ground using a shredder. (Carlsson al., 1999 quoted in Sjödin et al.,

1999). In the same study 2,2',3,4,4',5',6 HpBDPO was detected at levels of at most 0.08 ng/m^3 in the air at ordinary offices.

In conclusion, exposure to OBDPO during subsequent use of flame retarded equipments is likely to be negligible.

Table 4.1   Conclusion of occupational exposure

Scenario	External inhalation exposure (mg/m³)	External dermal exposure (mg/cm²/day)
1 Manufacture (bagging and cleaning activities)	5	1

2 Coumpounding and master batching
  - bag emptying
  - extrusion
	5
	extremely low
		1
		negligible

3 Moulding	extremely low	negligible
4 Equipment manufacture	extremely low	negligible
5 End uses of flame retarded products	negligible	negligible

4.1.1.3   Consumer exposure

4.1.1.3.1   Introduction

Polybrominated diphenyloxides (PBDPOs) have no direct use as consumer products but are widely used in consumer plastics to enhance their flame retarding properties.

PBDPOs are additive flame retardants in that they do not react with the substrate but are present as bromine releasing agents which reduce and retard flame development in the event of fire.

There are very few useful data on the potential exposure to OBDPO from consumer products.

4.1.1.3.2   Use of OBDPO in plastics

In plastics the flame retardant is incorporated into the molten plastic during manufacturing process, e.g. a TV or computer case, circuit boards and a variety of other plastic products. Typical levels of OBDPO used in plastics are 12-18% (EBFRIP, 1995).

There are no measured data for the indoor environment for OBDPO. On the other hand, quantitative measurements of PBDPOs in the air at offices were carried out which show concentrations of PBDPOs of at most 97 pg/m^3 (Ball et al., 1992) and of 2,2',3,4,4',5',6 HpBDPO (one component of commercial OBDPO) of at most 0.08 ng/m^3 (Carlsson al., 1999 quoted in Sjödin et al., 1999). This confirms that exposure to PBDPOs from polymer matrices will be very small; this will be because PBDPOs are immobile within the matrices (EBFRIP, 1995).

In summary, based on scattered pieces of evidence and in agreement with previous risk assessment conducted under the auspices of International Programme on chemical Safety (IPCS) (Brominated Diphenyl Ethers, EHP, 162, IPCS, 1994), it is felt that consumer exposure to OBDPO is likely to be negligible.

4.1.1.4   Humans exposed via the environment

The exposure to humans via environmental routes has been estimated using EUSES (see Appendix B). The results are reported in **Table 4.2** below.

Table 4.2   Predicted concentrations relevant to exposure of humans via the environment

Scenario	Route	Predicted concentration		Estimated daily dose (mg/kg bw/day)	
		1994 data	1999 data	1994 data	1999 data
Local - Polymer processing	Wet fish	$3.2 \cdot 10^{-4}$ mg/kg	$1.0 \cdot 10^{-4}$ mg/kg	$5.3 \cdot 10^{-7}$	$1.6 \cdot 10^{-7}$
	Root tissue of plants	1.86 mg/kg	1.82 mg/kg	0.010	0.010
	Leaves of plants	0.023 mg/kg	$6.9 \cdot 10^{-3}$ mg/kg	$4.0 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$
	Drinking water	$1.4 \cdot 10^{-4}$ mg/l	$1.4 \cdot 10^{-4}$ mg/kg	$3.9 \cdot 10^{-6}$	$3.9 \cdot 10^{-6}$
	Meat	0.11 mg/kg	0.054 mg/kg	$4.7 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
	Milk	0.035 mg/kg	0.017 mg/kg	$2.8 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
	Air	$1.5 \cdot 10^{-5}$ mg/m³	$4.3 \cdot 10^{-6}$ mg/m³	$3.2 \cdot 10^{-6}$	$9.5 \cdot 10^{-7}$
	Total local daily dose			0.011	0.011
Regional	Wet fish	$3.0 \cdot 10^{-5}$ mg/kg	$1.4 \cdot 10^{-5}$ mg/kg	$4.9 \cdot 10^{-8}$	$2.4 \cdot 10^{-8}$
	Root tissue of plants	0.069 mg/kg	0.026 mg/kg	$3.8 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
	Leaves of plants	$4.4 \cdot 10^{-4}$ mg/kg	$2.2 \cdot 10^{-4}$ mg/kg	$7.6 \cdot 10^{-6}$	$3.7 \cdot 10^{-6}$
	Drinking water	$5.1 \cdot 10^{-6}$ mg/l	$2.0 \cdot 10^{-6}$ mg/l	$1.5 \cdot 10^{-7}$	$5.6 \cdot 10^{-8}$
	Meat	$4.3 \cdot 10^{-3}$ mg/kg	$1.8 \cdot 10^{-3}$ mg/kg	$1.8 \cdot 10^{-5}$	$7.7 \cdot 10^{-6}$
	Milk	$1.4 \cdot 10^{-3}$ mg/kg	$5.6 \cdot 10^{-4}$ mg/kg	$1.1 \cdot 10^{-5}$	$4.5 \cdot 10^{-6}$
	Air	$2.8 \cdot 10^{-7}$ mg/m³	$1.4 \cdot 10^{-7}$ mg/m³	$6.1 \cdot 10^{-8}$	$3.0 \cdot 10^{-8}$
	Total regional daily dose			$4.2 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$

The other possible route for OBDPO into the human food chain is via direct absorption into fatty foods such as oils, margarine, butter etc. This route, however, requires the food to come into direct contact with OBDPO. Given the uses of OBDPO, it is considered very unlikely that this would be an important route into food.

The above doses of 11 µg/kg bw/day and 0.42 µg/kg bw/day estimated with 1994 data will be used in the risk characterisation.

4.1.1.5   Combined exposure

For combined exposure, it is the occupational exposure that is predominant. The estimated indirect exposure via environment is very low compared to occupational exposure and consumer is thought to be negligible, therefore they do not contribute significantly to the combined exposure.

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

No toxicological information on OBDPO is available from studies in humans. The composition of the substance used in toxicological studies has been indicated when provided.

4.1.2.1   Toxicokinetics, metabolism and distribution

4.1.2.1.1   Studies in animals

Xenobiotic metabolism

In study from Carlson (1980a), designed largely to investigate hepatic enzyme induction, groups of 4 male rats were administered commercial OBDPO (a mixture containing 1.1% of PeBDPO, 8.5% of HxBDPO, 45.1% of HpBDPO, 30.7% of OBDPO, 13% of NBDPO, 1.6% of DeBDPO) at 0.1 mmol/kg/day (corresponding to 76.6 mg/kg/day) for 14 days (with seven administrations). Control animals received vehicle only. No positive controls were included in this experiment. No indication on the randomisation was reported. A liver enlargement was observed with an increase in the activity of O-ethyl-O-p-nitrophenyl phenylphosphonothioate (EPN) detoxification (145% above control group), p-nitroanisole demethylation (182% above control group), UDP-glucuronyl transferase (66% above control group), NADPH-cytochrome c reductase (86% above control group), cytochrome P450 (135% above control group). OBDPO was without effect on benzo[a]pyrene hydroxylase and sorbitol dehydrogenase. It was concluded by the author that commercial brominated diphenyl ethers including OBDPO and PeBDPO are fairly potent inducers of xenobiotic metabolism (Carlson, 1980a).

Oral administration for 90 days also increased xenobiotic metabolism: increases in EPN detoxification and p-nitroanisole demethylation from 0.78 μmol/kg/day (corresponding to 0.60 mg/kg/day) and, increases of cytochrome P450 (15% above control group) and NADPH-cytochrome c reductase (8.5% above control group) at 3.13 μmol/kg/day (corresponding to 2.4 mg/kg/day). The increases in EPN detoxification and p-nitroanisole demethylation were respectively 75% and 61% above control group at 3.13 μmol/kg/day. These increases were dose-dependent and some changes were still observable 30 to 60 days after the latest dosage. Although measurements of tissue content were not made, it is suggested that this extended period of induction is the result of the potency of OBDPO to act as inducer and of accumulation in sites such as adipose tissue and liver (Carlson, 1980b). Light microscopic examination of livers from rats dosed with up 2.4 mg/kg/day did not reveal substance-related changes.

In a recent study from Zhou et al. (2001), designed to investigate hepatic enzyme activity and thyroid hormone concentrations, weanling rats were exposed to three commercial PBDPO mixtures: DE-71 (58.1% PeBDPO and 24.6% TeBDPO), DE-79 (30.7% OBDPO and 45.1% HpBDPO) and DE-83 R (98% DBDPO). Female Long-Evans rats, 28 days old, were orally administered various doses from 0.3 to 100 mg/kg/day of DE-79 and DE-83R and from 0.3 to 300 mg/kg/day of DE-71 for 4 days. 8 animals were allocated per dose except for 0.3 mg/kg/day for DE-71 where 4 animals were allocated. Serum and liver samples were collected 24 h after the last dose and analysed for serum total thyroxine (T$_4$), triiodothyronine (T$_3$), thyroid-stimulating hormone (TSH), hepatic microsomal ethoxy- and pentoxy-resorufin-O-deethylase (EROD and PROD), and uridinediphosphate-glucuronosyltransferase (UDPGT) activities. The PBDPO-treated groups did not exhibit significant changes in body weight; however, increased liver

weights were found in the DE-71– and DE-79–treated animals with a statistical significant increase from 10 mg/kg/day with DE-79 and from 30 mg/kg/day with De-71. 10- to 20-fold induction in EROD and 30- to 40-fold induction in PROD were found in the DE-71– and DE-79– treated animals. DE-71 and DE-79 caused dose-dependent depletion of T_4 (statistically significant from 10 mg/kg/day with DE-79 and from 30 mg/kg/day with DE-71) accompanied by up to 3- to 4-fold induction in UDPGT activities. Serum total T_4 was decreased a maximum of 80% for DE-71 and 70% for DE-79 in the highest dose (100 mg/kg/day). Dose-related effects in serum T_3 levels were less apparent (statistically significant from 60 mg/kg/day with DE-71 and from 100 mg/kg/day with DE-79), with maximal reductions of 25–30% at the highest dose for both DE-71 and DE-79. The two mixtures showed no effect on serum TSH levels. DE-83R was not effective in altering any of the measured parameters. The present study suggests that short-term exposure to some commercial PBDPO mixtures (including OBDPO and HpBDPO mixtures) interferes with the thyroid hormone system and that one of the mechanism by which PBDPOs interfere is via upregulation of UDPGTs.

OBDPO is an inducer of xenobiotic metabolism with dose and time dependent relationship.

Distribution and retention

Dose-related increases in total bromine levels in the liver were noted after 4 weeks of oral treatment at 100 or 1,000 ppm and ranged from 6 to 40 times the levels found in controls (Great Lakes, 1976a). These total bromine levels decreased rapidly during the recovery period but only in rats with the lowest level, the liver total bromine concentration approached the control levels after a 4-week withdrawal period. The total bromine content in the liver was also increased after 13 weeks of treatment at 100 - 1,000 and 10,000 ppm and decreased during the recovery period (8 weeks - 6 months) but remained higher (a six fold increase at 10,000 ppm) than the control values after one year of withdrawal. The slow decline of bromine in the tissues suggests a capacity for bioaccumulation with repeated exposure. In these studies, the nature of the bromine detected was not characterised. However, it may be assumed that the tissue detection of bromine is indicative of the presence of parent OBDPO or its metabolites since free bromine is water soluble (Great Lakes, 1977b).

After a 14-day inhalation exposure of OBDPO, the total bromine concentrations in lung, liver and fat were higher than in controls and it appeared that lung and fat accumulated OBDPO to a greater extent than the liver (1.5 to 12.5 times higher) (Great Lakes, 1978).

These data on distribution and retention show an absorption of OBDPO by oral or inhalation route. Pertaining to percutaneous absorption, no data are available on OBDPO neither on DBDPO, PeBDPO or polybrominated biphenyl compounds (Polybrominated biphenyls. Environmental Health Criteria 152, IPCS, 1994). Nevertheless based on OBDPO physicochemical properties and by analogy with PCBs, an estimation of dermal absorption might be done. Indeed it is commonly assumed that stratum corneum is the crucial barrier and the rate limiting step is either: 1) diffusion into and through the lipid-rich intercellular matrix of the stratum corneum, or 2) diffusion out of the stratum corneum into and through the relatively aqueous viable epidermis below. The predominance of either step appears to depend upon the lipophilicity or lipid solubility of the penetrant (Jackson et al., 1993). Moreover it is now generally accepted that relatively low molecular weight compounds (<500 dalton) of correctly balanced oil water partitioning are likely to have decent passive skin permeabilities (Guy, 1996).

With respect to those considerations and given physico-chemical properties of OBDPO, high log Kow (6.29), poor water solubility (<0.5μg/l) and high molecular weight (801) the dermal absorption is expected to be low.

In addition, the effects of halogen substitution on the dermal absorption have been studied with polychlorinated biphenyls. It was shown that dermal penetration varied inversely with degree of chlorination and at 48 hours ranged from 100% for monochlorobiphenyl to 30% for the hexachlorobiphenyl and penetration rate constants correlated well with log Kow. Moreover the authors assume that penetration of PCB with seven or more chlorine would be less than 1% (Garner and Matthews, 1998). If this pattern is also applied to OBDPO, this would lead to predict a maximum absorption of 4.5%. Indeed commercial OBDPO contains congeners with seven or more bromine (from 88 to 90%) and congeners with six or less bromine (only 10.5 to 12%). Assuming that this latter is mainly HxBDPO we may assume for this compound a dermal absorption of 30% and for the other congeners a dermal absorption lower than 1% which leads to a global dermal absorption of 4.5%.

Nevertheless, fatty chemicals tend to accumulate in the stratum corneum which behaves as a storage site and releases these chemicals over a long period of time, a phenomenon known as a reservoir effect (Leung et al., 1994). This reservoir effect was observed with high chlorinated PCBs. Indeed high-chlorinated PCBs such as tetrachlorobiphenyl and hexachlorobiphenyl are retained in the site of exposure and are very slowly absorbed systemically. Pertaining to commercial OBDPO, which contains in particular HxBDPO or HxBDPO/PeBDPO and HpBDPO, a possible reservoir effect cannot be dismissed.

In conclusion, dermal absorption of OBDPO is assumed to be low and may be estimated to be 4.5%, associated with a likely trend towards accumulation in the stratum corneum which behaves as a storage site, leading to a slow systemic release over the time.

4.1.2.1.2   Studies in humans

OBDPO was detected (70-8,000 pg/g) in human adipose tissue selected from the National Human Adipose Tissue Survey (FY 87 NHATS) Repository (Stanley et al., 1991). The samples analyzed were selected from composites of the fiscal year 1987 National Human Adipose Tissue Survey (FY87 NHATS) repository. No information is provided on the method of tissue sampling, nor on the number of individuals, on the pattern of exposure. Identification of the polyhalogenated diphenylethers (PHDPEs) was based on comparison of full scan mass spectra of the samples to the available standards, application of SIM (Selected Ion Monitoring) techniques to compare theorical ion ratios to observed ion ratios for characteristic ions, and measurement of fragment losses from the molecular ion clusters. The authors conclude that the presence of polybrominated diphenylethers (PBDPEs) in human adipose tissues suggests exposure to these compounds from commercial products as well as environmental pathways.

Since few human data are available on OBDPO compound, when qualitative and/or quantitative data were available on 2,2',4,4',5,5' hexabromodiphenyloxide, 2,2',3,4,4',5',6-heptabromodiphenyloxide and nonabromodiphenyloxide which are components of commercial octabromodiphenyl oxide product, those data were included in the report.

Polybrominated diphenyloxides including 2,2',4,4',5,5' hexabromodiphenyloxide were detected in pooled blood samples (40 men) taken from a random population (Klasson Wehler et al., 1997). However, only qualitative results were provided for this compound but no quantified data were reported for 2,2',4,4',5,5' hexabromodiphenyloxide. As a feasibility project, Lindström et al. (1997) monitored PBDPOs including TeBDPO, PeBDPO and HxBDPO in human in the adipose tissue of a small group of elderly patients with non-Hodgkin's lymphoma in Sweden. Concerning HxBDPO results, 2,2',4,4',5,5' HxBDPO was detected at levels of the order of ng/g of adipose tissue. In Haglund et al. (1997), identification and quantification of methoxy-polybrominated

diphenyl ethers and polybrominated diphenyl ethers including TeBDPO, PeBDPO and HxBDPO were mainly carried out in Baltic biota and in a less extent in human adipose tissue. 2,2',4,4',5,5' HxBDPO was detected at levels of the order of ng/g of adipose tissue (1.7 ng/g) in adipose tissue sampled in 1994 from a healthy Swedish 74-year old male. In Spanish general population (Meneses et al., 1999), PBDPOs including TeBDPO, PeBDPO and HxBDPO were also detected in human adipose tissues with levels of similar order (ng/g) adipose tissue. 2,2',4,4',5,5' HxBDPO compound was detected at level of 1.8 ng/g in lipid.

Contamination levels of polybrominated diphenyloxide were determined in the blood of Japanese people for the first time (Nagayama et al., 2001). Blood sample was obtained from 54 volunteers (27 males and 27 females) with the mean age of 43.9 years (37-49 years old) in 1998. PBDPOs were determined in all of the 54 blood samples. Usually contamination level was the highest in 2,2',4,4'-tetrabromodiphenyl oxide. However, in the blood of Japanese adults, 2,2',4,4',5,5'-hexabromodiphenyloxide was the highest with the median value of 2,300 pg/g lipid, 2,2',4,4',5-pentabromodiphenyloxide the second (1,200 pg/g lipid) and 2,2',4,4'-tetrabromodiphenyloxide the third (520 pg/g lipid). The median concentration of total PBDPOs was 4,500 pg/g lipid. No data on HpBDPO, OBDPO or DBDPO are reported. This total median PBDPOs level was comparable to those in Swedish breast milk (Darnerud et al., 1998).

In a well reported study (Sjödin et al., 1999), potential exposures to PBDPOs were determined for clerks working full-time at computer screens (20 females) and personnel at an electronics dismantling plant (15 males and 4 females), with hospital cleaners (20 females) as a control group (see **Table 4.3**). Five PBDPO congeners 2,2',4,4'-TeBDPO, 2,2',4,4',5,5'-HxBDPO, 2,2',4,4',5,6'-HxBDPO, 2,2',3,4,4',5',6-HpBDPO and DBDPO were quantified in blood serum from all categories of workers. In the electronics dismantling plant, the work includes manual dismantling of electronic goods such as personal computers, television sets and radio. Plastic goods were ground using a shredder. The personnel in charge of the shredder wore dust protection masks made of filter paper during this work; no respiratory protection was used for other work tasks.

- Subjects working at the dismantling plant (n=19) showed significantly higher levels of all PBDO congeners in their serum as compared to the control group with 2,2',3,4,4',5',6-HpBDPO as major compound. The relative increase for this compound was most pronounced (approximately 70 times the median value), whereas the corresponding values for the other compounds varied between two and seven times. DBDPO was present in concentrations of 5 pmol/g lipid weight (lw) in the personnel dismantling electronics; these concentrations are comparable to the concentrations of 2,2',4,4'-TeBDPO.

- Clusters of OBDPOs and NonaBDPOs were confirmed to be present in the blood samples of the electronics-dismantling workers but no quantitative measurements were performed because of the lack of authentic standards.

Table 4.3 Median and range serum concentrations (pmol/g lipid weight with ng/g lipid weight in parenthesis) of five PBDE congeners, total PBDEs, and CB-153 for subjects from three occupational settings (quoted in Sjödin et al., 1999)

Compound	Hospital cleaners (*n*=20)		Computer clerks (*n*=20)			Electronics dismantlers (*n*=19)		
	Median [a]	Range [a]	Median [a]	Range [a]	p [b]	Median [a]	Range [a]	p [b]
2,2',4,4'-tetraBDO	3.2 (1.6)	<1-34	3.0 (1.5)	<1-10	>0.5	5.9 (2.9)	<1-47	0.02
2,2',4,4',5,5'-hexaBDO	0.89 (0.57)	0.64-7.6	1.3 (0.85)	0.80-5.1	0.02	7.0 (4.5)	3.2-19	<0.001
2,2',4,4',5,6'-hexaBDO	0.59 (0.38)	0.25-1.4	0.79 (0.51)	0.43-1.5	0.04	1.9 (1.2)	0.74-7.4	<0.001
2,2',3,4,4',5',6-heptaBDO	0.16 (0.12)	0.025-0.39	0.24 (0.18)	<0.02-1.4	0.02	11 (7.8)	3.1-26	<0.001
2,2',3,3',4,4',5,5',6,6'- decaBDO	<0.7 (<0.7)	<0.3-3.9	<0.7 (<0.7)	<0.3-8.0	>0.5	5.0 (4.8)	<0.3-9.9	<0.001
Polybrominated diphenyl ethers [c]	5.4 (3.3)	3.1-39	7.1 (4.1)	3.9-17	0.1	37 (26)	15-75	<0.001
2,2',4,4',5,5'-hexaCB	330 (120)	120-1,000	480 (170)	130-1,300	0.08	760 (270)	190-2,200	<0.001

a) Amount present in blank samples subtracted
b) Level of significance derived from Mann-Whitney *U*-test hospital cleaners as control
c) Sum of the PBDE congeners quantified, using values obtained for limit of quantification and detection for non-quantified samples

- For the computer clerks (n=20), small but significantly elevated levels were observed for 2,2',3,4,4',5',6-HpBDPO as compared to the cleaners. The dominating PBDPO congener in the clerks and cleaners was TeBDPO. According to the authors, this is an indication that computer work may cause exposure to PBDPOs but these observations need to be confirmed.

- The total PBDPO median concentrations in the serum from workers at the electronics-dismantling plant, clerks and cleaners were 37, 7.1 and 5.4 pmol/g lw, respectively. The serum concentrations of all PBDPO congeners decreased during summer vacation in the electronics-dismantling workers (the median decreases between 14 and 66% for TeBDPO and DBDPO respectively). Those results show that DBDPO and other PBDPOs congeners are bioavailable and that occupational exposure to PBDPOs occurs at the electronics-dismantling plant. Interestingly, there seem to be different half-lives depending on bromination degree of the diphenyl oxides; the more bromine in the molecule, the shorter the half-live is.

- Those results indicate also that PBDPOs are environmental contaminants since PBDPOs were also present in human lipids extracted from serum of subjects who had been working in a potentially non-PBDPO contaminated environment. No correlations were observed for any of the PBDPO congeners with age or fish intake.

Hagmar and Bergman (2001) reported plasma levels of 2,2',4,4',5,5'-hexaBDO, 2,2',3,4,4',5',6-heptaBDO, 2,2',3,3',4,4',5,5',6,6'- decaBDO in occupational settings. These results indicate that dismantling old electronic equipment, intense work with brand new computers and smelting of electronics are related to increased plasma levels of some of those congeners (see **Table 4.4** below).

Table 4.4 Median and range plasma concentrations (ng/g lipid) of three PBDE congeners for subjects from three occupational settings (quoted in Hagmar and Bergman, 2001)

Compound	Smelter workers (*n*=9)		Computer technicians (*n*=19)		Electronics dismantlers (*n*=6)		
	Median	Range	Median	Range	Median	Range	p
2,2',4,4',5,5'-hexaBDO	1.3	0.77-2.5	2.6	<1.3-18	3.1	1.7-9.7	
2,2',3,4,4',5',6-heptaBDO	<0.5	<0.5-1.3	0.98	0.15-4.8	3.2	2.5-12	
2,2',3,3',4,4',5,5',6,6'-decaBDO	2.3	1.4-5.6	1.5	<1-6.8	No data	No data	

Hovander et al. (2001) reported plasma concentrations of 2,2',4,4',5,5'-hexaBDO and 2,2',3,4,4',5',6-heptaBDO in nine subjects (three office workers and six electronics dismantlers). The concentrations of 2,2',4,4',5,5'- hexaBDO and 2,2',3,4,4',5',6- heptaBDO, ranging between 0.9–9.7 ng/g and 0.4–12.2 ng/g lipid respectively were higher in the dismantler than in the office workers and also when compared to the control group of a previous study from Sjödin et al. (1999).

Plasma concentrations of polybrominated diphenyl oxide were also determined in three Norvegian occupational groups (Thomsen et al., 2001a; Thomsen et al., 2001b). Samples were obtained from three groups of five individuals each working a) at an electronics dismantling facility, b) in production of printed circuit boards, and c) in an analytical laboratory. 2,2',3,4,4',5',6-HpBDPO was only identified in plasma from electronics dismantling plant personnel whereas 2,2',4,4',5,5'-HxBDPO was detected in each occupational group with higher plasma levels at the electronics dismantling plant compared to the other groups (see **Table 4.5**). No data on OBDPO or DBPO are reported. The total amount of PBDPOs were 8.8, 3.9 and 3.0 ng/g lipids for the group of electronic dismantlers, circuit board producers and laboratory personnel, respectively. Generally large variations in the individual concentration levels were found within the groups, especially in the group of electronic dismantlers.

Table 4.5 Mean, range (ng/g lipid) and relative standard deviation (RSD) of the plasma concentrations of PBDOs congeners in three occupational groups.
The mean concentrations are given in pmol/g lipid weight in parentheses. Undetected compounds are marked with n.d. (quoted in Thomsen et al., 2001b)

Compound	Electronics dismantlers		Circuit board producers		Laboratory personnel	
	Mean [a]	Range (RSD,%) [a]	Mean [a]	Range (RSD,%)	Mean [a]	Range (RSD,%)
2,2',4,4'-tetraBDO	4.0 (8.2)	0.87-15 (147)	1.6 (3.3)	0.43-3.4 (73)	1.5 (3.1)	1.0-3.0 (55)
2,2',4,4',5,5'- hexaBDO	1.7 (2.6)	1.2-2.3 (23)	0.95 (1.5)	0.50-1.8 (52)	0.54 (0.84)	0.43-0.63 (14)
2,2',4,4',5,6'- hexaBDO	0.44 (0.68)	0.21-0.86 (62)	0.21 (0.33)	n.d.-0.30 (58)	n.d.	n.d.
2,2',3,4,4',5',6- heptaBDO	0.44 (0.61)	0.18-1.5 (141)	n.d.	n.d.	n.d.	n.d.
Sum of PBDPOs	8.8 (16)	3.8-24 (98)	3.9 (7.3)	1.6-7.3 (55)	3.0 (5.9)	2.4-5.1 (39)

a) Sum of PBDPOs quantified

One of these studies (Stanley et al., 1991) demonstrates absorption of the OBDPO compound in humans and that OBDPO is distributed to the adipose tissues and lipid. The other study available (Sjödin et al., 1999) confirms a systemic absorption of OBDPO and NonaBDPO since clusters of OBDPOs and NonaBDPOs were identified but not quantified. The other studies available on

PBDPOs including 2,2',4,4',5,5' hexabromodiphenyloxide which is a component of a commercial octabromodiphenyl oxide product, TeBDPO and PeBDPO confirms systemic absorption and distribution to the adipose tissues. As there is evidence that PeBDPO is highly persistent and bioaccumulative and as PeBDPO has been detected, albeit at relatively low levels, in human breast milk. It was deemed prudent to assess the potential excretion of OBDPO in the breast milk as well. Therefore PBDPOs data on breast milk excretion were included in this report.

In Meironyté et al. (1998; 1999) and Norén and Meironyté (1998) studies which focused mainly on analytical techniques and extraction and purification methods, samples of human milk were analysed for PBDPO content. The milk was collected during different periods from 1972 to 1997 and supplied by the Mothers' Milk Centre in Stockholm. The milk samples were collected from differing numbers (ranging from 20 to 116) of women with an average age between 27 and 31 years, over a 25-year period from 1972 to 1997. TriBDPO, TeBDPOs, PeBDPOs and HxBDPOs congeners were differentiated. Recovery studies were performed by adding a standard solution of TriBDPOs, TeBDPOs, PeBDPOs and HxBDPO to one of the samples before extraction. The average recoveries of these substances ranged from 86 to 102% except for one internal standard (3,3',4,4'-TeBDPO) with a recovery of 70-111%.

These data demonstrated an increase in total PBDPOs from 72 to 4,010 pg/g lipids during the last 25 years with TeBDPO as the predominant congener representing the greatest fraction of PBDPOs (about 60-70%) during the period 1976-1997. Two isomers of PeBDPOs were also detected at pg/g lipid concentrations and also showed an increase in concentration with time as well as for HxBDPO congeners. The concentrations in 1997 for PeBDPOs and HxBDPOs congeners were 1,100 pg/g lipid and 500 pg/g respectively. No data on HpBDPO, OBDPO or DBDPO are reported. It should be noticed that no information is given on the technique of preservation of the milk samples, a possible evolution with time of these samples, a possible silylation treatment of the glassware used for the storage of the samples and on the purity of the standard substances used. Moreover it is not obvious if the extraction yield was taken into account in the final results.

Meironyté et al. (2001) reported levels of hexabromodiphenyl ether congeners and heptabromodiphenyl ether congener in samples of human milk from Sweden over the years 1998 to 2000. The samples were analysed by the method described by Meyronité et al. (1999). Two pooled samples from each year were analysed (each pooled sample contained milk from 20 mothers). Detection of OBDPO and DBDPO was not carried out. The levels found were 0.02 ng/g lipid in 1998, 0.07 ng/g lipid in 1999 and 0.05 ng/g lipid in 2000 for 2,2',3,4,4',5',6-heptabromodiphenyl ether. 2,2',4,4',5,5'-hexabromodiphenyloxide was also detected at level of 0.47, 0.54 and 0.45 ng/g lipid respectively. These results show that the levels of PBDPOs in human milk tend to decline during the last years. The highest concentrations of PBDPOs were found in 1997, while the levels in 2000 are similar to those from 1995.

In a briefly summarised paper picograms/g fat concentrations of HxBDPOs (named PBDE-153 and PBDE-154) have been detected in breast milk samples from 39 women (Darnerud et al., 1998). The breast milk was obtained from primiparous mothers from Uppsala county, Sweden aged 22 to 36 years. The year of the collection was not indicated, however the study is part of a current and ongoing investigation on persistent and organic pollutants in blood and breast milk from mothers planning to include 250 mothers. The women had to answer a questionnaire focusing on the present pregnancy, including symptoms, dietary habits and other habits (including smoking and alcohol consumption). The levels of PBDPOs detected in the breast milk samples were generally within 1,000 to 10,000 pg/g fat weight with one individual presenting a high peak value (28,170 pg/g fat). Five major congeners (TeBDPO, PeBDPOs and HxBDPOs) were identified of which TeBDPO was the major congener in the breast milk (55% of PBDPOs).

The median PBDPOs and HxBDPOs values in breast milk were 3.4 ng/g fat and 538 pg/g fat respectively. It was reported that this value is more or less a hundred times smaller than that found for PCBs. Within this small group of samples there was no correlation between the concentrations of PBDPOs and mothers' age, alcohol or fish consumption, place of residence or birth weight of the child, computer usage frequency although an increase in concentration with increasing cigarette smoking was suggested. However it is not established if smoking habits are a causal effect for the increase of PBDPOs in human breast milk. No data on HpBDPO, OBDPO or DBDPO are reported. These results can be compared with that from Kruger (1988) who reported a range of values between 600 to 11,000 pg/g milk fat (these partial results were provided by Kemi, (1998)). In an extended study from Lind et al. (2001) HxBDPOs (2,2',4,4',5,5'-hexabromodiphenyl ether and 2,2',4,4',5,6'-hexabromodiphenyl ether) have been detected in breast milk samples from 93 women. The breast milk was obtained from primiparous mothers from Uppsala county, Sweden aged 20 to 35 years (mean 27) over a period from 1996-1999. The women had to answer a questionnaire focusing on their dietary habits and life style including smoking and alcohol consumption before and during the pregnancy. The mean concentration of PBDPOs was 4. ng/g fat. TeBDPO was the major congener detected in the breast milk samples (about 50–60%). 2,2',4,4',5,5'-hexabromodiphenyloxide and 2,2',4,4',5,6'-hexabromodiphenyloxide were detected with a mean value of 597 ng/kg fat and 68 ng/kg fat, respectively.

Ryan and Patry (2001) reported the findings from a recent survey of the levels of 2,2',3,4,4',5',6-heptabromodiphenyloxide and 2,3,3',4,4',5,6-heptabromodiphenyloxide in human milk and commercial foods from Canada. Human milks were collected in 1992 from all provinces of Canada. The methodology used was capable of quantifying most of the congeners of the PBDPOs except for the octa and nona homologues for which standards are not available. The analysis of the substances in these samples was reported to be difficult, and the presence of substances in laboratory blanks made quantification in the samples uncertain. Little or no 2,3,3',4,4',5,6-heptabromodiphenyl oxide could be detected in 72 human milk samples from 1992, however 2,2',3,4,4',5',6-heptabromodiphenyloxide was reported to be present at a median level of around 180 ng/kg lipid and 2,2',4,4',5,5'-hexabromodiphenyloxide of around 300 ng/kg lipid.

On the whole human data demonstrate systemic absorption of the OBDPO compound in humans and that OBDPO is distributed to the adipose tissues and lipid. The other studies available on PBDPOs including 2,2',4,4',5,5' hexabromodiphenyloxide which is a component of a commercial octabromodiphenyl oxide product, TeBDPO and PeBDPO confirm this distribution to the adipose tissues but also indicate an excretion of these latter compounds in the breast milk. Unfortunately, such measurements were not carried out on OBDPO. However, based on the high lipophilicity of OBDPO, its potential to bioaccumulate in adipose tissues and the breast milk measured data with HxBDPO which is one of the components of commercial OBDPO, excretion of OBDPO in the breast milk may be anticipated.

4.1.2.1.3 Summary of toxicokinetics, metabolism and distribution

Only limited data are available. Animal data show an absorption of OBDPO by oral or inhalation route with an accumulation of the parent compound or its metabolites in the liver and also in the adipose tissue and the lung following an inhalation administration. The extent of absorption and elimination cannot be assessed from the data available. No information on the metabolism of OBDPO is available. Following oral administration, OBDPO is an inducer of xenobiotic metabolism with dose and time dependent relationship. There are no measured data on OBDPO dermal absorption or on PeBDPO, DBDPO and polybrominated biphenyls compounds. However

based on OBDPO physicochemical properties and analogy with PCBs, a dermal absorption of 4.5% may be estimated associated with a likely trend towards accumulation in the stratum corneum.

Very limited data on human toxicokinetics are available. These data indicate that OBDPO, HxBDPO, HpBDPO and NonaBDPO which are components of commercial OBDPO can be absorbed into the body and are distributed to the blood. Distribution to the adipose tissue was evidenced at least for OBDPO and HxBDPO. There are no data available on the rate of elimination or of bioaccumulation of OBDPO from human adipose tissue neither for PeBDPO but given the high lipophilicity of these compounds and the adipose tissues accumulation observed in rats following oral or inhalation routes, it can be assumed that in humans OBDPO might bioaccumulate in these tissues as well. Following pregnancy HxBDPO and others PBDPOs such as TeBDPO and PeBDPOs are excreted in the breast milk. Unfortunately, such measurements were not carried out on OBDPO. However, based on the high lipophilicity of OBDPO, its potential to bioaccumulate in adipose tissues and the breast milk measured data with HxBDPO (one component of commercial OBDPO), excretion of OBDPO in the breast milk may be anticipated.

4.1.2.2 Acute toxicity

4.1.2.2.1 Oral route (rat)

LD50 > 28,000 mg/kg body weight (Chem. Fabrik Kalk, 1982). No more information is available.

LD50 > 10,000 mg/kg body weight = no death during the study (72 hours) up to 10,000 mg/kg (Ethyl Corp., 1984a) (remark: the report was not available, a summary was only provided).

LD50 > 5,000 mg/kg body weight = no death and normal weight gain during the study (14 days) with commercial OBDPO suspended in corn oil when 50, 500 and 5,000 mg/kg were administered to five male Charles River CD rats respectively (Great Lakes, 1987).

LD50 > 5,000 mg/kg body weight = no death, no test article related lesions observed upon terminal necropsy at a dose level of 5,000 mg/kg administered to ten Sprague Dawley rats (5 males and 5 females). Decreased activity was observed immediately after dosing and one hour post treatment. The observation period was 14 days. This test was conducted in conformity with Good Laboratory Practices (GLP) (Ethyl Corp., 1983a).

4.1.2.2.2 Dermal route (rabbit)

LD50 > 2,000 mg/kg body weight = no death, normal weight gain during the study (14 days). OBDPO was administered neat under occlusive wraps for 24 hours to the clipped abraded or intact skin of New Zealand white rabbits at concentrations of 200 or 2,000 mg/kg bw. Necropsies were not performed and local or general signs of toxicity were not examined (Great Lakes, 1975a).

4.1.2.2.3 Inhalation route (rat)

LC50 (SAYTEX 111) > 50 mg/l (US EPA, 1986).

LC50 > 60 mg/l. One-hour exposure of 2 or 60 mg/l results in survival of all rats. Decreased motor activity, erythema and eye squint during exposure were observed from 2 mg/l and tachypnea at 60 mg/l. The animals exhibited normal body weight gain and no significant toxicity signs (observation period of 14 days). No necropsy results were provided. The physical properties of the substance precluded administration at levels higher than 60 mg/l. No data on particle size are given (Great Lakes, 1975b).

LC50 (SAYTEX 111 unmilled) > 17.3 mg/l (gravimetric concentration) (mass median diameter = 6.46 µm). 17.3 mg/l one-hour exposure results in survival of all rats. Crusty eye was observed in one test female and crusty nose in one male one day post exposure. No other reactions were noted in any test rats during the course of the investigation (14 days). Gross necropsy was carried out in particular on nasal cavity, paranasal sinuses, bronchi and lungs. Diffuse discolouration of the lung was only observed at necropsy in one test rat but this abnormality appeared not to be related to exposure to test article. This test was done in conformity with the GLP (Ethyl Corp., 1984b). The results of this test are consistent with the other available LC50.

4.1.2.2.4 Summary of acute toxicity

The acute toxicity of OBDPO is very low.

4.1.2.3 Irritation

4.1.2.3.1 Skin

OBDPO (500 mg) was applied for 24 hours to the clipped and occluded intact or abraded skin of 6 New Zealand white rabbits and followed by an observation period of 72 hours. Very slight erythema (grade 1) was observed in one animal (non abraded skin) at 72 hours. The remaining rabbits did not have skin changes (Great Lakes, 1975c).

Another study was carried out with Saytex 111 (500 mg), applied moistened with 0.9% saline for 24 hours under occlusion, to 2 intact and 2 abraded skin sites on each of 6 New Zealand White rabbits (3 males and females). Slight erythema (grade 1) in 3 animals and very slight edema (grade 1) in 2 animals were observed at 24 hours following application of the test article. No dermal examination was carried out at 48 hours after treatment but all sites returned to normal at 72 hours after treatment. This study was well reported, carried out in conformity with GLP standard. Even if, no dermal examination was carried out at 48 hours after treatment, this study is considered as appropriate to assess the irritation potency of OBDPO since no dermal irritation is observed at 72 hours (Ethyl Corp., 1983b).

4.1.2.3.2 Eye

The eye irritation studies conducted with 3 male and 3 female New Zealand white rabbits showed that single application of 100 mg of OBDPO caused a slight transient conjunctival irritation. The cornea and iris were unaffected (Ethyl Corp., 1983c; Great Lakes, 1975d). In Ethyl Corp. (1983c), conjunctival redness (grade 1) was observed at one hour only. No other positive responses were observed at 24, 48, 72 hours and at 7 days. This study was well reported and carried out in conformity with GLP standard. In Great Lakes (1975d), a slight discharge was noted from the eyes of two rabbits at 24 hours and a slight conjonctival redness (grade 1) was

noted in the eye of one rabbit at 48 hours. No other positive responses were observed at 72 hours and at 7 days.

OBDPO is not a dermal or an ocular irritant.

4.1.2.3.3   Respiratory tract

In an acute inhalation study on rats (Ethyl Corp., 1984b), gross necropsy was carried out on nasal cavity, paranasal sinuses, bronchi and lungs. Diffuse discolouration of the lung was observed at necropsy in one test rat among 10 animals but this abnormality appeared not to be related to exposure to test article. Moreover, in an inhalation sub-acute toxicity study in rats, histopathology of the respiratory tract was carried out on nasal turbinate area, lung and trachea and did not detect microscopically compound related lesions (Great Lakes, 1978).

Following 2 weeks of exposure by inhalation, local toxicity was demonstrated with hyperplasia/hypertrophy of the goblet cells from 1 mg/m^3 (Great Lakes, 2000). Chronic active lung inflammation and alveolar histiocytosis were observed within 13 weeks of exposure from 1.1 and 202 mg/m^3 respectively (analytical concentrations) in Great Lakes (2001), (see also Section 4.1.2.5).

4.1.2.4   Sensitisation

No human data on cutaneous or respiratory sensitisation are available.

A Magnusson and Kligman test was carried out. Twenty male guinea pigs were exposed to OBDPO intradermally (at a concentration of 2.5% in corn oil) and topically (with neat article moistened in corn oil) at induction and challenge. The test substance was a mixture of three samples of OBDPO, composition was provided and is representative of the current commercial products (as described in Chapter 1). No animals were sensitised. This test was conducted in conformity with GLP. The experimental design complied with the OECD Guidelines 406 for testing of chemicals (Chemical Manufacturers Association, 1996a).

OBDPO is not considered as a skin sensitiser.

4.1.2.5   Repeated dose toxicity

4.1.2.5.1   Oral sub-acute toxicity studies (rat)

In a 28-day study, groups of ten Charles River CD rats of each sex were fed diets containing 0 - 100 - 1,000 ppm OBDPO (which correspond respectively to 8.1 and 82.2 mg/kg/day for the males and to 8.4 and 88.3 mg/kg/day for the females). No changes in appearance, behaviour, mortality, feed consumption or body weight gain were observed. Hematology, blood chemistry and urinalysis parameters were not studied. No compound-related increase in organ weights except in the liver and no gross pathological lesions were noted.

Absolute and relative liver weights were increased in female rats given 100 ppm and in both sexes at 1,000 ppm diet. Compound-related histopathological liver lesions were observed: enlarged centrolobular and midzonal liver parenchymal cells in which the cytoplasm had large areas of finely granular "ground glass" structures containing eosinophilic "round bodies". These

changes occurred with a higher frequency and with greater severity in male animals. Their incidence and severity were dose-related.

Rats given 1,000 ppm had a slight to moderate hyperplasia of the thyroid (most of the follicles were very small, devoid of colloid and lined by basophilic columnar follicular epithelium) but it was not clear whether it was compound-related. Dose-related increase in total bromine levels of the liver was noted in both male and female rats and ranged from 6 to 40 times the levels found in controls (Great Lakes, 1976a).

The No Observed Adverse Effect Level (NOAEL) is not established in this study and the Lowest Observed Adverse Effect level (LOAEL) is 100 ppm (8.1 mg/kg/day approximately).

In a second 28-day feeding study, 10 Charles River CD rats of each sex were fed diets containing 0 - 100 - 1,000 or 10,000 ppm commercial OBDPO which corresponds respectively to 9.8, 97 and 1,003 mg/kg/day for the males and 9.9, 106 and 1,007 mg/kg/day for the females.

No changes in appearance, behaviour or mortality were observed. The food consumption and body weight gain were slightly lower in the treated groups than in the control group.

Clinical chemistry values were normal except a slight increase of serum urea nitrogen levels at 10,000 ppm.

An increase in absolute and relative liver weights was observed in some of the rats from 1,000 ppm group and enhanced lobulization and discolouration were observed at necropsy in the liver of some rats at 10,000 ppm. An enlargement of the centrolobular and midzonal hepatocytes was noticed from 100 ppm. Their cytoplasm had large areas of finely granular appearance and frequently contained eosinophilic "round bodies" which occurred with a dose related incidence and severity. Moreover in the 10,000 ppm group vacuolisation of hepatocytes and necrosis of scattered individual hepatocytes were seen. This kind of necrosis also occurred in one rat from the 1,000 ppm level. No significant increases in hepatic biochemical parameters (Alanine Aminotransferase (ALAT) or Aspartate Aminotransferase (ASAT) were observed at any dose level. These liver lesions were less severe at the end of the recovery period (4 weeks). A dose-related increase in liver total bromine content was seen from 100 ppm after 4 weeks of treatment, with a rapid decrease in the recovery period. However, only in rats with the lowest dose level liver total bromine concentration approached the control levels after a 4-week withdrawal period (Great Lakes, 1977).

The NOAEL is not established in this study and the LOAEL is 100 ppm (9.8 mg/kg/day approximately).

In study from Carlson (1980a) (also reported in Section 4.1.2.1.1), designed largely to investigate hepatic enzyme induction, groups of 4 male rats were administered commercial OBDPO at 0.1 mmol/kg/day (corresponding to 76.6 mg/kg/day) for 14 days (with seven administration). Control animals received vehicle only. No positive controls were included in this experiment. No indication on the randomisation was reported. A liver enlargement was observed with an increase in the activity of O-ethyl-O-*p*-nitrophenyl phenylphosphonothioate (EPN) detoxification (145% above control group), p-nitroanisole demethylation (182% above control group), UDP-glucuronyl transferase (66% above control group), NADPH-cytochrome c reductase (86% above control group), cytochrome P450 (135% above control group). OBDPO was without effect on benzo[a]pyrene hydroxylase and sorbitol dehydrogenase.

In a recent study from Zhou et al. (2001), designed to investigate hepatic enzyme activity and thyroid hormone concentrations, weanling rats were exposed to three commercial PBDPO

mixtures: DE-71 (58.1% PeBDPO and 24.6% TeBDPO), DE-79 (30.7% OBDPO and 45.1% HpBDPO) and DE-83 R (98% DBDPO). Female Long-Evans rats, 28 days old, were orally administered various doses from 0.3 to 100 mg/kg/day of DE-79 and DE-83R and from 0.3 to 300 mg/kg/day of DE-71 for 4 days. 8 animals were allocated per dose except for 0.3 mg/kg/day for DE-71 where 4 animals were allocated. Serum and liver samples were collected 24 h after the last dose and analysed for serum total thyroxine (T_4), triiodothyronine (T_3), thyroid-stimulating hormone (TSH), hepatic microsomal ethoxy- and pentoxy-resorufin-O-deethylase (EROD and PROD), and uridinediphosphate-glucuronosyltransferase (UDPGT) activities. The PBDPO-treated groups did not exhibit significant changes in body weight; however, increased liver weights were found in the DE-71– and DE-79–treated animals with a statistical significant increase from 10 mg/kg/day with DE-79 and from 30 mg/kg/day with DE-71. 10- to 20-fold induction in EROD and 30- to 40-fold induction in PROD were found in the DE-71– and DE-79–treated animals. DE-71 and DE-79 caused dose-dependent depletion of T_4 (statistically significant from 10 mg/kg/day with DE-79 and from 30 mg/kg/day with DE-71) accompanied by up to 3- to 4-fold induction in UDPGT activities. Serum total T_4 was decreased a maximum of 80% for DE-71 and 70% for DE-79 in the highest dose (100 mg/kg/day). Dose-related effects in serum T_3 levels were less apparent (statistically significant from 60 mg/kg/day with DE-71 and from 100 mg/kg/day with DE-79), with maximal reductions of 25–30% at the highest dose for both DE-71 and DE-79. The two mixtures showed no effect on serum TSH levels. DE-83R was not effective in altering any of the measured parameters. The present study suggests that short-term exposure to some commercial PBDPO mixtures (including OBDPO and HpBDPO mixtures) interferes with the thyroid hormone system and that one of the mechanism by which PBDPOs interfere is via upregulation of UDPGTs.

4.1.2.5.2   Oral sub-chronic toxicity study (rat)

Charles River CD rats were fed for up to 13 weeks commercial OBDPO at dietary dose levels of 0 - 100 - 1,000 or 10,000 ppm which corresponds respectively to 7.2, 73.7 and 781 mg/kg/day for the males and 8.3, 85.6 and 834 mg/kg/day for the females (25 males, 25 females / dose group). Clinical signs, body weight, food consumption, blood and urine chemistry were studied after 1 and 2 months and at the end of the study. A recovery period of 8 weeks or 6 months followed the 13-week dosing period.

A decrease in body weight gain was found during the treatment from 1,000 ppm and during recovery at 10,000 ppm.

Clinical chemistry: slight changes in serum chemistry values were detected at 10,000 ppm (a slight decrease of the blood glucose levels and a slight increase in the ASAT and ALAT activities after 2 months treatment). Orange discolouration of the urine was observed from weeks 13 to 39.

Kidney examination: at 10,000 ppm, increase in absolute and relative kidney weight, brownish discolouration, histopathological changes including the occurrence of small to moderate numbers of cortical regenerative tubules, severe tubular nephrosis in one male; these histopathological changes were reversible after 8-week withdrawal.

Thyroid examination: increase in absolute and relative thyroid weights at 13 weeks from 1,000 ppm and at the end of the 8-week recovery period at 10,000 ppm, histopathological changes at 10,000 ppm (some rats had most follicles composed of epithelium which was tall columnar in type rather than cuboidal with very pale staining colloid). These cellular changes were probably compound-related and were reversible after 8-week withdrawal. The effects on

the thyroid gland might be considered to be a consequence of the induction of hepatic enzymes. Indeed this induction enhances T_4 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 (1980a), which specifically demonstrated the induction of hepatic UDP-glucuronyl transferase in rats administered OBDPO and PeBDPO. This enzyme catalyses the conjugation of free thyroid hormones and enhances their excretion in the bile. Human plasma contains a primary binding protein, thyroxine binding globulin (TBG), which binds T_4 with a relatively high binding affinity and T_3 with a lower binding affinity. A second transport protein, called thyroxine-binding prealbumin (also called transthyretin or TTR), although present in higher amounts than TBG, has a lower binding affinity for the thyroid hormones than TBG and is considered of secondary physiologic importance (Thomas and Thomas, 1994). In rodents TBG is not found but TTR is the major transport protein in nonmammalian vertebrates, (Cheek et al., 1999). In humans and most other mammals, the thyroid hormones also can bind to albumin following occupation of the higher affinity binding sites. Pertaining to T_3, this hormone is only bound to albumin in mouse and rat whereas in human beings and monkeys, T_3 is transported to albumin but also to TBG. As a consequence of these differences in plasma protein binding less than 0.1 % of the total plasma thyroid hormones exist in a free or unbound form (Thomas and Thomas, 1994). Binding of thyroid hormones to plasma proteins protects the hormones from metabolism and excretion, resulting in their long half-lives in the circulation (Farwell and Braverman, 1996). Whereas, in a species such as the rat, which does not possess a thyroxine binding globulin (i.e. high affinity binding protein), lower plasma levels of protein-bound thyroid hormone exist (Capen et al., 1996). Therefore these differences in plasma half-life of thyroid hormones and binding to transport proteins between rats and human beings may be one factor in the greater sensitivity of the rat thyroid in response to chronic TSH stimulation (Capen et al., 1996). Hence it is unlikely that the treatment related effects on thyroid status via an induction of the hepatic enzymes would occur in human. However the T_4-depleting effects are likely to involve multiple mechanisms of interference in addition to thyroid hormone metabolism. In Zhou et al. (2001), a dose-related reduction in plasma T_4 concentrations was observed consistent with a dose-related induction in hepatic UDPGT activity, suggesting that T_4 glucuronidation was one factor contributing to the reduction in serum T_4. But mixture of OBDPO and HpBDPO (DE-79) showed potency comparable to a mixture of TeBDPO and PEBDPO (DE-71) in plasma T_4 depletion, with an induction of UDPGT only approximately half as much as DE-71. This suggests mechanisms other than T_4 glucuronidation may also contribute to the plasma T_4 depletion.

Liver examination: increase in absolute and relative liver weights from 100 ppm, reversible at the end of the recovery period except for the 10,000 ppm group. Histopathological lesions were observed: granular cytoplasmic changes from 100 ppm, cytoplasmic vacuolisation from 1,000 ppm which probably represents fatty degeneration, scattered necrosis of parenchymal cells or of centrolobular cells, centrolobular fibrosis and pigmented Küppfer cells at 10,000 ppm, accentuated lobulation and yellowish mottling of livers and brownish discolouration. A hyperplastic nodule was found after 8-week withdrawal in a female rat at 10,000 ppm and after 6-month withdrawal in one rat each from the 1,000 and 10,000 ppm group. After one-year recovery, no hyperplastic nodules or neoplasms were observed. During recovery, the histological changes decreased in severity and frequency.

Liver total bromine was dose-related increased at 13 weeks from 100 ppm and declined during the recovery period but remained higher (6 fold increase) than the control values after one year for the 10,000 ppm group (Great Lakes, 1977).

The NOAEL is not established in this study and the LOAEL is 100 ppm (7.2 mg/kg/day approximately).

In a study from Carlson (1980b) (previously reported in Section 4.1.2.1.1), designed largely to investigate hepatic enzyme induction, oral administration of commercial OBDPO for 90 days increased xenobiotic metabolism: increase in EPN detoxification and p-nitroanisole from 0.78 μmol/kg/day (corresponding to 0.60 mg/kg/day) and, increase of cytochrome P450 (15% above control group) and NADPH-cytochrome c reductase (8.5% above control group) at 3.13 μmol/kg/day (corresponding to 2.4 mg/kg/day). The increases in EPN detoxification and p-nitroanisole demethylation were respectively 75% and 61% above control group at 3.13 μmol/kg/day. These increases are dose-dependent and some changes were still observable 30 to 60 days after the latest dosage. Although measurements of tissue content were not made, it is suggested that this extended period of induction is the result of the potency of OBDPO to act as inducer and of accumulation in sites such as adipose tissue and liver. It was briefly reported in this study that light microscopic examination of livers from rats dosed with up 2.4 mg/kg/day did not reveal substance-related changes. Given the limited range of investigations in this study no firm conclusions can be drawn for the determination of a N(L)OAEL.

In these oral toxicity studies, the effects observed at the highest tested doses were insufficient for applying a Xn-R48/20 labelling and it can be assumed from these studies whatever the duration of treatment (28 or 90 days), that a NOAEL cannot be established and that the LOAEL is 100 ppm. This LOAEL of 100 ppm was determined based on liver effects (histopathological findings concurrently with or without increased liver weights) observed from 100 ppm.

4.1.2.5.3   Inhalation sub-acute toxicity study (rat)

In a 14-day study, groups of 5 Charles River CD rats of each sex were whole body-exposed to a micronized dust of commercial OBDPO at nominal concentrations of 0, 1.2, 12, 120 and 1,200 mg/m^3 for 8 hours/day for 14 consecutive days. No study of reversibility was carried out. The analytical concentrations of the airborne particles were respectively 0.6, 3.7, 23.9 and 165.2 mg/m^3. The AMMD (aerodynamic mass median diameter) of the dusts was estimated to be 3.5 μm with a geometric standard deviation of 2. Over 90% of the airborne particles had a diameter equal or lower than 11 μm.

By the end of the 8-hour exposure period all animals in the 23.9 and 165.2 mg/m^3 groups exhibited a fast breathing pattern that disappeared by the morning following exposure. Food consumption, body weight gain, hematology, blood and urine chemistry in all dose groups were normal. The total bromine concentrations in lung, liver and fat of all of the exposed rats (except at 0.6 mg/m^3 in the liver tissues) were higher than in the controls on a dose related basis. The lung and fat tissue accumulate OBDPO to a greater extent than the liver as the average total bromine concentration in lung and fat ranged from 1.5 to 12.5 times higher than in the liver. The relative liver weights were increased from 3.7 mg/m^3 dose group in a dose-related manner. Increase of absolute liver weights were also observed from 3.7 mg/m^3 dose group. These changes were accompanied by histological lesions consisting in focal (0 animal/10 animals, 2/10 (very slight), 0/10, 1/10 (very slight), 1/10 (very slight) and 1/10 (slight) for the 0-0.6, 3.7, 23.9 and 165.2 mg/m^3 groups, respectively) to multifocal (0 animal/10 animals, 0/10, 0/10, 1/10 (very slight), 7/10 (very slight) - 1/10 (slight) and, 3/10 (very slight) - 1/10 (slight)) cytoplasmic enlargement of the hepatocytes, and focal acidophilic degeneration (0/10, 0/10, 0/10, 3/10 (very slight)- 2/10 (slight) and, 5/10 (very slight)- 4/10 (slight)) of individual to small groups of liver cells. At the two highest dose levels, the enlargement of the hepatocytes was multifocal to diffuse (in 3 animals (slight) at the highest dose) in distribution and small to large areas of

necrosis of very slight (in one animal at the highest dose), slight (in 1/10 and 4/10 at 23.9 mg/m^3 and 165.2 mg/m^3 respectively), moderate (in 1/10 at 23.9 mg/m^3) to marked degree (a marked focal hepatocellular necrosis in one animal at 165.2 mg/m^3 dose group) were observed in the centrolobular regions of the affected liver lobules, especially in the 165.2 mg/m^3 group without clinical chemistry changes (alkaline phosphatase, ASAT, ALAT). No other compound-related effects were observed in other tissues examined including thyroid gland. Histopathology of the respiratory tract was carried out on nasal turbinate area, lung and trachea and did not detect microscopically compound related lesions. It can be assumed that the No Observed Adverse Effect Concentration (NOAEC) is 0.6 mg/m^3 (analytical concentration).

In a recent 2-week inhalation toxicity range finding study (Great Lakes, 2000), conducted according to GLP procedures and well reported, groups of 5 Crl:CD(SD)IGS BR rats of each sex were nose-only exposed to OBDPO dust aerosol for 6 hours/day, five days per week, for two consecutive weeks. The targeted exposure concentrations were 1.0, 10, 100 and 250 mg/m^3 and the analytical concentrations were respectively 1.0, 10, 110 and 250 mg/m^3 with mass median aerodynamic diameters of 2.9, 3.2, 2.9 and 2.9 μm respectively. Bromine content of the test article was 78.7%. A concurrent control group of identical design received clean, filtered air on a comparable regimen. All animals survived to the scheduled necropsy. No toxicologically significant clinical signs were observed. There were no significant changes in body weight data or food consumption. There were no test article-related macroscopic findings. No hematological or clinical biochemistry tests and no study of reversibility were carried out. Total bromine concentration in tissues like lung, liver and fat was not determined.

Test article-related increased mean absolute and/or relative liver weights were noted from 10 mg/ m^3 in males and from 110 mg/m^3 in females. The increases were greatest in the 110 and 250 mg/m^3 groups (21–44 %). Correlating test article-related centrilobular hypertrophy of hepatocytes (minimal to mild) was observed microscopically for all males from 10 mg/m^3 and for 4/5 females in both 110 and 250 mg/m^3 groups. The only other test article-related finding consisted of minimal to mild goblet cell hyperplasia and/or hypertrophy in the nasal tissues from 10 mg/m^3 in females and from 1 mg/m^3 in all treated males. The goblet cell hyperplasia/hypertrophy was present in nasal levels 2 and 3 of the 1 mg/m^3 group males and generally present in nasal levels 2-6 of the 10, 110 and 250 mg/m^3 groups. The remaining squamous, respiratory and olfactory epithelium appeared intact for all treated animals. This effect on the nasal tissues was considered to be very slight irritation.

No other compound-related effects were observed in other weighed organs including testes and ovaries nor in examined tissues (adrenals, brain, kidneys, larynx, lungs, ovaries, spleen, testes preserved in Bouin's solution, trachea). Heart was not examined histologically and the thyroid gland was neither weighed nor microscopically examined.

Based on the increased liver weights and the liver microscopic findings, a NOAEC of 1 mg/m^3 is considered for systemic toxicity. Regarding local toxicity, no NOAEC can be determined but only a Low Observed Adverse Effect Concentration (LOAEC) of 1 mg/m^3 based on the minimal goblet cell hyperplasia and/or hypertrophy in the nasal tissues.

In a recent 90-day inhalation toxicity study (Great Lakes, 2001), well reported and conducted according to GLP procedures and to OECD 413 Technical Guideline, groups of 10 Crl:CD(SD)IGS BR rats of each sex were nose-only exposed to dust aerosol for 6 hours/day, five days per week, for 13 consecutive weeks. The targeted exposure concentrations were 1.0, 15 and 200 mg/m^3 and the analytical concentrations were respectively 1.1, 16 and 202 mg/m^3 with mass median aerodynamic diameters of 2.0, 2.7 and 2.8 μm respectively. Bromine content of the test article was 78.7%. A concurrent control group of identical design received clean, filtered air on a

comparable regimen. Special endpoints were included in the study design to optimise the microscopic examinations for potential effects on the male and female reproductive tract and to evaluate effects on thyroid hormones and thyroid stimulating hormone. Microscopic examination was conducted on tissues stained with hematoxylin and eosin except for the testes and epididymides stained with PAS (Periodic Acid-Schiff) and fixed in Bouin's solution. Neither study of reversibility nor total bromine concentration in tissues like lung, liver and fat were carried out.

All animals survived to the scheduled necropsy. No toxicologically significant clinical signs or oculopathic findings were observed. There were no significant changes in body weight data or food consumption. No treatment-related findings on hematologic or clinical biochemistry were observed. The only observed effect was an increase of the serum cholesterol level in the 202 mg/m^3 group females. Test article-related decreased mean T_4 values were observed at 16 mg/m^3 (30% and 16% in males and females respectively) confirmed at 202 mg/m^3 (68% and 61% in males and females respectively). Increased mean TSH values (approximately 2 fold increase) were also noted from 16 mg/m^3 in males and at 202 mg/m^3 in females. These changes were consistent with chemical-induced hypothyroidism although no effects on organ weight or microscopic appearance of the thyroid gland and no thyroid hormone-related clinical signs of disease or effects on body weight were detected.

A dose-related centrilobular hepatocellular hypertrophy was observed in 3/10 males and 3/10 females in the 16 mg/m^3 group (severity: minimal) and in all males and 6/10 females in the 202 mg/m^3 group (severity: minimal to moderate) with a treatment-related increased mean liver weights (absolute and relative) in the 202 mg/m^3 group in both sexes. Increased mean kidney weight (relative) was noted at 202 mg/m^3 in females only. However, no histopathological lesions in the kidneys and no similar findings were observed in the males group, therefore this difference is unlikely to be related to treatment.

In the lung, alveolar histiocytosis and chronic active inflammation were noted at 202 mg/m^3 in all animals and where correlated with the increases in lung weights (absolute and relative) and gross findings (white areas) in the lungs. Minimal chronic active inflammation of the lungs was observed in one male at 1.1 mg/m^3 and in 3 animals (combined sexes) at 16 mg/m^3. At necropsy, macroscopic findings also included firmness, white discoloration and/or enlargement in the bronchial and/or mediastinal lymph nodes in both sexes at the same dose level. These finding correlated with the histopathological finding of granulomatous inflammation in these lymph nodes in this group. Examination of the nasal tissues (nasal levels I to VI) did not reveal a clear treatment-related effect. A slight increased incidence goblet cell hypertrophy in the nasal tissues (minimal/mild) was noted from 1.1 mg/m^3 in both sexes in nasal level 2 but without a dose-related trend and at 202 mg/m^3 in level 3 limited to males. Histological examination of spleen, marrow and thymus did not show any treatment related anomalies.

Absence of corpora lutea was reported in 3/10 females at 202 mg/m^3 vs 0/10 in the control group. This effect was considered treatment-related. No microscopic evidence of cell loss or inappropriate cell presence in the seminiferous tubules was shown at 202 mg/m^3 at the microscopic examination of the testes fixed in Bouin's solution and stained with PAS and hematoxylin nor treatment-related effects on testes and epididymis weights.

Based on the decreased thyroxin levels, increased TSH levels and the slight centrilobular hepatocellular hypertrophy observed from 16 mg/m^3, a NOAEC for systemic toxicity was considered to be 1.1 mg/m^3. Regarding local toxicity, a LOAEC of 1.1 mg/m^3 can be determined based on the increased incidence of chronic active inflammation even if a trend is only identified at the lowest tested doses (1.1 and 16 mg/m^3) with a minimal chronic active inflammation.

Table 4.6 Synthesis of subacute and subchronic toxicity results of studies conducted in rats on commercial OBDPO

Duration treatment	Doses tested by oral route	Body weight	Clinic. signs	Organ weight	Macros-copy	Microscopy	Br content	Biochem Parameters	Hematol Parameters	Urine parameters	NOAEL / NOAEC	LOAEL	Bibliogr. Refer.
28 days	0-100-1,000 ppm in diet	No change	No change	Increased liver weight from 100 ppm		Thyroid hyperplasia at 1,000 ppm liver lesions from 100 ppm	↑ in liver from 100 ppm	-	-	-	Not established	100 ppm (≈8.1mg/kg/d)	Great Lakes, 1976a
28 days	0-100-1,000-10,000 ppm in diet	Slight ↓	No change	↑of liver weights from 1,000 ppm	Liver (enlarge-ment)	Liver changes ("round bodies" from 100 ppm and, hepatocytes vacuolisation and necrosis mainly at 10,000 ppm); partially reversible	↑ in liver from 100 ppm, partially reversible	Slight ↑ of urea at 10,000 ppm			Not established	100 ppm (≈ 9.8 mg/kg/d)	Great Lakes, 1977
13 weeks	0-100-1,000-10,000 ppm in diet	↓ from 1,000 ppm		↑of liver weights from 100 ppm, thyroid weights from 1,000 ppm and kidney weights at 10,000 ppm	Kidney and liver changes: brownish discoloration	Liver changes (granular cytoplasmic changes from 100 ppm and cytoplasmic vacuolisation from 1,000 ppm and, scattered necrosis and fibrosis at 10,000 ppm); partially reversible. Thyroid changes (follicles with pale staining colloid) at 10,000 ppm. Kidney changes at 10,000 ppm, reversible	↑ in liver from 100 ppm, partially reversible	Slight ↓ of blood glucose Slight ↑ of ASAT and ALAT at 10,000 ppm		Orange discolora-tion	Not established	100 ppm (≈ 7.2 mg/kg/d)	Great Lakes, 1977
14 days	Nominal concentrations: 0-1,2-12-120-1,200 mg/m³ (≈ analytical concentrations: 0-0.6-3.7-23.9-165.2 mg/m³)	No change		↑of liver weights from 3.7 mg/m³	No change	No change on the respiratory tract Liver lesions (cytoplasmic enlargement, focal acidophilic degeneration, hepatocytes enlargement, areas of necrosis)	↑ in liver, lung and fat.	No change	No change	No change	0.6 mg/m³ analytical concen-tration		Great Lakes, 1978

Table 4.6 continued overleaf

Table 4.6 continued Synthesis of subacute and subchronic toxicity results of studies conducted in rats on commercial OBDPO

Duration treatment	Concentrations tested by inhalation route	Body weight	Clinical signs	Organ weight	Macroscopy	Microscopy	Br content	Biochem. Parameters	Hematol Parameters	Urine parameters	NOAEC	LOAEC	Bibliogr. references
14 days	Nominal concentrations: 0-1,0-10-100-250 mg/m³ (≈ analytical concentrations: 0-1.0-10-110-250 mg/m³)	No change	No change	↑ liver weight from 10 mg/m³		Hepatocytes centrilobular hypertrophy from 1 mg/m³ Goblet cell hyperplasia / hypertrophy from 1 mg/m³	Not determined	-	-	-	For systemic toxicity: 1 mg/m³	For local toxicity: 1 mg/m³	Great Lakes, 2000
90 days	Nominal concentrations: 0-1.0-15-200 mg/m³ (≈ analytical concentrations: 0-1.1-16-202 mg/m³)	No change	No change	↑ liver and lung weights at 202 mg/m³	Macroscopic anomalies in the bronchial and/or mediastinal lymph nodes at 202 mg/m³.	Hepatocytes centrilobular hypertrophy from 16 mg/m³ Chronic active lung inflammation from 1.1 mg/m³ associated with alveolar histiocytosis at 202 mg/m³. Absence of corpora lutea at 202 mg/m³.	Not determined	No treatment related changes. ↑ TSH values and ↓ T₄ from 16 mg/m³	No change	No treatment related changes	For systemic toxicity: 1.1 mg/m³	For local toxicity: 1.1 mg/m³	Great Lakes, 2001

4.1.2.5.4   Summary of subacute and subchronic results

Results from the different subacute and subchronic studies are summarized in **Table 4.6**. The information concerning the effects of repeated oral and inhalation exposure to OBDPO comes from studies in rats involving administration of commercial OBDPO. These studies consistently indicate that the liver is the key target organ affected by OBDPO. The effects observed include increases in liver weight and liver enlargement, cellular microscopic changes, scattered incidence of hyperplastic nodules during the withdrawal period (8 weeks and 6 months) and induction of a range of liver enzymes. It was also shown that OBDPO exhibits a strong porphyrinogenic effect in vitro (see Section 4.1.2.9.1).

Following oral administration, thyroid gland effects are observed including increases in thyroid weight and histopathological changes suggesting an increase in thyroid gland stimulation. It should be noticed that no thyroid hormonal measurement was carried out in this study. In a recent study, especially designed to investigate thyroid hormone concentrations in weanling rats, oral exposure to a mixture of OBDPO 30.7% and HpBDPO 45.1% for 4 days, induced a dose-dependent depletion of T_4 from 10 mg/kg/day as well as a decrease of serum T_3 from 100 mg/kg/day without effect on TSH level. In the recent inhalation studies, it was shown a thyroid hormonal disturbance with a decreased T_4 level and an increased TSH level from 16 mg/m3 without thyroid weight or histopathological changes up to 202 mg/m3. Due to species differences in thyroid metabolism it is unlikely that the effects on thyroid status via an induction of the hepatic enzymes would occur in human. However mechanisms other than T4 glucuronidation may not be completely disregarded.

Dose-related increases in total bromine levels in the liver were observed after 4 and 13 weeks of oral treatment from 100 ppm. Following 2 weeks of inhalation exposure, increase in total bromine concentrations were reported in the liver and in the fat and the lung as well. Moreover it was shown that fat and lung accumulate OBDPO to a greater extent than the liver.

Absence of corpora lutea was only exhibited following inhalation exposure at the highest tested concentration of 202 mg/m3 (analytical concentration) within 13 weeks of exposure.

Local toxicity was demonstrated with hyperplasia/hypertrophy of the goblet cells within 2 weeks of exposure and with chronic active lung inflammation and alveolar histiocytosis within 13 weeks of exposure. It is obvious that observed effect at *1.1 mg/m^3* is minimal and reveal only a trend to a chronic inflammation however this value has been taken to set up the *LOAEC.*

Regarding systemic toxicity, the liver changes produced by commercial OBDPO, apparent within 4 and 13 weeks of repeated oral dosing and within 14 days and 90 days of inhalation exposure, are observed in the latter study from 16 mg/m3 (analytical concentration). The changes in thyroid status are apparent within 4 and 13 weeks of repeated oral dosing at 1,000 ppm and above and within 13 weeks of repeated inhalation dosing from 16 mg/m3 (analytical concentration). Thus the *NOAEC* was considered at the dose below: *1.1 mg/m^3.*

The effects observed in these sub-acute or sub-chronic studies were insufficient for applying a Xn - R48/20/22 labelling.

4.1.2.6   Mutagenicity

4.1.2.6.1   *In vitro* assays

Studies in bacteria

OBDPO was tested in *Salmonella typhimurium* TA98-100-1535-1537-1538 strains and Saccharomyces cerevisae (D4) in the presence or absence of an exogenous metabolic system from Aroclor 1254 induced male rat - liver S9 following the Ames method at concentrations of 0.25, 0.5, 5 and 50 μg/plate (in DMSO). The results of this test were negative.

This test presents strong limitations: no duplication, only one plate per dose performed, no toxicity observed at the maximum concentration tested, dose levels in the positive controls without metabolic activation seemed too high to check the sensitivity of the test system, no increase in the number of revertant colonies per plate in D4 strain with the positive control with metabolic activation. As no cytotoxicity was observed and no precipitation reported, the maximum concentration tested (50 μg/plate) should have been increased (Great Lakes, 1976b).

Other Ames tests on Muster 13, Muster 82 and Muster 84 referenced in EPA's file as OBDPO (CAS No 32536-52-0) and submitted by BASF as OBDPO (CAS No 32536-52-0) were available. It should be noticed that in these reports only the name of the samples namely Muster 13, 82 and 84 were indicated and not the CAS number or the chemical name of the substance tested. In those studies Muster 84 and Muster 13 did not induce an increase in the number of revertant colonies in *Salmonella typhimurium* TA 98-100-1535 in the presence or absence of an exogenous metabolic system at concentrations ranging from 50 to 5,000 μg/plate (in DMSO) and from 2 to 2,000 μg/plate, respectively. These tests were not duplicated. Precipitate was observed at the highest concentration tested. The test conducted on Muster 13 is not reliable as it presents too high limitations (EPA/OTS, Doc # 86-9000004040 and Doc # 86-900000402).

Muster 82 shows evidence of weak mutagenic activity without metabolic activation on TA100. Muster 82 was tested in Salmonella typhimurium TA98-100-1535 in the presence or absence of an exogenous metabolic system from Aroclor 1254 induced rat-liver S9 at concentrations ranging from 50 to 5,000 μg/plate (in DMSO) in the main experiment and from 2,500 to 10,000 μg/plate in repeated tests on TA 100 without metabolic activation (precipitate was observed from 5,000 μg/plate) (EPA/OTS, Doc # 86-900000403).

An assay was performed on OBDPO (a mixture of three samples of OBDPO: composition of the test substance was provided and it is representative of the current commercial products) using the plate incorporation method. A preliminary toxicity assay was carried out with Salmonella typhimurium TA98-100-1535-1537 (one plate per dose) on selective minimal agar in both the presence and absence of rat liver S9 activation up to the maximum dose tested of 5,000 μg/plate. Precipitate was observed at ≥ 667 μg/plate but no appreciable toxicity was observed. In the mutagenicity assay, Salmonella typhimurium TA98-100-1535-1537 were exposed to OBDPO concentrations of 33, 100, 333, 1,000, 5,000 μg/plate (in DMSO) in the presence and absence of an exogenous metabolic system from Aroclor 1254-induced male rat liver S9. All dose levels of test article, vehicle controls and positive controls were plated in triplicate. Precipitate was observed at ≥ 1,000 μg/plate but no appreciable toxicity was observed. This test was not duplicated. No positive responses were observed with any of the tester strains in the presence and absence of S9 activation. This test was conducted in conformity with GLP (Chemical Manufacturers Association, 1996b).

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Studies in mammalian cells

OBDPO did not induce UDS (*Unscheduled DNA Synthesis*) in WI-38 human fibroblasts cells in vitro at concentrations ranging from 60 to 300 μg/ml in the presence or absence of exogenous metabolic activation system. In the main experiment (assay without duplication) no decrease in survival percentage was noted at the maximal tested concentration, thus limiting the value of the test (Great Lakes, 1983).

OBDPO did not induce SCE (*Sister Chromatid Exchanges*) in Chinese hamster ovary cells in vitro in the presence or absence of an exogenous metabolic activation system at concentrations ranging from 7.5 to 750 μg/ml (in DMSO) for 2-hour exposure followed by a 24-hour expression period. As cytotoxicity was moderate without activation, the maximum concentration tested could have been higher (Great Lakes, 1982).

OBDPO was tested in a cytogenetic assay using human peripheral blood lymphocytes in both the absence and presence of an exogenous metabolic system from Aroclor 1254 induced male Sprague Dawley rat -liver S9 at concentrations of 125-250 and 500 μg/ml in the absence of S9 and at concentrations of 32-63 and 125 μg/ml in the presence of S9. The cells were treated for 4 and 20 hours without metabolic activation and for 4 hours with metabolic activation and all cells were harvested at 20 hours after treatment initiation. Visible precipitate was observed in treatment medium from 500 μg/ml without metabolic activation and from 250 μg/ml with metabolic activation. Additional dose levels were included: 1,000 μg/ml without and 250 and 1,000 μg/ml with metabolic activation. But they were not analysed due to excessive precipitation without metabolic activation for a 4-hour exposure period and due to excessive toxicity with metabolic activation. Cytotoxicity was observed with metabolic activation at 125 μg/ml (51% mitotic inhibition) and without metabolic activation for a 4-hour exposure period at 1,000 μg/ml (43% mitotic inhibition) and for a 20-hour exposure at 500 μg/ml (32% mitotic inhibition). Positive, untreated and solvent controls gave results in the expected ranges. No statistically significant increases in structural and numerical chromosome aberrations were observed with or without metabolic activation relative to the solvent control group. This study was conducted in compliance with GLP procedures (Great Lakes, 1999).

4.1.2.6.2 *In vivo* assays

No available data.

On the whole, results from different Salmonella tests can be considered as negative. OBDPO did not induce UDS or SCE in vitro neither cytogenetic effects in vitro. It is noticeable that some of these tests present some limitations in particular the UDS and SCE assays. However, given the negative results obtained in recent Ames and cytogenetic assays conducted in compliance with GLP procedures and the negative results obtained in the mutagenicity tests with PeBDPO and DBDPO, no concern for mutagenicity may be assumed.

4.1.2.7 Carcinogenicity

No chronic or carcinogenicity studies in animals are available. Only subchronic studies area available to anticipate carcinogenic potential of the substance, thus no firm conclusion can be drawn on carcinogenicity.

4.1.2.8   Toxicity for reproduction

4.1.2.8.1   Effects on fertility

No specific fertility studies have been conducted. However, when rats were treated for 13 weeks, no histological changes were noted in testes, prostate, ovaries or uterus up to dietary level of 10,000 ppm (781 mg/kg/day for the males and 834 mg/kg/day for the females), but histopathological examination was limited to examination of hematoxylin and eosin stained paraffin sections of tissues and the fixation method was unknown limiting the assessment of the adverse effects on the reproductive organs. Moreover, an increase in absolute and relative testes weights was observed at 10,000 ppm in this study. Absolute and relative (% body weight) organ weights were respectively 3.55 gr and 0.84% at 10,000 ppm, versus 3.26 gr and 0.64% in the control group. The increase of the absolute testes weight was statistically significant ($p<0.05$) and the relative testes weight was also statistically significant ($p<0.01$). However, at 8-week withdrawal following a 13-week treatment, no difference was observed between the control group and 10,000 ppm group (Great Lakes, 1977). In a 14-day inhalation toxicity range finding study recently conducted (Great Lakes, 2000), no treatment-related effects were observed neither on female or male reproductive weight organs nor at the histopathological examinations (ovaries and testes preserved in Bouin's solution) up to 250 mg/m^3. In a recent 90-day inhalation toxicity study (Great Lakes, 2001b), well reported, conducted according to GLP procedures and to OECD 413 Technical Guideline, designed to investigate potential effects on the male and female reproductive tract, groups of 10 Crl:CD(SD)IGS BR rats of each sex were nose-only exposed to OBDPO dust aerosol for 6 hours/day, five days per week, for 13 consecutive weeks. Testes were examined with attention to spermatogenic stages in an attempt to identify cell loss or inappropriate cell presence in the seminiferous tubules. Neither treatment-related effects on testes and epididymis weights nor microscopic evidence of cell loss or inappropriate cell presence in the seminiferous tubules were shown up to 202 mg/m^3. No weighing of prostate and seminal vesicles was carried out but histopathological examination did not reveal any treatment-related effects. Pertaining to female reproductive organs, no treatment-related effects were shown on mean ovaries or uterus weights. However, absence of corpora lutea was reported in 3/10 females at 202 mg/m^3 vs 0/10 in the control group associated in the affected females to an individual decrease of the ovaries absolute weight of 29 to 33%. Since the absence of corpora lutea is considered to be an unusual finding in rats at 20 weeks of age, the 30% incidence in this group was considered treatment-related and therefore a NOAEC of 16 mg/m^3 was considered.

In summary: the only information concerning the potential effects of OBDPO on fertility comes from sub-acute or sub-chronic studies in rats involving administration of commercial OBDPO by oral or inhalation routes. No specific fertility studies have been conducted. The oral sub-chronic study indicates a reversible increase of the absolute and relative testes weight (Great Lakes, 1977). However in recent sub-acute and sub-chronic inhalation studies (Great Lakes, 2000 and 2001), no treatment-related effects on testes and epididymis weights nor microscopic evidence of cell loss or inappropriate cell presence in the seminiferous tubules were shown up to 202 mg/m^3 or 250 mg/m^3. Since this recent sub-chronic study, well conducted and specifically designed to investigate reproductive organs, did not demonstrate adverse effects on male reproductive organs, no concern is assumed for male fertility. Regarding female reproductive organs, absence of corpora lutea was shown at 202 mg/m^3 in the recent 90-day inhalation study. This effect is taken into account although only observed in the one study well conducted and specifically designed to investigate reproductive organs and a NOAEC for female fertility of 16 mg/m^3 is assumed for this end-point. With respect to this effect, it was deemed cautious to apply a classification toxic for reproduction Cat. 3 R62.

4.1.2.8.2   Developmental toxicity studies (rat)

In a *range finding study*, five groups of ten bred Charles River COBS CD female rats were dosed daily by gavage from days 6 through 15 of gestation with 0 - 2.5 - 10 - 15 - 25 and 50 mg commercial OBDPO (DE-79) / kg/day.

Maternal effects: at 50 mg/kg/day, after cessation of the dosage, decrease in maternal body weight gain during gestation days 16-20 (43 versus 72 grams). It was partially due to an increased number of late resorptions and a reduced mean fetal weight. Administration of DE-79 did not affect ASAT, ALAT, alkaline phosphatase or total bilirubin levels at any dosage. Serum bromide levels were increased from 25 mg/kg/day groups. There were no remarkable macroscopic changes at the scheduled necropsy to indicate any toxic effects in any of the treated groups. No microscopic findings were seen in liver or thyroid, considered to be related to DE-79 administrations.

Conceptus effects

At 50 mg/kg/day:

- reduction in the mean fetal weight (2.2 versus 3.6 grams);

- increase of post-implantation loss: 14/137 implantation sites (10.2%) versus 10/150 (6.6%) mainly due to late resorption (8 versus 0). This increase (1.55/dam) was not statistically significant, however, it exceeded the laboratory historical control range (0.1-1.2/dam);

- fetal anasarca, bent limb bones and unilateral absence of the 13th rib were noted as single instances. Reduced ossification of the skull, various unossified bones and two instances of bent ribs were also noted. Bent limb bones and bent ribs are not considered to be true malformations or variations but reversible pathological findings related to retarded ossification.

Administration of commercial OBDPO to the dams resulted in effects on the conceptuses including reduced average fetal body weights, increased embryo/fetal death (resorption) and retarded ossification at a dose of 50 mg/kg/day. Decrease of maternal body weight gain which was partially due to the adverse effects observed on the fetuses was observed during days 16-20 of gestation at 50 mg/kg/day. It can be assumed that the NOAEL for the conceptuses is 25 mg/kg/day and the NOAEL for the dams 50 mg/kg/day (Great Lakes, 1986).

In a *developmental toxicity study*, four groups of 25 pregnant Charles River Crl:COBS CD (SD)BR rats were administered by gavage corn oil suspensions of commercial OBDPO (Saytex 111: composition of the test substance was provided and is representative of the current commercial products) at doses of 0 - 2.5 - 10 or 25 mg/kg/day on days 6-15 of gestation. Dosage volumes were adjusted daily for changes in body weight. The female rats were observed for viability, clinical signs and/or general appearance throughout the study period, for abortion (days 6 through 20 of presumed gestation) and/or natural delivery. The dams were sacrificed at day 20 of gestation, one half of the fetuses was examined for gross visceral abnormalities and the remaining fetuses for skeletal abnormalities.

The average numbers of corpora lutea or implantations were not affected at any dose.

Maternal effects: after cessation of dosage, a decrease was observed in the average maternal body weight and body weight gain for the 25 mg/kg/day dosage group dams (38.8 versus 63 grams). These observations were interrelated with the high incidence of resorption and small average fetal body weights observed for litters of the high dosage group dams. They were not

indicative of a direct toxic effect of the test substance on the dams. At 25 mg/kg/day, red or brown vaginal exudate was observed associated with resorption of conceptuses.

Conceptus effects

- decrease of the average fetal body weights per litter was observed from10 mg/kg/day: fetal body weights averaged 3.38 - 3.34 - 3.25 2.10 grams for the 0 - 2.5 - 10 - 25 mg/kg/day dosage group litters, respectively;

- significant lethal effect at 25 mg/kg/day: increase in dead or resorbed conceptuses per litter: 33.2% versus 4.3%; there was one or more resorptions observed for 18 dams (75%) versus 10 (40%); whole litter resorptions occurred in 2/25 pregnant dams; decrease in the average number of live fetuses per litter: 8.9 versus 14.6;

- fetal malformation/variations and delayed skeletal ossification at 25 mg/kg/day: significant increases in the incidences of fetuses with enlarged heart, rear limb malformation (shortened, bent and/or incompletely ossified femur, tibia and/or fibula) and with remarkable delays in ossification of the skull, vertebrae, ribs and pelvis. The fetal incidences of slight dilatation of the lateral ventricles of the brain and of malformed and incompletely ossified scapulae were also significantly increased. Significantly retarded ossification of the fetal sacral and caudal vertebrae, manubrium, sternal and xiphoid centers, metacarpals, metatarsals and both fore- and hindpaw phalanges also occurred for litters of the high dosage group dams.

The substance is more toxic to the conceptus than to the dam. It can be assumed that the embryo/fetal NOAEL is 10 mg/kg/day and the maternal NOAEL $\geq$ 25 mg/kg/day. As compared with control values, administration of 10 and 25 mg/kg/day dosages to the dams results in dosage-dependent effects on the conceptuses including reduced average fetal body weights (10 and 25 mg/kg/day dosage group litters), increased embryo/fetal death (resorption), fetal malformation/variations and delayed skeletal ossification (25 mg/kg/day dosage group). These effects are statistically significant only for the high dosage group, as compared with control (Ethyl Corp., 1985).

In an other *developmental toxicity study*, four groups of 22 females mated CD rats (of Sprague-Dawley origin) were dosed with OBDPO (FR-1208), in corn oil, by intragastric gavage, at dosages of 0, 2.5, 10 and 25 mg/kg/day, respectively, from day 6 to day 15 post coitum, inclusive. The dams were sacrificed at day 20 of gestation. Composition of the test substance was provided: it is a mixture of the same components as the current commercial OBDPO, even though percentage of heptabromodiphenyl oxide is slightly higher and percentages of octa- and nonabromodiphenyl oxides slightly smaller.

No adverse maternal effects were elicited at any dosage, in terms of gross observable signs, food consumption or body weight gain.

Statistically significant fetal death (post-implantation loss) was observed among litters from dams dosed at 10 (5.9% of post implantation loss) or 25 mg/kg/day (6.0%) in comparison to concurrent controls (4.4%). The biological significance of this finding is not clear, as all values fell within the range of historical control values of the laboratory (4.4-7.0%). No treatment-related skeletal malformations or variations and no indication of delayed or retarded ossification were observed in any treated group.

No treatment-related fetal visceral malformations or variations were found at sectioning. A single case of hydrocephalus occurred in the highest dosage group but this is considered as

incidental by the laboratory. A second fetus in the same litter showed an "apparent intracerebral cyst" but the precise nature of this anomaly remains unclear.

It can be assumed that the maternal NOEL is ≥ 25 mg/kg/day and that the fetal NOEL and NOAEL are 2.5 mg/kg/day. Indeed, the higher doses (10 and 25 mg/kg/day) cannot be considered as NOAEL since it cannot be shown that the observed effects are without toxicological significance (Dead Sea Bromine Co, Ltd, 1987).

4.1.2.8.3 Developmental toxicity studies (rabbit)

Groups of 26 inseminated adult New Zealand white rabbits were treated with 0 (corn oil), 2 - 5 or 15 mg commercial OBDPO (Saytex 111)/kg bw/day by gavage on days 7-19 of gestation. Saytex 111 was a mixture containing: 0.2% PeBDPO, 8.6% HxBDPO, 45% HpBDPO, 33.5% OBDPO, 11.2% NBDPO and 1.4% DeBDPO. Body weight gain was recorded on gestation day 0, 7, 10, 13, 16, 20 and 28. Maternal liver, kidneys and gravid uterine weights were measured at sacrifice. The offspring were examined on day 28 of gestation.

An increase in liver weight and a decrease in body weight gain (not statistically identified) during gestation days 0-28 was observed in the 15 mg/kg/day group. Early deliveries were observed in the 5 mg/kg/day dose group (one rabbit) and in the 15 mg/kg/day dose group (two rabbits). An additional rabbit from the 15 mg/kg/day dose group was terminated after exhibiting signs of abortion; multiple resorption sites were noted in the uterus.

There was no statistically significant deviation in maternal mortality (death of one pregnant rabbit from each of the 0, 2 and 5 mg/kg/day dose groups was observed), number of pregnancies, number of litters with viable pups, corpora lutea/dam, implantations/dam, live fetuses/litter, percentage of resorptions.

From 5 mg/kg/day, a slight fetal toxicity was observed, evidenced by a slight decrease of the fetal body weight (37.3, 33.4 and 33.8 grams for 0, 5 and 15 mg/kg/day group) and by an increase in delayed ossification of the sternebrae (38 delayed ossifications / 131 fetuses, 74 / 175, 62 / 132 for 0, 5 and 15 mg/kg/day group). There was an increase in the incidence of retrocaval ureter in the 5 and 15 mg/kg groups and fused sternebrae in the 5 mg/kg group but these increases were not dose-related (Breslin et al., 1989).

There is no evidence for teratogenic activity but slight fetotoxicity at 5 and 15 mg/kg/day with decreased body weight gain (not statistically identified) of the dams at the highest dose tested. It can be assumed that the NOAEL for the conceptuses is 2 mg/kg/day and the NOAEL for the dams 15 mg/kg/day as the decrease of bodyweight gain is observed before the beginning of the treatment (from day 0 of gestation) in the 15 mg/kg/day dose group.

In summary, developmental effects are observed in rats in two studies and they do not seem to be related to maternal toxicity (only decrease in maternal body weight gain during days 16-20 of gestation or decrease in body weight gain interrelated with resorptions and small fetal body weights). These developmental effects are not confirmed in a third assay in rats which was conducted with a test article containing a lesser percentage of octabrominateddiphenyl oxide component. In rabbits, the substance produces only slight foetotoxicity along with a decreased bodyweight gain of the dams at the highest dose. However it must be noticed that this decrease had already happened before the treatment. The lowest identified NOAEL is considered for the risk characterisation i.e. 2 mg/kg/day as obtained in the rabbit. Some of the above mentioned results are considered as borderline but since some of these results are indicative of

developmental effects which are most likely unrelated to maternal toxicity, it was deemed cautious to apply a classification: Toxic for reproduction cat. 2 R61.

4.1.2.9   Additional comments

4.1.2.9.1   Porphyrinogenic action of Fire Retardants

Koster et al. (1980) found a strong porphyrinogenic effect in cultures of chick embryo liver cells at concentrations of 10 µg commercial OBDPO (in DMSO)/ml medium, with and without pretreatment by ß-naphtoflavone, an inducer of cytochrome P450, P448 and delta-aminolevulinic acid synthetase. The effect was determined semiquantitatively with fluorescence microscopy 24 hours after addition of the flame retardant (Koster et al, 1980).

4.1.2.9.2   Immunotoxicity

The reported studies have shown no immunotoxic properties but it is recognised that lymphoid tissues are affected by polybrominated biphenyls (Polybrominated biphenyls. Environmental Health Criteria 152, IPCS, 1994, p. 451).

4.1.2.9.3   Endocrine disruptor potential

Alterations in thyroid homeostasis were reported with organochlorine compounds and a thyroid hormonelike affinity for the serum transport protein transthyretin (TTR) was explored. So it was deemed useful to gather some data on organochlorine compounds and PBDPOs congeners on this end-point.

It was reported by Cheek et al. (1999) that alterations in thyroid homeostasis by organochlorine compounds have been documented for many species, including humans. In most cases, exposure to organochlorine compounds is correlated with decreased serum levels of thyroid hormone, particularly T_4. Exposure to PCBs has been correlated with decreased serum T_4 concentrations in rats and humans. Evidence from rat studies indicates that organochlorines such as chloroacetanilides acetochlor and alochlor, DDT and, PCB induced decreases in serum T_4 which are the result of increased metabolism by UDPGT. Because of their physiological effects and their resemblance to thyroid hormones, several studies have investigated the ability of PCBs to bind to the serum transport proteins transthyretin and thyroxine binding globulin (TBG) and to the rat thyroid receptor. PCBs have different affinities for transthyretin and TBG (Lans et al., 1994). Hydroxylated PCBs are potent ligands for transthyretin. Few hydroxylated PCBs bind TBG and few unmetabolised PCBs have strong affinities for either TTR or TBG. Like the transport proteins, the rat thyroid receptor appears to have a higher affinity for hydroxylated versus parent PCBs. Cheek et al. (1999) examined the ability of PCBs to bind a recombinant human thyroid receptor and to human transthyretin and TBG. Their results show that hydroxylated PCBs have a thyroid hormonelike affinity for the serum transport protein transthyretin with a relatively low affinity for the human thyroid receptor *in vitro*. Interestingly, TBG deficiency in humans does not interfere with euthyroid status, suggesting that transthyretin is also important for T_4 transport in humans (Larsson et al., 1985). Moreover TTR is the principal T_4 binding protein in cerebrospinal fluid and may play a similar role in the central nervous system (Cavalieri, 1997). It has also been suggested that TTR plays an important role in

mediating the delivery of T_4 across the blood-brain barrier and in maternal-to-fetal transfer over the placenta (Calvo et al., 1990; Southwell et al., 1993).

Concerning PBDPOs, certain PBDPO congeners namely BDE-15 (DiBDBPO) and BDE-77 (TeBDPO) after in vitro microsomal transformation into metabolites compete with thyroxin for a transport protein (TTR) suggesting a potential endocrine disturbing effect of these PBDPO metabolites. No competition was observed for any of the parent PBDPO congeners neither for BDE-32 (TriBDPO) metabolites (Bergman et al., 1997a).

A series of papers at Dioxin 98 reported on interaction of various PBDPO congeners with aspects of the thyroid axis. 17 PBDPO congeners were synthesized and included di, tri, tetra, penta, hexa and hepta isomers. All 17 PBDE congeners were tested *in vitro* for competition with T4 in binding to human transthyretin (Meerts et al., 1998 and 2000). None of the 17 PBDPO parent compounds competed with T4 for binding to human TTR (results not shown in the publication). The 17 congeners were then incubated with rat microsomes induced with phenobarbital (PB), beta naphthaflavone (NF), or clofibrate (CL). The products of the incubation were tested for competition with T4.

With rat microsomes induced with NF and/or Cl, BDE-15 and BDE-30 metabolites competed with T4-TTR (with approximately 60% of inhibition) and BDE-28, 32, 71, 75 and 77 with T4-TTR (with approximately 20% of inhibition) but none of the higher brominated PBDPO congeners (i.e., 2,2',3,4,4',5-HxBDPO, 2,2',4,4',5,5'-HxBDPO, 2,3,4,4,5,6-HxBDPO, and 2,3,3'4,4',5,6-HpBDPO) incubated with NF or CL microsomes generated products which competed with T4 for binding to human TTR.

With PB induction 9 of the 17 PBDE congeners induced rat microsomes generated products which competed with T4 for binding to human TTR (with approximately 60% of inhibition) and 4 of the remaining congeners (including BDE-166: 2,3,4,4,5,6-HxBDPO) competed with T4–TTR (with approximately 20% of inhibition). Only 2,3,3',4,4',5,6-heptabromodiphenylether, 2,2',4,4',5,5'-hexabromodiphenylether, BDE-138 and BDE-32 did not inhibit T4-TTR after rat microsomal incubations.

In conclusion, Meerts et al. (2000) hypothesized that either these PBDPOs are not metabolised by the differently enriched microsomal preparations or that the metabolites formed where not able to compete with T4 for binding to TTR and that further studies should be focused on the elucidation of the chemical identity of these PBDPOs metabolites. Moreover to our knowledge, no studies on transthyretin-T_4 competition have been carried out on OBDPO neither on DBDPO. In consequence a transtyretin-T4 competition may not be completely disregarded as far as sufficient metabolism data are not available to indicate whether a dehalogenation might occur with production of analogues that are better ligants than high brominated congeners. It should be reminded that TTR may play in important role in mediating the delivery of T4 across the placenta to the foetus. Therefore it might be hypothesised that the impact of compounds binding to TTR might be lower in humans and non-human primates that possess TBG as the major thyroxin carrier. However the binding of compounds such as PCBs/HO-PBDOs to TTR may be involved in facilitated transfer of these compounds across the placenta and the blood brain-brain barrier, leading to relatively high levels in the foetus and especially the foetal brain (Brouwer, 1998; Meerts et al., 2000).

In Meerts et al. (2001), antiestrogenic potency of PBDPOs was determined in the ER-CALUX bioassay by treating T47D.Luc cells with 0.01 to 10 µM concentrations of PBDPOs in the presence of 10 pM of E_2 (17β–Estradiol). Alone, this E_2 concentration produced a luciferase induction of 63.3 +- 7.5% of the maximum. Among the PBDPOs tested only 2,2',4,4',5,5'-

HxBDPO, 2,3,4,4',5,6-HxBDPO and 2,3,3',4,4',5,6-HpBDPO which did not induce luciferase activity alone (up to 10 µM), reduced E_2 –induced luciferase activity. Moreover, these three PBDPOs congeners inhibited the E_2–induced activity in a dose-dependent manner with concentrations resulting in 50% inhibition (IC50 values) ranging from 0.8 to 3.1 µM.

4.1.2.9.4   Neurotoxicity

In a study designed to assess behaviour and nicotinic receptor modification (Viberg, 2001), hexabromo-diphenyl ether (PBDE 153) (purity not given) was orally administered as one single dose to neonatal NMRI mice on postnatal day 10. The three doses used were 0.45, 0.9 and 9.0 mg/kg b.wt (0.7, 1.4 or 14 µmol/kg b.wt). Mice serving as controls received 10 ml/kg b.wt of the 20 % fat emulsion vehicle.

Spontaneous motor behaviour test was conducted at 2, 4 and 6 months of age. The test measures *locomotion*: horizontal movements, *rearing*: vertical movements, and *total activity*: all types of vibrations within the test cage. Swim maze test (Morris Water maze type) was performed at 6 months of age. The test measures spatial learning ability and memory. Nicotinic receptors were analysed by measuring α-Bungarotoxin binding sites in the P2-fraction of the hippocampus in 6-month-old mice.

The spontaneous motor behaviour data showed a dose-response related disruption of habituation in adult mice, neonatally exposed to PBDE 153. Habituation, defined here as a decrease in *locomotion, rearing* and *total activity* variables in response to the diminishing novelty of the test chamber over the 60-min test period, was demonstrated in the control group of the three age categories as well as in animals exposed to the lowest dose at 2 and 4 months of age. At six months of age mice exposed to the lowest dose of PBDE 153 showed the spontaneous behaviour significantly altered and mice exposed to the two highest doses of PBDE 153 displayed a non-habituating behaviour at 2, 4 and 6 months of age; in addition mice exposed to highest dose of PBDE 153 showed the most pronounced deviation from normal behaviour.

The ability of adult mice to learn and memorize spatial navigation task was studied using swim maze test. The swim maze allowed a 4-day acquisition period followed by reversal learning on the fifth day. All mice improved their ability to locate the platform during the acquisition period, but animals exposed neonatally to 0.9 or 9.0 mg PBDE 153/kg b.wt displayed significantly longer latencies to locate the platform on day 2 and 3 during the acquisition period.

α-Bungarotoxin binding sites were assayed in the P2-fraction of the hippocampus in 6-month-old mice using ^{3}H-α-bungarotoxin/α-bungarotoxin. Mice exposed to the highest dose of PBDE 153 (9.0 mg/kg b.wt) showed a significant decrease in the density of specific [^{3}H]-α-bungarotoxin binding sites of hippocampus. Neonatal exposure to certain PCBs has also been shown to affect the nicotinic receptors in the adult mouse brain.

The author concludes that PBDE 153 can induce neurotoxic effects in the adult animal when neonatal exposed: functional disorder is dose-response related and worsen with age; learning and memory functions are also affected these changes are dose-response related. In addition; nicotinic α-Bungarotoxin binding sites are also affected in the adult mouse, by the neonatal exposure to PBDE 153 on postnatal day 10 at the highest tested dose.

Number of uncertainties and weakness in this study make the toxicological significance of these findings unreliable. 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. Moreover only an abstract of this study is available and some major information is lacking such as the housing condition, randomisation, number of animals. It is also noticeable that description of the severity of the effects pending on the dose quantitative data is not indicated. Moreover no statistical treatment of the results, no standard deviation data are presented, so it is difficult to judge the degree of variability that might be expected within this study. Finally no details regarding the historical negative control are reported.

4.1.3 Risk Characterisation

4.1.3.1 General aspects

Animal data show an absorption of OBDPO by oral or inhalation route with an accumulation of the parent compound or its metabolites in the liver and also in the adipose tissue and the lung following an inhalation administration. The extent of absorption and elimination cannot be assessed from the data available. No information on the metabolism of OBDPO is available. Following oral administration, OBDPO is an inducer of xenobiotic metabolism with dose and time dependent relationship. There are no measured data on OBDPO dermal absorption nor on PeBDPO, DBDPO and polybrominated biphenyls compounds. However based on OBDPO physicochemical properties and analogy with PCBs, a dermal absorption of 4.5% may be estimated associated with a likely trend towards accumulation in the stratum corneum.

No data regarding the quantification of absorption, metabolism or excretion of OBDPO in humans following exposure are available. However, evidence from humans indicates that OBDPO, HxBDPO, HpBDPO and NonaBDPO which are components of commercial OBDPO can be absorbed into the body and distributed into the blood. Distribution to the adipose tissue was evidenced at least for OBDPO and HxBDPO. There are no data available on the rate of elimination or on bioaccumulation of OBDPO from human adipose tissue neither for PeBDPO but given the high lipophilicity of these compounds and the adipose tissue accumulation observed in rats following oral or inhalation routes, it can be assumed that in humans OBDPO might bioaccumulate in these tissues as well. Following pregnancy HxBDPO and others PBDPOs such as TeBDPO and PeBDPOs are excreted in the breast milk. Unfortunately, such measurements were not carried out on OBDPO. However, based on the high lipophilicity of OBDPO, its potential to bioaccumulate in adipose tissues and the breast milk measured data with HxBDPO (one component of commercial OBDPO) excretion of OBDPO in the breast milk may be anticipated. Thus these end-points have been considered for risk assessment purposes.

Assessment of the available data clearly indicates that OBDPO is of low acute toxicity in animals and does not cause skin or eye irritation nor sensitisation in animal studies. There is no information on respiratory or cutaneous sensitisation in human.

The only information concerning the effects of repeated oral and inhalation exposure to OBDPO comes from studies in rats involving administration of commercial OBDPO. These studies consistently indicate that the liver is the key target organ affected by OBDPO. The effects observed include increases in liver weight and liver enlargement, cellular microscopic changes, scattered incidence of hyperplastic nodules during the withdrawal period (8 weeks and 6 months) and induction of a range of liver enzymes. It was also shown that OBDPO exhibits a strong porphyrinogenic effect in vitro. Following oral administration, thyroid gland effects are also observed including increases in thyroid weight and histopathological changes in adult rats and a dose-dependent depletion of T_4 as well as a decrease of serum T_3 level in weanling rats showing a thyroid homeostasis disturbance. In a recent inhalation study, administration up to 202 mg/m^3

does not lead to thyroid weight or histopathological changes but to a thyroid hormonal disturbance with a decreased T_4 level and an increased TSH level. However, due to species differences in thyroid metabolism it is unlikely that the effects on thyroid status via an induction of the hepatic enzymes would occur in human. However mechanisms other than T_4 glucuronidation may not be completely disregarded. Dose-related increases in total bromine levels in the liver were observed after 4 and 13 weeks of oral treatment from 100 ppm. Following 2 weeks of inhalation exposure, increase in total bromine concentrations were reported in the liver and in the fat and the lung as well. Moreover it was shown that fat and lung accumulate OBDPO to a greater extent than the liver. Following inhalation exposure only, absence of corpora lutea was exhibited at the highest tested concentration of 202 mg/m^3 (analytical concentration) within 13 weeks of exposure. Local toxicity was demonstrated with hyperplasia/hypertrophy of the goblet cells within 2 weeks of exposure and with chronic active lung inflammation and alveolar histiocytosis within 13 weeks of exposure. It is obvious that observed effect at *1.1 mg/m^3* is minimal and reveal only a trend to a chronic inflammation however this value has been taken to set up the LOAEC for local toxicity for the risk characterisation. For systemic toxicity, the liver changes produced by commercial OBDPO are apparent within 4 and 13 weeks of repeated oral dosing and within 14 days and 90 days of inhalation exposure, with effects from 100 ppm and 1 mg/m^3 (analytical concentration) respectively. The changes in thyroid status are apparent within 4 and 13 weeks of repeated oral dosing from 1,000 ppm and within 13 weeks of repeated inhalation dosing from 16 mg/m^3 (analytical concentration). For risk characterisation, the LOAEL is considered to be 100 ppm $\approx$ 7.2 mg/kg/day in the 90-day study by oral route and the NOAEC for systemic toxicity to be 1.1 mg/m^3 in the 90-day study by inhalation route.

Regarding mutagenicity, results from different Salmonella tests taken as a whole can be considered as negative. OBDPO did not induce UDS or SCE in vitro neither cytogenetic effects in vitro. It is noticeable that some of these tests present some limitations in particular the UDS and SCE assays. However, given the negative results obtained in recent Ames and cytogenetic assays conducted in compliance with GLP procedures and the negative results obtained in the mutagenicity tests with PeBDPO and DBDPO, no concern for mutagenicity may be assumed.

No chronic or carcinogenicity studies in animals are available. Only subchronic studies are available to anticipate carcinogenic potential of the substance, thus no firm conclusion can be drawn on carcinogenicity.

No specific fertility study is available. The information concerning the potential effects of OBDPO on fertility comes from sub-acute or sub-chronic studies in rats involving administration of commercial OBDPO by oral or inhalation routes. The oral sub-chronic study indicates a reversible increase of the absolute and relative testes weight (Great Lakes, 1977). However in recent sub-acute and sub-chronic inhalation studies (Great Lakes, 2000 and 2001), no treatment-related effects on testes and epididymis weights nor microscopic evidence of cell loss or inappropriate cell presence in the seminiferous tubules were shown up to 202 mg/m^3 or 250 mg/m^3. Since this recent sub-chronic study, well conducted and specifically designed to investigate reproductive organs, did not demonstrate adverse effects on male reproductive organs, no concern is assumed for male fertility. Regarding female reproductive organs, absence of corpora lutea was shown at 202 mg/m^3 in the recent 90-day inhalation study, thus a NOAEC for female fertility of 16 mg/m^3 is considered for risk characterisation.

Developmental effects are observed in rats in two studies and they do not seem to be related to maternal toxicity (only decrease in maternal body weight gain during days 16-20 of gestation or decrease in body weight gain interrelated with resorptions and small fetal body weights).

However, these developmental effects are not confirmed in a third assay in rats conducted with a test article containing a less percentage of octabrominateddiphenyl oxide component. In rabbits, the substance produces only slight foetotoxicity along with a decreased bodyweight gain of the dams at the highest dose. However it must be noticed that this decrease had already happened before the treatment. The lowest identified NOAEL is considered for the risk characterisation i.e. 2 mg/kg/day as obtained in the rabbit.

With regard to endocrine disruptor potential: alterations in thyroid homeostasis were reported with organochlorine compounds for many species, including humans and a thyroid hormonelike affinity for the serum transport protein transthyretin was shown for hydroxylated PCBs. Concerning PBDPOs, certain PBDPO congeners namely BDE-15 (DiBDPO) and BDE-77 (TeBDPO) after in vitro microsomal transformation into metabolites compete with thyroxin for a transport protein (TTR) suggesting a potential endocrine disturbing effect of these PBDPO metabolites. However, to our knowledge, no studies on transthyretin-T_4 competition have been carried out on OBDPO neither on DBDPO.

With regard to neurotoxicity: recently it has been reported behavioural disturbances when mice (10 days old) were exposed to a single dose of hexabromo-diphenyl ether (0.45, 0.9 and 9 mg/kg b.wt) those effects are observed at 2, 4 but also 6 months of age. Nicotinic receptors were also affected in adult mouse in the previous conditions of exposure. The toxicological significant of these findings is not obvious since a clear interpretation of the significance for human health of the behavioural difference seen in mice has not been established. Moreover only an abstract of this study is available and some major information is lacking such as housing condition, randomisation, number of animals. It is also noticeable that description of the severity of the effects pending on the dose as well as quantitative data are not indicated. Moreover no statistical treatment of the results and no standard deviation data are presented, so it is difficult to judge the degree of variability that might be expected within this study. Finally no details regarding the historical negative control are reported.

No firm conclusion can be drawn from the previous data.

4.1.3.2 Workers

For the purpose of the risk characterisation, it is assumed that inhalation of dust and skin exposure are the main routes of exposure. Oral exposure is not considered to be a significant route of exposure under normal working practice.

Taking into account the poor available qualitative information, the highest exposure levels are likely to occur while handling the dry substance during manufacture and compounding or master batching (bagging, bag emptying). Afterwards the substance is incorporated in the polymer matrix and the polymer is in a non dusty form; therefore the potential for exposure is likely to be negligible.

In case of heating during processing, release of OBDPO fumes is unlikely to be a significant source of exposure.

For dust exposure, a full-shift exposure of 5 mg/m^3 will be used to describe a reasonable worst-case scenario during manufacture and compounding.

No information is available on the extent of absorption of OBDPO following inhalation. But animal data fairly support an extended absorption by this route of administration. Therefore on

the side of caution a 100 % absorption will be assumed. Assuming a 100 % absorption and a 70 kg worker breathes 10 m^3/working day, a body burden of 0.7 mg/kg/day is achieved.

Maximum skin exposures of 1 mg/cm^2/day is predicted by the EASE model. Assuming that the skin exposed on the hands represents 840 cm^2, a worker weighs 70 kg and a skin absorption of 4.5% (based on physicochemical properties and analogy with PCBs), body burdens of 0.54 mg/kg/day.

It should be noted that these exposure levels are assumed to be reached when the substance is in the form of a powder. Exposure will be significantly reduced when the substance is flaked.

4.1.3.2.1   Acute toxicity

Given the effects observed in the acute oral, dermal and inhalation studies it is concluded that OBDPO is of no concern for workers with regard to acute effects (**conclusion (ii)**).

4.1.3.2.2   Irritation

Given the effects observed in the skin and eye irritation studies, it is concluded that OBDPO is of no concern for workers with regard to irritating effects (**conclusion (ii)**).

4.1.3.2.3   Sensitisation

Given the results from the dermal sensitisation studies it is concluded that OBDPO is of no concern for workers with regard to skin sensitisation (**conclusion (ii)**).

There are neither data from human experience on dermal sensitisation nor other indications for respiratory sensitisation.

4.1.3.2.4   Repeated dose toxicity

With respect to repeated dose toxicity, each route of exposure will be considered separately for the initial assessment.

<u>Inhalation route</u>

A NOAEC of 1 mg/m^3 for systemic toxicity and a LOAEC of 1 mg/m^3 for local effects was identified in the recent 90-day inhalation toxicity study in rats, (6 hours/day, 5 days/week). The calculated MOSs and conclusions are given in **Table 4.7**.

Table 4.7   MOS for repeated dose toxicity and inhalation exposure

Scenario	External inhalation exposure (mg/m³)	NOAEC (mg/m³) (systemic) LOAEC (mg/m³) (local)	MOS	Ccl
1-Manufacture (bagging)	5	1	<1	iii
2-Coumpounding and master batching (bag emptying)	5	1	<1	iii

The calculated MOSs lower than 1 are of concern. Hence **conclusion (iii)** is reached for inhalation exposure for bagging during manufacture and for bag emptying during compounding and master batching.

Provided that the substance is labelled with appropriate risk and safety phrases (see proposal at Section 1), appropriate precautions can be expected to be taken during handling (according to the risk reduction measures already applied in EU). However it may still be necessary to recommend further risk reduction measures like the setting of an occupational exposure limit value or dust suppression methods, such as the use of the substance in flaked form.

Dermal route

No dermal toxicological data are available neither in human nor in animals. Therefore on the side of caution, the dermal and oral NOAEL or LOAEL for repeated doses will be assumed to be the same. Since no quantitative information is available on the extent of absorption of OBDPO following oral administration, a conservative value of 50% of absorption may be assumed. The LOAEL of 7.2 mg/kg/day based on oral studies (28 or 90 days) leads to an "internal" LOAEL of 3.6 mg/kg/day.

The calculated MOSs and conclusions are given in **Table 4.8**.

Table 4.8 MOS for repeated dose toxicity and dermal exposure

Scenario	Internal dermal exposure (mg/kg bw/d)	Internal LOAEL (mg/kg bw/d)	MOS	Ccl
1-Manufacture (bagging and cleaning activities)	0.54	3.6	7	iii
2-Compounding and master batching (bag emptying)	0.54	3.6	7	iii

The calculated MOS for scenario 1 and 2 is of concern. Hence **conclusion (iii)** is reached for dermal exposure for bagging and cleaning activities during manufacture and for bag emptying during compounding and master batching.

It should be noticed that the estimated exposure does not take into account the normal safety practices which should strongly reduce the exposure and provided that the substance is labelled with appropriate risk and safety phrases (see proposal at Section 1), appropriate precautions can be expected to be taken during handling (according to the risk reduction measures already applied in the EU).

4.1.3.2.5   Immunotoxicity

It is recognised that lymphoid tissues are affected by polybrominated biphenyls (Polybrominated biphenyls. Environmental Health Criteria 152, IPCS, 1994, p. 451), but no indication of immunotoxicity was reported in the studies available on OBDPO (**conclusion (ii)**).

4.1.3.2.6   Mutagenicity

Given the results from the mutagenicity studies it is concluded that OBDPO is of no concern for workers with regard to mutagenicity (**conclusion (ii)**).

4.1.3.2.7   Reproductive toxicity

Fertility

No specific fertility study is available. The only information concerning the potential effects of OBDPO on fertility comes from sub-acute or sub-chronic studies in rats involving administration of commercial OBDPO by oral or inhalation routes.

Based on these studies, no concern is assumed for male fertility and therefore no concern for workers with regard to male fertility effects is anticipated (**conclusion (ii)**).

Regarding female reproductive organs, absence of corpora lutea was shown at 202 mg/m³, and a NOAEC for female fertility of 16 mg/m³ was considered. With respect to female fertility, each route of exposure will be considered separately for the initial assessment.

Inhalation route

A NOAEC of 16 mg/m³ was identified in a 90-day inhalation study in rats (6 hours/day, 5 days/week). The calculated MOSs and conclusions are given in **Table 4.9**.

Table 4.9   MOS for female fertility toxicity and inhalation exposure

Scenario	External inhalation exposure (mg/m³)	NOAEC (mg/m³)	MOS	Ccl
1-Manufacture (bagging)	5	16	3	iii
2-Coumpounding and master batching (bag emptying)	5	16	3	iii

These values are of concern. Hence **conclusion (iii)** is reached for inhalation exposure for bagging during manufacture and bag emptying during compounding and master batching.

Provided that the substance is labelled with appropriate risk and safety phrases (see proposal at Section 1), appropriate precautions can be expected to be taken during handling (according to the risk reduction measures already applied in the EU). However it may still be necessary to recommend further risk reduction measures like the setting of an occupational exposure limit value or dust suppression methods, such as the use of the substance in flaked form.

Dermal route

No dermal toxicological data are available neither in human nor in animals. Therefore the inhalation NOAEC (16 mg/m³) for female fertility toxicity will be used. Since no quantitative information is available on the extent of absorption of OBDPO following inhalation administration, a conservative value of 100% of absorption may be assumed which leads to "internal" NOAEL of 4.6 mg/kg/day (rat respiratory rate of 0.8 l/mn/kg, 6 h/d).

The calculated MOSs and conclusions are given in **Table 4.10**.

Table 4.10 MOS for female fertility toxicity and dermal exposure

Scenario	Internal dermal exposure (mg/kg bw/d)	Internal NOAEL (mg/kg bw/d)	MOS	Ccl
1-Manufacture (bagging and cleaning activities)	0.54	4.6	< 9	iii
2-Coumpounding and master batching (bag emptying)	0.54	4.6	< 9	iii

The calculated MOS for scenario 1 and 2 is of concern. Hence **conclusion (iii)** is reached for dermal exposure for bagging, cleaning activities during manufacture and for bag emptying during compounding and master batching.

It should be noticed that the estimated exposure does not take into account the normal safety practices which should strongly reduce the exposure and provided that the substance is labelled with appropriate risk and safety phrases (see proposal at Section 1), appropriate precautions can be expected to be taken during handling (according to the risk reduction measures already applied in the EU).

Developmental toxicity

With respect to developmental toxicity, each route of exposure will be considered separately for the initial assessment. A NOAEL of 2 mg/kg/day for the conceptuses, lower than the NOAEL for maternal toxicity, was established in a developmental toxicity study by oral route.

With regard to dermal and inhalation exposures, no developmental toxicological data are available for these routes of exposures. Therefore, the oral NOAEL for developmental toxicity will be used to determined the internal NOAEL. Since no quantitative information is available on the extent of absorption of OBDPO following oral administration, a conservative value of 50% of absorption may be assumed which leads to "internal" NOAEL of 1 mg/kg/day. The calculated MOSs and conclusions are given in **Table 4.11** and **Table 4.12**.

Table 4.11 MOS for developmental toxicity and inhalation exposure

Scenario	Internal inhalation exposure (mg/kg bw/d)	Internal NOAEL (mg/kg bw/d)	MOS	Ccl
1-Manufacture (bagging)	0.7	1	1	iii
2-Coumpounding and master batching (bag emptying)	0.7	1	1	iii

Table 4.12 MOS for developmental toxicity and dermal exposure

Scenario	Internal dermal exposure (mg/kg bw/d)	Internal NOAEL (mg/kg bw/d)	MOS	Ccl
1-Manufacture (bagging and cleaning activities)	0.54	1	2	iii
2-Coumpounding and master batching (bag emptying)	0.54	1	2	iii

These values are of concern and risk reduction measures (**conclusion (iii)**) should be considered for dermal and inhalation exposures for bagging and cleaning activities during manufacture and bag emptying during compounding and master batching.

Provided that the substance is labelled with appropriate risk and safety phrases (as proposed at Section 1), appropriate precautions can be expected to be taken (according to the risk reduction measures already applied in the EU). However it could still be necessary to recommend further risk reduction measures like the setting of an exposure limit value or dust suppression methods such as the use of the substance in flaked form.

4.1.3.2.8   Breast feeding

Following pregnancy HxBDPO and others PBDPOs such as TeBDPO and PeBDPOs have been identified in breast milk but unfortunately such measurements were not carried out on OBDPO neither on DBDPO. Based on the high lipophilicity of OBDPO, its potential to bioaccumulate in adipose tissues and its similar toxicological pattern with PeBDPO, we may anticipate an excretion of this compound in breast milk. However as no quantified data on OBDPO are available, an attempt of risk characterisation is not possible. Therefore information on the extent of excretion of commercial OBDPO into the breast milk is necessary. Moreover since no metabolism data are available on OBDPO, no appraisal on the different metabolites formed and especially on lower brominated congeners could be done. Therefore estimation of the excretion data on OBDPO and its metabolites into milk would be improved if toxicokinetics data including metabolism and distribution data were available.

Hence **conclusion (i)** is reached.

Recommended action/testing:

- Information on the extent of excretion of commercial OBDPO into the breast milk. Depending upon the results submitted by Industry further information might be requested.

4.1.3.2.9   Endocrine disruptor potential

Pertaining to endocrine disruptor potential, no studies on transthyretin-T_4 competition have been carried out on OBDPO. Moreover since no chronic or carcinogenicity studies are available, alterations in thyroid homeostasis could not be appraised. Therefore it is not possible to conclude for risk assessment at this time. Therefore it would be useful to explore this end-point to reassure that there is no concern about an endocrine disruptor potential. Hence **conclusion (i)** is reached.

Recommended action/testing:

- Information is needed on transthyretin-T_4 competition with OBDPO.

4.1.3.2.10   Effects of prolonged exposure

Given the high lipophilicity of OBDPO and the adipose tissue accumulation observed in rats following oral or inhalation routes, it can be assumed that in humans OBDPO might bioaccumulate in these tissues as well. Since body burden may increase with time until steady state levels are reached, the calculation and use as a comparator of a daily body burden is likely to be inappropriate for this substance. 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 toxicological information available, the LOAEL used is from a 90-day study. Given the bioaccumulative nature of this compound, it is unknown whether or not such a LOAEL would be appropriate for much long-term exposures. Thus information from a chronic repeat-dose study may be required. Overall, these uncertainties indicate that the method used to calculate MOS has significant limitations and that further information, including the development of a suitable methodology for the risk assessment of bioaccumulative substances is required. Hence **conclusion (i)** is reached.

Recommended action/testing:

- Information on the effects of prolonged exposure: 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.

4.1.3.2.11   Summary of the risk characterisation for workers

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

This conclusion is reached since information is needed on transthyretin-T4 competition with OBDPO as well as information on the extent of excretion of commercial OBDPO into the breast milk and information on the effects of prolonged exposure.

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

This conclusion is reached for manufacture (bagging and cleaning activities) and for compounding and master batching (bag emptying). There are concerns for:

- systemic effects after inhalation and dermal repeated exposure,
- local effects in the respiratory tract after inhalation repeated exposure,
- effects on female fertility after inhalation and dermal repeated exposure.

4.1.3.3   Consumers

Due to the lack of detailed information about consumer exposure to OBDPO, it is not possible to conduct a sound risk assessment for the consumer.

However, based on scattered pieces of evidence, and in agreement with the previous risk assessment conducted under the auspices of IPCS (Brominated Diphenyl Ethers EHP, vol 162, IPCS, 1994), it is felt that consumer exposure to OBDPO is likely to be negligible, with no resulting risk for consumers. Hence **conclusion (ii)** is reached.

4.1.3.4   Humans exposed via the environment

The estimated maximum human intake from local environmental sources is around 11 μg/kg bw/day from polymer processing. At a regional level, the estimated human intake figure is around 0.42 μg/kg bw/day.

4.1.3.4.1   Repeated dose toxicity

Comparison with the available LOAEL derived from the oral subchronic toxicity study (7.2 mg/kg/day) leads for polymer processing to a ratio of 654 at the local level and 17 142 at the regional level.

These ratios are considered to be sufficient to provide reassurance that adverse health effects will not occur (**conclusion (ii)**).

4.1.3.4.2   Reproductive toxicity

Fertility

No specific fertility study is available. The only information concerning the potential effects of OBDPO on fertility comes from sub-acute or sub-chronic studies in rats involving administration of commercial OBDPO by oral or inhalation routes.

Based on these studies, no concern is assumed for male fertility and therefore no concern for humans exposed indirectly via the environment with regard to male fertility effects is anticipated (**conclusion (ii)**).

Regarding female reproductive organs, absence of corpora lutea was shown at 202 mg/m³, and a NOAEC for female fertility of 16 mg/m³ was considered which corresponds to an internal NOAEL of 4.6 mg/kg/day. Comparison between the exposure and this internal NOAEL leads for polymer processing to a ratio of 418 at the local level and 10 952 at the regional level.

These ratios are considered to be sufficient to provide reassurance that adverse health effects will not occur (**conclusion (ii)**).

Developmental toxicity

Comparison with the NOAEL derived from the developmental toxicity studies (2 mg/kg/day) leads for polymer processing to ratios of 182 for local level and 4 762 at the regional level.

The ratio derived for local exposure is of insufficient magnitude to provide reassurance that adverse health effects will not occur. There is concern for human health with respect to exposure via the environment. In order to refine this estimate, further information is needed either regarding emissions into the environment from use or regarding soil-plant transfer as the exposure is mostly due to high estimated concentrations in root crops. Hence **conclusion (i)** is reached.

Recommended action/testing:

- Further information is needed on emissions into the environment from use or on soil-plant transfer.

4.1.3.4.3   Exposure to infants via milk

Breast feeding

Following pregnancy HxBDPO and others PBDPOs such as TeBDPO and PeBDPOs have been identified in breast milk but unfortunately such measurements were not carried out on OBDPO

neither on DBDPO. Based on the high lipophilicity of OBDPO, its potential to bioaccumulate in adipose tissues and its similar toxicological pattern with PeBDPO, we may anticipate an excretion of this compound in breast milk. However as no quantified data on OBDPO are available, an attempt of risk characterisation is not possible. Therefore information on the extent of excretion of commercial OBDPO into the breast milk is necessary. Moreover since no metabolism data are available on OBDPO, no appraisal on the different metabolites formed and especially on lower brominated congeners could be done. Therefore estimation of the excretion data on OBDPO and its metabolites into milk would be improved if toxicokinetics data including metabolism and distribution data were available.

- Information on the extent of excretion of commercial OBDPO into the breast milk. Depending upon the results submitted by Industry further information might be requested.

Cows' milk

Estimates for the concentration of OBDPO in cows' milk using the EUSES model are presented in Section 4.1.1.4. The concentration estimated for local sources is 35 µg/kg, which is higher than the measured levels found in human breast milk for HxBDPO (generally 0.5 µg/kg lipid) which is a component of commercial OBDPO. The concentration estimated for regional sources is about 1.4 µg/kg, which is also higher than 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, it is considered that in addition to some of the information required in the conclusion i for exposure to human breast milk, the exposure estimates for cows' milk should be investigated further in order to improve the accuracy of the risk characterisation. Moreover since no metabolism data are available on OBDPO, no appraisal on the different metabolites formed and especially on lower brominated congeners could be done. Therefore estimation of the excretion data on OBDPO and its metabolites into milk would be improved if toxicokinetics data including metabolism and distribution data were available. Hence **conclusion (i)** is reached.

Recommended action/testing:

- Information on the extent of excretion of commercial OBDPO into the breast milk.
- Information on the extent of excretion of commercial OBDPO into cows' milk. Depending upon the results submitted by Industry on milk excretion further information might be requested.
- There is a need for exposure information from local and regional sources on the concentration of OBDPO in cows' milk.

4.1.3.4.4 Endocrine disruptor potential

Pertaining to endocrine disruptor potential, no studies on transthyretin-T_4 competition have been carried out on OBDPO. Moreover since no chronic or carcinogenicity studies are available, alterations in thyroid homeostasis could not be appraised. Therefore it is not possible to conclude for risk assessment at this time. Therefore it would be useful to explore this end-point to reassure that there is no concern about an endocrine disruptor potential. Hence **conclusion (i)** is reached.

Recommended action/testing:

- Information is needed on transthyretin-T_4 competition with OBDPO.

4.1.3.4.5   Effects of prolonged exposure

Given the high lipophilicity of OBDPO and the adipose tissue accumulation observed in rats following oral or inhalation routes, it can be assumed that in humans OBDPO might bioaccumulate in these tissues as well. Since body burden may increase with time until steady state levels are reached, the calculation and use as a comparator of a daily body burden is likely to be inappropriate for this substance. 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 toxicological information available, the LOAEL used is from a 90-day study. Given the bioaccumulative nature of this compound, it is unknown whether or not such a LOAEL would be appropriate for much long-term exposures. Thus information from a chronic repeat-dose study may be required. Overall, these uncertainties indicate that the method used to calculate MOS has significant limitations and that further information, including the development of a suitable methodology for the risk assessment of bioaccumulative substances is required. Hence **conclusion (i)** is reached.

Recommended action/testing:

- Information on the effects of prolonged exposure: 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.

4.1.3.4.6   Summary of the risk characterisation for humans exposed via the environment

Conclusion (i)   There is a need for further information.

Recommended action/testing:

- Further information is needed on emissions into the environment from use or on soil-plant transfer.
- Information on the extent of excretion of commercial OBDPO into the breast milk.
- Information on the extent of excretion of commercial OBDPO into cows' milk. Depending upon the results submitted by Industry on milk excretion further information might be requested.
- There is a need for exposure information from local and regional sources on the concentration of OBDPE in cows' milk.
- Information is needed on transthyretin-T_4 competition with OBDPO.
- Information on the effects of prolonged exposure: 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.

4.1.3.5   Combined exposure

Combined environmental exposure and occupational exposure will not influence the characterisation of the risks which are outlined above in Sections 4.1.3.2 and 4.1.3.4.

4.2   HUMAN HEALTH (PHYSICO-CHEMICAL PROPERTIES)

4.2.1   Exposure assessment

Exposure occurs only in the workplace where the substance is produced or at the first step of its use (compounding).

4.2.2   Effect assessment

4.2.2.1   Explosivity

Explosive properties have not been tested. Due to its chemical structure, the substance is not expected to be explosive.

4.2.2.2   Flammability

OBDPO will not sustain combustion on its own, however it may burn in association with another fuel giving off corrosive gases (Great lakes Chemical (Europe) Ltd, 1995). Although no test has been conducted, it is expected to give a negative result. The substance is used as a flame retardant and is known for its stability.

4.2.2.3   Oxidizing properties

No oxidizing properties are expected due to the chemical structure of the substance.

4.2.3   Risk characterisation

OBDPO gives no reason for concern in relation with its physico-chemical properties. There is no need for further information and/or testing. 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 RESULTS

5.1 INTRODUCTION

Octabromodiphenyl ether is mainly used in the plastics industry as an additive flame retardant for acrylonitrile-butadiene-styrene (ABS) polymers. The commercially supplied product is a mixture of brominated diphenyl ethers typically consisting of 31-36% octabromodiphenyl ether. The other main components are hexabromodiphenyl ether (up to 10.5-12%), heptabromodiphenyl ether (around 44%), nonabromodiphenyl ether (9.5-11.3%) and decabromodiphenyl ether (0-0.7%). The actual composition of the product varies between manufacturers. Recently, a composite sample from three current suppliers of octabromodiphenyl ether to the EU has been used in various physico-chemical and ecotoxicity tests and this had the following composition: 5.5% hexabromodiphenyl ether, 42.3% heptabromodiphenyl ether, 36.1% octabromodiphenyl ether, 13.9% nonabromodiphenyl ether and 2.1% decabromodiphenyl ether. The product is a solid of low water solubility and vapour pressure.

No production of octabromodiphenyl ether currently occurs in the EU. The substance used is imported from outside the EU. Information on the actual amounts currently used within the EU would be useful for the assessment.

5.2 ENVIRONMENT

Local releases to the environment may occur from polymer processing. In addition, volatilisation of the flame retardant from plastic articles and particulate loss of plastic containing the substance may occur during the lifetime of the article. These releases have been quantified in the assessment and used to calculate PECs for various environmental compartments.

The possible environmental effects of the lower brominated components (e.g. hexabromodiphenyl ether) present in the commercial products is considered in the environmental assessment, along with those of the commercial product as a whole.

For the aquatic compartment, the risk from exposure via surface water is thought to be low. Exposure to organisms via sediment is thought to be much more relevant for this substance and the risk to sediment-dwelling organisms was also found to be low. The risk to wastewater treatment processes was low.

For the terrestrial compartment, no risk was indicated from a worst-case PEC/PNEC comparison.

No adverse effects are expected on the atmosphere from the use of octabromodiphenyl ether.

The available information indicates that the risk of secondary poisoning resulting from the use of octabromodiphenyl ether itself is low using the conventional PEC/PNEC approach. However, when the hexabromodiphenyl ether component present in commercial octabromodiphenyl ether products is considered, a possible risk of secondary poisoning via the earthworm route is indicated.

There are considerable uncertainties in the secondary poisoning assessment for octabromodiphenyl ether, and a strict PEC/PNEC approach may not be appropriate for this substance. In addition, the possibility of octabromodiphenyl ether degrading in the environment to give more toxic lower brominated diphenyl ethers cannot be completely ruled out over extended time periods with the available data. The combination of uncertainties raises a concern about the possibility of long-term environmental effects that cannot easily be predicted. Although

further information is necessary to help clarify the concern, the inherent difficulties and time required to complete the work mean that there may be a need at a policy level to consider precautionary risk reduction action for this endpoint.

Overall results

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

This conclusion applies to the risk of secondary poisoning from all sources of octabromodiphenyl ether. The additional information needed is:

a)   A more widespread monitoring project to determine whether the finding in top predators (including birds' eggs) is a widespread or localised phenomenon, and trends (if possible).

b)   Further toxicity testing. The existence of a mammalian toxicity data set means that testing could be considered on birds (e.g. an avian reproduction test (OECD 206), with appropriate tissue analysis). Overall, the benefit of further vertebrate testing is open to question due to expected difficulties in achieving sufficiently high exposures. This leaves the toxicity issue with some unresolved uncertainty.

c)   An investigation of the rate of formation of degradation products under environmentally relevant conditions over a suitably prolonged time period (e.g. years) - for example, an extended monitoring programme to determine trends in degradation product levels in various environmental compartments. This could be coupled with analysis of the parent compound to detect whether it is building up in the environment or has achieved equilibrium. A controlled field study (or studies) might be the way forward, with controlled continuous input of the substance and regular monitoring of other components.

d)   Further toxicological work on the non-diphenyl ether degradation products, to determine if they pose a hazard or risk.

[N.B. A number of technical experts from EU member states consider that this uncertainty is sufficient to warrant risk reduction measures directly (conclusion (iii)) based on the information currently provided in this assessment.]

The possible long-term increase in levels as a result of releases from waste sites might need to be considered further in any future revision of this risk assessment report.

5.3   HUMAN HEALTH

This assessment does not take into account the risks related to the breakdown products formed during processing at elevated temperatures. These risks are assessed elsewhere in this report (see Appendix D).

5.3.1   Human health (toxicity)

5.3.1.1   Workers

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

This conclusion is reached since information is needed on transthyretin-T4 competition with OBDPO as well as information on the extent of excretion of commercial OBDPO into the breast milk and information on the effects of prolonged exposure.

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

This conclusion is reached for manufacture (bagging and cleaning activities) and compounding and master batching (bag emptying), because:

- systemic effects after inhalation and dermal repeated exposure,
- local effects in the respiratory tract after inhalation repeated exposure and
- developmental effects after repeated dermal and inhalation exposure cannot be excluded at the workplace.

5.3.1.2   Consumers

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

This conclusion is reached because consumer exposure is considered negligible.

5.3.1.3   Humans exposed via the environment

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

This conclusion is reached since further information is needed on emissions into the environment from use or on soil-plant transfer; on the extent of excretion of commercial OBDPO into the breast milk and cow's milk. Depending upon the results submitted by Industry on milk excretion further information might be requested. There is a need for exposure information from local and regional sources on the concentration of OBDPE in cows' milk. Information is needed as well on transthyretin-T$_4$ competition with OBDPO and on the effects of prolonged exposure. 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   Human health (risks from 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.

Human health assessment: Note for all information required under conclusion (i)

It is noted that much of the information required under conclusion (i) would take a long time to be generated or gathered, in particular for breast feeding and effects of prolonged exposure, and that a considerable amount of uncertainty could remain in the risk assessment once the further information had been provided. As a consequence of the environmental and human health (occupational exposure) risk assessment, a risk reduction strategy has been developed for this substance which proposes a restriction of the marketing and use under Directive 76/769/EEC. If this strategy is adopted, then the information requirement should be adjourned.

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ABBREVIATIONS

ADI	Acceptable Daily Intake
AF	Assessment Factor
ALAT	Alanine Amino Transferase
ASAT	Aspartate Amino Transferase
ASTM	American Society for Testing and Materials
ATP	Adaptation to Technical Progress
AUC	Area Under The Curve
B	Bioaccumulation
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
BCF	Bioconcentration Factor
BMC	Benchmark Concentration
BMD	Benchmark Dose
BMF	Biomagnification Factor
bw	body weight / *Bw, b.w.*
C	Corrosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
CA	Chromosome Aberration
CA	Competent Authority
CAS	Chemical Abstract Services
CAT	Camitine Acetyltransferase
CEC	Commission of the European Communities
CEN	European Standards Organisation / European Committee for Normalisation
CMR	Carcinogenic, Mutagenic and toxic to Reproduction
CNS	Central Nervous System
COD	Chemical Oxygen Demand
CSTEE	Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO)
CT_{50}	Clearance Time, elimination or depuration expressed as half-life
d.wt	dry weight / dw
dfi	daily food intake
DG	Directorate General
DIN	Deutsche Industrie Norm (German norm)
DNA	DeoxyriboNucleic Acid
DOC	Dissolved Organic Carbon
DT50	Degradation half-life or period required for 50 percent dissipation / degradation
DT90	Period required for 90 percent dissipation / degradation

E	Explosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
EASE	Estimation and Assessment of Substance Exposure Physico-chemical properties [Model]
EbC50	Effect Concentration measured as 50% reduction in biomass growth in algae tests
EC	European Communities
EC10	Effect Concentration measured as 10% effect
EC50	median Effect Concentration
ECB	European Chemicals Bureau
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECVAM	European Centre for the Validation of Alternative Methods
EDC	Endocrine Disrupting Chemical
EEC	European Economic Communities
EINECS	European Inventory of Existing Commercial Chemical Substances
ELINCS	European List of New Chemical Substances
EN	European Norm
EPA	Environmental Protection Agency (USA)
ErC50	Effect Concentration measured as 50% reduction in growth rate in algae tests
ESD	Emission Scenario Document
EU	European Union
EUSES	European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment]
F(+)	(Highly) flammable (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
FAO	Food and Agriculture Organisation of the United Nations
FELS	Fish Early Life Stage
GLP	Good Laboratory Practice
HEDSET	EC/OECD Harmonised Electronic Data Set (for data collection of existing substances)
HELCOM	Helsinki Commission -Baltic Marine Environment Protection Commission
HpBDPO	Heptabromodiphenyloxide
HPLC	High Pressure Liquid Chromatography
HPVC	High Production Volume Chemical (> 1000 t/a)
HxBDPO	Hexaabromodiphenyloxide
IARC	International Agency for Research on Cancer
IC	Industrial Category
IC50	median Immobilisation Concentration or median Inhibitory Concentration
ILO	International Labour Organisation
IPCS	International Programme on Chemical Safety
ISO	International Organisation for Standardisation

IUCLID	International Uniform Chemical Information Database (existing substances)
IUPAC	International Union for Pure and Applied Chemistry
JEFCA	Joint FAO/WHO Expert Committee on Food Additives
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
Koc	organic carbon normalised distribution coefficient
Kow	octanol/water partition coefficient
Kp	solids-water partition coefficient
L(E)C50	median Lethal (Effect) Concentration
LAEL	Lowest Adverse Effect Level
LC50	median Lethal Concentration
LD50	median Lethal Dose
LEV	Local Exhaust Ventilation
LLNA	Local Lymph Node Assay
LOAEL	Lowest Observed Adverse Effect Level
LOEC	Lowest Observed Effect Concentration
LOED	Lowest Observed Effect Dose
LOEL	Lowest Observed Effect Level
lw	lipid weight
MAC	Maximum Allowable Concentration
MATC	Maximum Acceptable Toxic Concentration
MC	Main Category
MITI	Ministry of International Trade and Industry, Japan
MOE	Margin of Exposure
MOS	Margin of Safety
MW	Molecular Weight
N	Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC
NAEL	No Adverse Effect Level
NOAEL	No Observed Adverse Effect Level
NOEL	No Observed Effect Level
NOEC	No Observed Effect Concentration
nonaBDPO	Nonabromodiphenyloxide
NTP	National Toxicology Program (USA)
O	Oxidizing (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
OECD	Organisation for Economic Cooperation and Development
OEL	Occupational Exposure Limit
OJ	Official Journal

OSPAR	Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic
P	Persistent
PBT	Persistent, Bioaccumulative and Toxic
PBPK	Physiologically Based PharmacoKinetic modelling
PBTK	Physiologically Based ToxicoKinetic modelling
PCBs	Polychlorinated biphenyls
PeBDPO	Pentabromodiphenyloxide
PEC	Predicted Environmental Concentration
pH	logarithm (to the base 10) (of the hydrogen ion concentration $\{H^+\}$
PHAHs	Polyhalogenated aromatic hydrocarbons
pKa	logarithm (to the base 10) of the acid dissociation constant
pKb	logarithm (to the base 10) of the base dissociation constant
PNEC	Predicted No Effect Concentration
POP	Persistent Organic Pollutant
PPE	Personal Protective Equipment
QSAR	(Quantitative) Structure-Activity Relationship
R phrases	Risk phrases according to Annex III of Directive 67/548/EEC
RAR	Risk Assessment Report
RC	Risk Characterisation
RfC	Reference Concentration
RfD	Reference Dose
RNA	RiboNucleic Acid
RPE	Respiratory Protective Equipment
RWC	Reasonable Worst Case
S phrases	Safety phrases according to Annex III of Directive 67/548/EEC
SAR	Structure-Activity Relationships
SBR	Standardised birth ratio
SCE	Sister Chromatic Exchange
SDS	Safety Data Sheet
SETAC	Society of Environmental Toxicology And Chemistry
SNIF	Summary Notification Interchange Format (new substances)
SSD	Species Sensitivity Distribution
STP	Sewage Treatment Plant
T_3	Tri-iodothyronine
T_4	Thyroxine
T(+)	(Very) Toxic (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)

TBG	Thyroxine-Binding Globulin
TDI	Tolerable Daily Intake
TeBDPO	Tetrabromodiphenyloxide
TG	Test Guideline
TGD	Technical Guidance Document [1]
TNsG	Technical Notes for Guidance (for Biocides)
TNO	The Netherlands Organisation for Applied Scientific Research
Transthyretin (TTR)	Thyroxine-binding prealbumin
TriBDPO	Tribromodiphenyloxide
UC	Use Category
UDPGT	Uridine diphosphate glucuronysyltransferase
UDS	Unscheduled DNA Synthesis
UN	United Nations
UNEP	United Nations Environment Programme
US EPA	Environmental Protection Agency, USA
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products of Biological material
vB	very Bioaccumulative
vP	very Persistent
vPvB	very Persistent and very Bioaccumulative
v/v	volume per volume ratio
w/w	weight per weight ratio
WHO	World Health Organization
WWTP	Waste Water Treatment Plant
Xn	Harmful (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
Xi	Irritant (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)

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	-	Monobromodibenzo-*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°C for 60 seconds, of which 3-5 seconds were within 20°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°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°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°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°C, 800°C 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 concentrations. The results of the experiment are shown in **Table A1**. The results at 800°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 **Table A1**, 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 amount 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$_3$BDF	243621	177124	131149	54744	71009	87808	199400	150000	120500	nd	nd	nd
T$_3$BDD	95825	54880	19967	28202	23557	14258	92300	42300	25700	nd	nd	nd
T$_4$BDF	211709	181624	98575	95131	109402	105013	330400	213600	176900	26	93	nd
T$_4$BDD	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$_7$BDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	482	1304	4357
H$_7$BDD	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

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°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°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

Dumler et al. (1989b and 1989c) studied the decomposition of decabromodiphenyl ether at temperatures between 300 and 800°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°C. The results of the experiments are shown in **Table A3**.

Table A3 Results of Dumler 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

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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 $100 \text{ cm}^3/\text{min}$, 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 $400 \text{ cm}^3/\text{min}$, only a small amount of decomposition of the decabromodiphenyl ether was seen. At higher temperatures ($800\text{-}1,000^{o}C$), 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 ($75\text{-}300^{o}C$). 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 $650^{o}C$	Air atmosphere $625^{o}C$
DBBF	0.03%	ND
DBDD	ND	0.04%
T$_3$BDF	0.03%	0.03%
T$_3$BDD	ND	0.04%
T$_4$BDF	0.03%	0.03%
T$_4$BDD	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 $100^{o}C$ 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$_4$BDD	5,300 mg/kg	41,000 mg/kg	4,100 mg/kg	110 mg/kg
T$_4$BDF	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$_6$BDD	-	1,000 mg/kg	23,000 mg/kg	380 mg/kg
H$_6$BDF	-	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 a 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°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 Dumler 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°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
T₃BDF	58	145	14	0.41	0.85	20.2	397	102	nd
T₃BDD				0.034	0.11	5.0	5	48	nd
T₄BDF	151	52	51	0.88	0.71	4.9	305	1547	nd
T₄BDD				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									
H₇BDF	3	8	nd						
H₇BDD									
OBDF									
OBDD									

nd = not detected

Dumler et al. (1989b; 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 Dumler 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 Dumler 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 Dumler 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$_3$BDF	-	15,033	15,952	1,738	36	15
T$_4$BDF	-	17,836	17,463	901	9	12
PBDF	-	9,127	3,349	391		-
H$_6$BDF	464	2,457	901	82	-	-
H$_7$BDF	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$_2$O$_3$	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)				
	400ºC	500ºC	600ºC	700ºC	800ºC
MBDF	100	300	100	50	nd
DBDF	500	400	200	10	nd
T₃BDF	3000	2000	400	nd	nd
T₄BDF	4000	3000	600	nd	nd
PBDF	4000	1000	200	nd	nd
H₆BDF	1000	200	nd	nd	nd
H₇BDF	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 400ºC 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$_2$O$_3$ (Luijk et al., 1991)

Atmosphere	Temp.	Concentration of PBDF (mg/kg polymer)						
	(^{o}C)	DBDF	T$_3$BDF	T$_4$BDF	PBDF	H$_6$BDF	H$_7$BDF	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°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 manufacture

Most of the information reported in this 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.

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).

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.

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

Note: 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.

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$_4$BDF=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$_4$BDF=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$_4$BDF=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$_4$BDF=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$_4$BDF=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$_4$BDF=1.02-2.59 Total PeBDF=68.2-82.8 Total HxBDF=272-708 Total HpBDF=72.5-108
PTBT with 5.2% decabromodiphenyl ether and antimony trioxide	Normal moulding conditions: 250°C	Total T$_4$BDF=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
PTBT with 7.0% decabromodiphenyl ether and antimony trioxide	Normal conditions: 250°C	Total T$_4$BDF=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$_4$BDF=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

Table A17 continued overleaf

Table A17 continued Formation of brominated dibenzo-*p*-dioxins and dibenzofurans from processing of plastics containing polybrominated diphenyl ethers

Formulation	Conditions	Brominated dioxin/furan concentration (mg/kg polymer)
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$_4$BDF=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$_4$BDF=0.15-0.17 Total PeBDF=29-34 Total HxBDF=8.2-10 Total HpBDF=0.5-0.92 Total OBDF=19

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 m³ 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 m³). 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/m³)
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/m³ 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 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 loads 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°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.

A recent study by Söderström and Markland (2001) compared bromine and chlorine in their ability to form halogenated dibenzo-*p*-dioxins and furans during co-combustion of decabromodiphenyl ether or other brominated flame retardants (hexabromocyclododecane and tetrabromobisphenol-A) as a source of bromine with municipal solid waste. The results showed that, using either a bromine source or chlorine source alone, more brominated dibenzofurans are formed than chlorinated ones under equal combustion conditions. The co-combustion of bromine- and chlorine-containing waste resulted in the formation of mixed chloro-bromo products. The results also indicated that under normal combustion conditions, the flame retardants were completely destroyed and that no differences could be seen between the three flame retardants studied in the formation of halogenated dibenzo-*p*-dioxins and furans. The report concluded that it is likely to be unfavourable to co-combust (batchwise) large amounts of bromine with municipal solid waste due to the increased formation of halogenated dibenzo-*p*-dioxins and furans.

Tange et al. (2001) reported the results of studies to investigate the effect on different bromine loads in the formation of halogenated dibenzo-*p*-dioxins and furans using a small-scale model grate combustion furnace. The materials tested included printed wiring board mixtures, TV backplates and other mixed electronic waste typically found at dismantlers. The actual brominated flame retardants present were not given. In the experiments the amount of electrical and electronic equipment in the waste feed was artificially increased to 20-25% of the total feed, resulting in increased bromine levels in the feed of up to 2,750 mg/kg compared with the typical levels in waste of around 30-100 mg/kg. The formation of bromine-containing dibenzo-*p*-dioxins and especially furans was found to increase with increasing bromine input into the reactor feed, but appeared to reach a constant level at bromine loads of ~500-1,000 mg/kg. The major products found contained 1 bromine atom/molecule and it was shown that the total load of

halogenated dioxins remained almost constant during the experiments despite the increased load of bromine-containing material. Overall it was concluded that the formation of halogenated dibenzo-*p*-dioxins and furans was dependent on the products of incomplete combustion and if the burnout of the reactor is optimised, the amounts of halogen present in the fuel had no significant influence on the amounts of halogenated dibenzo-*p*-dioxins or furans formed.

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 most 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°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 with 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

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 175-210ºC and injection moulded at 199-227ºC	Deca alone (composite sample from three suppliers)	HIPS containing 12% deca and Sb₂O₃, extruded at 175-210ºC and injection moulded at 199-227ºC	HIPS containing 12% deca and Sb₂O₃, extruded at 175-210ºC and injection moulded at 199-227ºC, 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), although industry (personal communication) have indicated that decabromodiphenyl ether is not used for this application, 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).

Impurities present in polybrominated diphenyl ethers

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 Appendix D.

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 US EPA. 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 have 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 Appendix D. 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 are 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 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

Part A - 1994 data

Part B - 1999 data

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 polymers
USE Pattern 1 [private use]   release over service life of polymers
USE Pattern 1 [recovery]   "waste remaining in the environment" from polymers

The disperse release of octabromodiphenyl ether from polymers in use are included in the regional and continental release figures.

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

Appendix C   SAMS soil model for octabromodiphenyl ether

The SAMS soil model was run to give an indication of the likely leaching behaviour of octabromodiphenyl ether in soil. The model was run over 730 days at one day intervals. The initial concentration of octabromodiphenyl ether was taken to be a nominal value of 1 kg/m^3 in the soil.

The input data and the predicted concentrations in soil at various depths after 730 days are shown below.

```
CAS    = 32536-52-0
# CAS registry number (CAS: Chemical Abstract Services)
Name   = Octabromodiphenyl ether
# Substance name
SumFor = C12H2Br8O
# Chemical sum formula
MolW   =       801.4 # [g/mol] Molecular mass
SolW   =      5e-007 # [g/l] Solubility in water
VP     =   6.59e-006 # [Pascal] Vapor pressure at 20 centigrades
MP     =         343 # [Kelvin] Melting point
BP     =         505 # [Kelvin] Boiling point at 100000 Pascal
Koc    = 1.363e+006 # [cm3 H2O/g] Partition coefficient organic carbon -
water
logKow =        6.29
# Logarithm of the n-octanol - water - partition coefficient
BCF    =           4 # 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	m^3/m^3	m	kg/m^3	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	VolW	Temp	WFlux	pH	KD
kg/kg	m^3/m^3 soil	K	mm/d		cm^3 H2O/g
0.02586	0.3	293	0.3	6.8	20450
0.0862	0.3	293	0.3	6.8	68150
0.0862	0.3	293	0.3	6.8	68150

RDeg
1/d
0
0
0

```
SOIL_ConcTop =      0.9618 # [kg/m3] Concentration in top layer
# This value has been estimated
SOIL_ConcBot =  2.86e-241 # [kg/m3] Concentration in bottom layer
# This value has been estimated
SOIL_SumSorb =      556.5 # [kg/m2] Total of substance sorbed to soil matrix
# This value has been estimated
SOIL_SumSolv =    0.02722 # [kg/m2] Total of substance solved in soil water
# This value has been estimated
SOIL_SumAir =   0.000118 # [kg/m2] Total of substance in soil air
# This value has been estimated
SOIL_SumTot =   0.009781 # [kg/m2] Total of substance remaining in soil
# This value has been estimated
```

	Flow	Balance
	$kg/m^2/d$	kg/m^2
Input	0	0.01
Runoff	0	0
Volatilisation	2.917e-007	0.000219
Degradation	0	0
Leaching	9.896e-250	1.215e-248
Remaining	-2.917e-007	0.009781

Depth	Conc	ConcA	ConcW	ConcS
m	kg/m3	kg/m3 air	kg/m3 H2O	kg/kg soil
0.01	0.9618	1.558e-007	3.594e-005	0.0005615
0.02	0.01612	2.611e-009	6.022e-007	9.407e-006
0.03	0.0001347	2.183e-011	5.034e-009	7.864e-008
0.04	7.504e-007	1.216e-013	2.804e-011	4.381e-010
0.05	3.134e-009	5.078e-016	1.171e-013	1.83e-012
0.06	1.047e-011	1.697e-018	3.913e-016	6.113e-015
0.07	2.915e-014	4.724e-021	1.089e-018	1.702e-017
0.08	6.957e-017	1.127e-023	2.6e-021	4.061e-020
0.09	1.452e-019	2.353e-026	5.428e-024	8.479e-023
0.1	2.696e-022	4.368e-029	1.007e-026	1.574e-025
0.11	4.502e-025	7.295e-032	1.682e-029	2.628e-028
0.12	6.836e-028	1.108e-034	2.555e-032	3.991e-031
0.13	9.515e-031	1.542e-037	3.556e-035	5.554e-034
0.14	1.223e-033	1.981e-040	4.568e-038	7.136e-037
0.15	1.458e-036	2.363e-043	5.45e-041	8.514e-040
0.16	1.624e-039	2.631e-046	6.069e-044	9.48e-043
0.17	1.695e-042	2.747e-049	6.335e-047	9.896e-046
0.18	1.665e-045	2.699e-052	6.224e-050	9.722e-049

```
0.19 1.545e-048 2.504e-055 5.775e-053 9.021e-052
 0.2 9.064e-052 1.469e-058 3.387e-056 5.291e-055
0.22 1.942e-055 9.719e-063 2.241e-060 1.202e-058
0.24 1.224e-059 6.124e-067 1.412e-064 7.573e-063
0.26  7.36e-064 3.684e-071 8.496e-069 4.555e-067
0.28 4.234e-068 2.119e-075 4.887e-073  2.62e-071
 0.3 2.334e-072 1.168e-079 2.694e-077 1.444e-075
0.32 1.235e-076 6.181e-084 1.426e-081 7.643e-080
0.34 6.283e-081 3.145e-088 7.253e-086 3.889e-084
0.36 3.078e-085 1.541e-092 3.553e-090 1.905e-088
0.38 1.454e-089 7.277e-097 1.678e-094 8.999e-093
 0.4 6.631e-094 3.319e-101 7.654e-099 4.104e-097
0.42 2.923e-098 1.463e-105 3.374e-103 1.809e-101
0.44 1.247e-102 6.242e-110 1.439e-107 7.718e-106
0.46 5.153e-107 2.579e-114 5.949e-112 3.189e-110
0.48 2.065e-111 1.034e-118 2.384e-116 1.278e-114
 0.5 8.032e-116  4.02e-123 9.271e-121 4.971e-119
0.52 3.034e-120 1.519e-127 3.503e-125 1.878e-123
0.54 1.114e-124 5.578e-132 1.287e-129 6.898e-128
0.56 3.983e-129 1.993e-136 4.597e-134 2.465e-132
0.58 1.386e-133 6.936e-141    1.6e-138 8.577e-137
 0.6 3.132e-138 1.568e-145 3.616e-143 1.939e-141
0.64 2.713e-143 1.358e-150 3.132e-148 1.679e-146
0.68 2.293e-148 1.148e-155 2.647e-153 1.419e-151
0.72 1.892e-153 9.468e-161 2.184e-158 1.171e-156
0.76 1.524e-158 7.629e-166 1.759e-163 9.434e-162
 0.8   1.2e-163 6.008e-171 1.386e-168 7.428e-167
0.84 9.241e-169 4.625e-176 1.067e-173 5.719e-172
0.88  6.96e-174 3.484e-181 8.035e-179 4.308e-177
0.92 5.131e-179 2.568e-186 5.923e-184 3.176e-182
0.96 3.703e-184 1.854e-191 4.275e-189 2.292e-187
   1 2.618e-189 1.311e-196 3.023e-194 1.621e-192
1.04 1.814e-194 9.081e-202 2.094e-199 1.123e-197
1.08 1.232e-199 6.169e-207 1.423e-204 7.628e-203
1.12 8.211e-205  4.11e-212 9.479e-210 5.082e-208
1.16 5.367e-210 2.687e-217 6.196e-215 3.322e-213
 1.2 3.443e-215 1.724e-222 3.975e-220 2.131e-218
1.24 2.169e-220 1.086e-227 2.504e-225 1.342e-223
1.28 1.342e-225 6.716e-233 1.549e-230 8.304e-229
1.32 8.155e-231 4.082e-238 9.414e-236 5.047e-234
1.36 4.871e-236 2.438e-243 5.623e-241 3.015e-239
 1.4  2.86e-241 1.431e-248 3.301e-246  1.77e-244
```

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Appendix D   Risk assessment associated with polybrominated dibenzodioxins (PBDDs) and -furans (PBDFs) during industrial use of OBDPO and DBDPO flame retardants

Exposure assessment of workers to PBDDs and PBDFs in the manufacture or use of polybrominated flame retardants

Since 1986, polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) are known to be formed from pure polybrominated diphenyl oxides by thermal reaction involving a free radical mechanism :

(1)

(2)
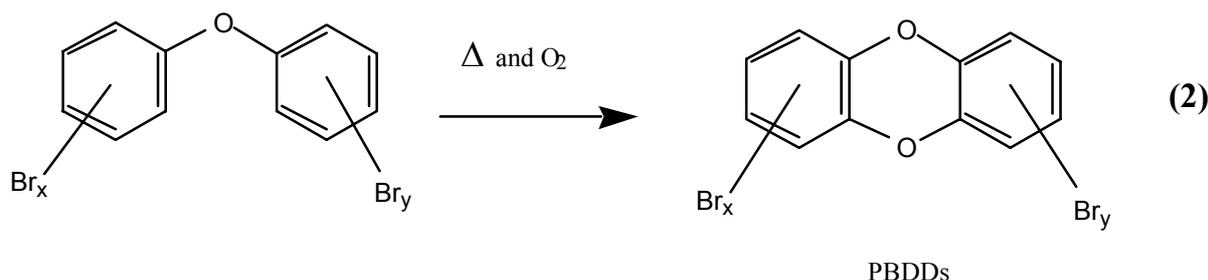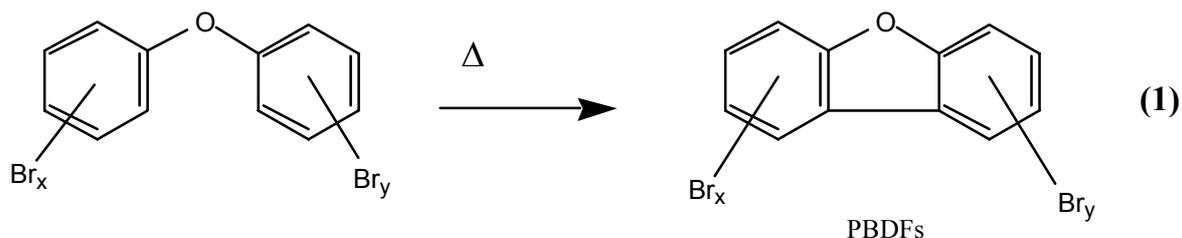
Reaction (1) occurs in pure thermic conditions and reaction (2) in oxidative ones. Toxicity of PBDFs and PBDDs being of several orders greater than that of brominated flame retardants themselves, the risk for industry workers linked to these compounds during manufacture and use has to be considered. In particular, it must be noticed that blending of flame retardants in powder form to thermoplastic polymers is performed by extrusion at temperatures in the range 200-300°C and that decomposition fumes are often emitted by the extruder heads, resulting in a visible pollution in this type of workshops in the plastic industry.

Thermal degradation of OBDPO and DBDPO (laboratory studies)

Degradation of flame retardants alone

This part has been treated in detail in Appendix A. General conclusions are:

- The possibility of formation of PBDFs and -Ds is clearly demonstrated and confirmed (7 references) with yields of few percent (reaching for example a maximum of 5% at 700°C).
- PBDFs are formed in much higher quantities than PBDDs.
- Mostly, the major components are congeners of tetra substituted compounds and when tetra substituted compounds are present the 2,3,7,8 isomer is a minor component.
- The amount of PBDFs and -Ds formed from the pyrolysis of DBDPO is much lower than with OBDPO.

Degradation of flame retarded polymers

This part has been treated in Appendix A with detailed review of laboratory experiments (8 references) with polyethylene, polypropylene, polyvinylchloride, polyester, polybutylene terephtalate, Acrylonitrile Butadiene Styrene copolymer (A.B.S.) and polyurethane blended with OBDPO or DBDPO in proportion varying from 3 to 25% and, in some cases, in presence of the synergistic flame retardant antimony trioxide Sb_2O_3. General conclusions are:

- Yields of formation of PBDFs and -Ds are at least as important as in the experiments with flame retardants alone, when based on the amount of flame retardant initially present in the polymer. It results in a concentration of PBDFs and -Ds in the residues of pyrolysis of blended polymers at ppm level (mg/kg).
- Antimony trioxide seems to play a catalytic role in the formation of PBDFs.

Formation of PBDFs and PBDDs under industrial use

PBDFs and -Ds present as impurities in commercial flame retardants

OBDPO and DBDPO flame retardants are elaborated in the chemical industry by bromination of diphenyl oxide, during which secondary dehydrobromination could be expected, leading to cyclisation and formation of furannic or dioxannic heterocycles.

Analysis of DBDPO performed by Ranken et al. (1994) for the presence of PBDFs (or Ds) with 2,3,7,8- substitution in multiple samples of DBDPO collected at random by each of the 3 producers (Albemarle, Eurobrom and Great Lakes) led to negative results: none of the fifteen 2,3,7,8-substituted compounds were detected at or above the limits of quantitation ruled by EPA (TSCA, 1987), which are at ppb level (ng/g).

Analysis of OBDPO (which is in fact a mixture of penta-, hexa-, hepta-, octa-, nona- and deca-BDPO) given by Companies at the request of the French rapporteur for the presence of the same fifteen 2,3,7,8-substituted PBDFs (or -Ds) showed the presence of some of these compounds at or above the limits of quantitation ruled by EPA (TSCA,1987) in some samples: tetrabromo dibenzodioxin or tetra-, penta-, hexa- or heptabromo dibenzofurans were detected at amount ranging from not detected to 80 ng/g whereas some batches seemed to be free of any of these compounds. In one case the sample contained only 2,3,7,8-TBDD just above the EPA level of 0.1 ng/g.

Formation of PBDFs and -Ds during production of flame retarded polymers

Extrusion occurs in the thermosetting plastics industry first with mixing additives (e.g. flame retardants) into the polymer matrix and, at a further step, with shaping a final product. During extrusion the polymer melts under pressure, but overheating may occur, resulting in thermal degradation or specific chemical reaction for both polymer and additives. In the case of polybrominated diphenyl ethers, elimination reactions of H_2, HBr or Br_2 resulting in ring-closure reactions shown in reaction. (1) or (2) could be expected.

Analysis of polymers after hot-processing

McAllister et al. (1990) analysed 3 commercial flame retarded plastic formulations after injection moulding in 3 different conditions: a high impact polystyrene with 12% DBDPO at 215-220°, 235-240° and 267-270°C; a polybutylene terephtalate with 6.5% DBDPO at 255°C in a normal 23 second cycle or extended ones to 5 or 7 minutes and an acrylonitrile-butadiene-styrene (ABS)

copolymer with 16% OBDPO at 225°C (1 min. cycle) and 245°C (10 min. cycle). All formulations contained 4-5% of antimony trioxide as "synergist". Detailed results are given in Appendix A (**Table A16**). Conclusions are:

- Normal conditions (simulating usual industrial conditions in laboratory) resulted in no increase of the PBDFs/Ds content.
- Forced conditions produced higher concentrations of PBDFs/Ds, but these concentrations were lower than values reported from laboratory pyrolysis studies: between ppm (mg/kg of polymer) and ppb (μg/kg) level.
- Like in pyrolysis studies, less brominated diphenyl ether (OBDPO) gives rise to a higher yield of PBDFs/Ds than saturated DBDPO.

Bonilla et al. (1990), performing the same type of experiment with ABS resins blended with brominated flame retardants of four different chemical families and antimony trioxide, observed that PBDFs level in the case of OBDPO exceeded by orders of magnitude levels found in any other flame retardant system (2,3,7,8-substituted PBDFs were detected after extrusion at level just above their quantitation limits).

Donnelly et al. (1989) reported a set of experiments on various formulations very similar to those of McAllister et al. (1990), and confirmed a ppb level of PBDFs in all samples after extrusion.

Luijk et al. (1991; 1992a; 1992b) made a proposal for the mechanism of formation of PBDFs/Ds in a polymer matrix with OBDPO or DBDPO and tried to explain the relative high yield of these compounds during degradation of polymers at relatively low temperatures (<300°C) compared to the optimal temperature of formation about 600°C in pyrolysis of pure polybrominated diphenyl ethers. They put forwards the idea that the formation of PBDFs is initiated by radical degradation of the polymer matrix and that, as a consequence, this formation seems inevitable either during industrial compounding of flame retardant into the polymer matrix or during shaping of final OBDPO or DBDPO flame-retarded products.

All these studies show that PBDFs and PBDDs can be generated but they don't give any evidence that workers could be significantly exposed.

Atmospheric monitoring in workshops

Only a limited number of occupational exposure data are available.

Brenner and Knies (1990; 1993) performed static atmospheric measurements during extrusion production around 250-300°C of a polybutylene terephtalate resin blended with $DBDPO/Sb_2O_3$ at the head of the extruder, at workplace area (the most probable stay of the operator) and in the atmosphere of the building. Complementary analyses of resins before and after processing showed that the major part (98.5%) of the PBDFs/Ds formed stays in the polymer matrix (resulting in weight concentrations in the polymer between 1 ppb and 0.5 ppm, as described above in other publications). A local concentration of 73 $\mu g/m^3$ (Σ PBDFs) at the head of the extruder and the following detectable concentrations at the workplace area (samples taken from a fixed location) were:

- PBDFs (di, tri, tetra, penta, hexa and hepta): about 1 $\mu g/m^3$ among which 34 ng/m^3 of Σ tetra-BDFs.
- Σ PBDDs (tetra, penta and hexa): 30 ng/m^3 among which 2 ng/m^3 of Σ tetra-BDDs and <0.5 ng/m^3 of 2,3,7,8-tetra-BDD.

The BASF Company (Germany), who performed these pilot plant tests, declared to have stopped this production and the use of polybrominated diphenyl ethers in general after examination of these data with the German Governmental Authorities (1989).

In the United States, the "Brominated Flame Retardant Industry Panel" (BFRIP), a subgroup of the Chemical Manufacturers Association, compiled several corporate non-published reports on this issue. A document of 1990, reviewed in the 1994 IPCS (International Programme on Chemical Safety) "Environmental Health Criteria" for brominated diphenyl ethers (IPCS, 1994), describes atmospheric monitoring performed in 1988 at the Bishop (Texas) facility of Hoechst-Celanese: three personal air sampling were performed during extrusion of a formulation containing polybutylene terephtalate polymer blended with DBDPO/Sb_2O_3, with the following results (from IPCS (1994), Table 20 p. 97):

	Worker 1	Worker 2	Worker 3
Σ PBDFs (tetra, penta, hexa)	13 ng/m^3	69 ng/m^3	117 ng/m^3
Σ PBDDs (penta and hexa)	0	0.003 ng/m^3	0

Biological monitoring of exposed workers

Zober et al. (1992) described blood monitoring of 42 production workers employed at BASF in extrusion-blending of polybutylene terephtalate with OBDPO and DBDPO for many years to determine internal exposure and immunological findings. Concentrations in the lipid content of the blood ranged from non-detectable to 112 ppt (pg/g) and from non-detectable to 478 ppt respectively for 2,3,7,8-Tetra BDF and 2,3,7,8-Tetra BDD, giving a statistical evidence of internal exposure when compared with referents employed at a similar job without PBDOs use. Individual concentrations were also significantly correlated with durations of exposure.

The finding of a higher burden in TBDD than in TBDF (since air monitoring revealed a much lower presence of dioxins than of furans) is at first surprising. One explanation might be given by toxicokinetic estimation of a mean biological half-time of 5.9 years for 2,3,7,8-TBDD and of only 1.5 years for 2,3,7,8-TBDF.

Conclusions on exposure assessment for workers

Very few workers of the chemical industry can be assumed to be exposed directly to OBDPO and/or DBDPO in a powder form during dry handling (bagging or weighing) of pure compounds in the three plants existing in Europe.

A more important number of workers, but only in small specialized companies (compounders) or in specialized workshops of big companies, are concerned with "extrusion-blending" where pellets of flame-retarded thermosetting polymers are produced.

The most important number of workers potentially exposed to PBDFs/Ds are in of the plastic industry where flame retarded polymeric final products are manufactured by shaping them using extrusion and injection-moulding.

In these three situations, it is clear that presence or emission of compounds of the PBDFs/Ds family may occur in only trace amounts. Moreover the chemical analyses able to identify the most potent toxics of this family (tetra-substituted congeners and isomers with 2,3,7,8-substitution) are often tentative trace analyses among a lot of chromatographic or mass spectrometric signals, with interference and calibration problems. Therefore, evaluation of quantitative data could lead to a number of discussions.

Hazard assessment of brominated dibenzofurans and -dioxins

The toxicity of the compounds of the halogenated dioxins and related chemicals family is not discussed in this Appendix, as there is a plethora of studies and reviews in the scientific literature. We will only consider any existing guide figures, established by experts of national or international bodies, which provide index currently used to measure the toxic potential of dioxins and furans.

In this assessment we will use the International Toxicity Equivalency Factors (I-TEF) elaborated by the NATO "Committee on the challenges of modern society" (1988), which provides the possibility of an overall toxicological risk assessment for complex mixtures of chlorinated dioxins and related compounds, in reference to 2,3,7,8-tetrachlorodibenzodioxin (TCDD), the dioxin involved in the Seveso accident in 1976, which is the most investigated compound of the family. These are shown in **Table D1**.

Table D1 International Toxicity Equivalency Factors (I-TEF)

I-TEF according NATO-CCMS (15)		
	PCDD/PCDF	**I-TEF**
Dioxins	2,3,7,8-TetraCDD (« SEVESO DIOXIN »)	1.0
	1,2,3,7,8-PentaCDD	0.5
	1,2,3,4,7,8-HexaCDD	0.1
	1,2,3,6,7,8-HexaCDD	0.1
	1,2,3,7,8,9-HexaCDD	0.1
	1,2,3,4,6,7,8-HeptaCDD	0.01
	OctaCDD	0.001
	Others Substitutions (than 2,3,7,8-)	0.000
Furans	2,3,7,8-TetraCDF	0.1
	1,2,3,7,8-PentaCDF	0.05
	2,3,4,7,8-PentaCDF	0.5
	1,2,3,4,7,8-HexaCDF	0.1
	1,2,3,6,7,8-HexaCDF	0.1
	1,2,3,7,8,9-HexaCDF	0.1
	2,3,4,6,7,8-HexaCDF	0.1
	1,2,3,4,6,7,8-HeptaCDF	0.01
	1,2,3,4,7,8,9-heptaCDF	0.01
	OctaCDF	0.001
	Others Substitutions (than 2,3,7,8-)	0.000

Long-term administration of TCDD causes liver tumours in rodents. The question whether this chemical increases the cancer risk in humans is a matter of debate. TCDD is considered a non-genotoxic carcinogen since it does not form DNA adducts and gives negative results in "in vitro" tests for genetic toxicity. However, TCDD is a very potent tumour-promoting agent, even if it is a weak - or non-initiator.

Although the mechanism of toxicity is not completely understood, it is believed that the effects of TCDD are mediated by the binding to a cellular protein, the Ah receptor, which is at the origin of the overall toxicity (Sewall and Lucier, 1995). The US-Environmental Protection Agency (EPA), in the 1994 review-draft of the dioxin scientific reassessment (EPA, 1994), tries to elaborate for this kind of receptor-mediated substances an appropriate model leading to an acceptable exposure level. Depending on the various approaches, allowable intake established by US regulatory agencies ranges from 0.005 to 10 pg/kg/day (0.01 pg/kg/day in the EPA Draft).

An overall equivalency of toxicity will be assumed for brominated dibenzofurans and dibenzodioxins as for chlorinated homologous compounds.

It was first suggested by Safe (1990), who reviewed comparative toxic potencies of halogenated compounds of the family, that the I-TEFs established for the PCDDs and PCDFs can be similarly used for the bromo and bromo-chloro analogues. Several literature reviews (Minnear and Lee, 1994; Weber and Greim, 1997) concluded in this way, considering similar, if not identical, biological effects and equipotency on a molar concentration basis in binding on receptors expected to mediate the toxicity.

The teratogenic potency of brominated homologous has been demonstrated to be equivalent to that of chlorinated dibenzo-p-dioxins and dibenzofurans in mice (Birnbaum et al., 1991). However the acnegenic activity was reported to be at one or two orders of magnitude less potent for TBDFs and TCDDs than for chlorinated ones, in a rabbit ear dermal comedogenicity (Pinkerton et al., 1989).

For carcinogenic properties not well known for each particular chemical species, this assimilation of brominated to chlorinated analogues provides a suitable safety factor for risk assessment.

We will also use the value of 10 pg TEQ[4]/kg/day established by the World Health Organisation(WHO,1990) as acceptable lifetime daily intake of polychlorinated dioxins and furans for the human organism. This value has been retained as a means of managing the public health risk of dioxins and furans by the French Académie des Sciences in a recent assessment report (1994), in spite of the imperfections of TEQ mentioned by this body.

In Germany a proximate value of 7 pg/kg/day is the ground of an occupational threshold limit value (TRK[5] value) of 50 pg/m³ on the basis of 10 m³ inhalated air during an 8-hour workshift and a mean bodyweight of 70 kg for adult males ([7 x 70] /10 = 49). This occupational exposure limit is proposed by the Federal Department of Labour [22] on workplaces where halogenated wastes could be incinerated in municipal or industrial waste incinerators, during recycling of metals (for instance when electrical wires insulation is burned) and where electric capacitors are emptied. It is specified that the atmospheric concentrations to be compared to this 50 pg/m³ value have to be calculated as "dioxin equivalent" according to the International Toxicology Equivalent Factors (I-TEF) on the basis of additive effects of the congeners.

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[4] TEQ = Toxicity Equivalent vs. 2,3,7,8 TCDD
[5] TRK = Technische Risk Konzentrationen (indicative technical concentrations)

Risk assessment associated with polybrominated dioxins and - furans during industrial use of OBDPO and DBDPO

Precise exposure data are in limited number in this dossier, and correspond in some cases to extreme or abusive exposure situations (temperatures higher than usual during extrusion pilot testing). Nevertheless they will be taken into account, even if they are not representative of all situations, because they provide a suitable safety factor for ordinary situations.

Exposure during manufacture in chemical industry

PBDFs and PBDDs, like brominated flame retardants themselves, have a very low vapour pressure and exposure may occur only by dust inhalation or skin contact.

Particle size of commercial DBDPO in powder are below 5 μm, i.e. inhalable, but all current commercial batches are assumed not to be contaminated by PBDFs/Ds. It follows that there is no exposure to PBDFs or PBDDs during handling of pure DBDPO.

Particles of commercial OBDPO in powder are of higher size, but 45% of the particles are minor than 10 μm and it is assumed that the substance is able to generate inhalable dust. Air samplings have been carried out during intermittent tasks of bagging and check-weighing in a facility in the UK (HSE, 1995), resulting in dust concentrations ranging from 2 to 7 mg/m^3.

Considering on the one hand the worst-case scenario exposure of 5 mg/m^3 during manufacture (derived from these results and the EASE prediction) and on the other hand the available detailed analysis of the PBDFs and Ds content of an OBDPO sample given by EPA (Remmers and al., 1993) (with the identified compounds either just at the EPA limit of quantitation or at their individual measured maximal value) and applying the corresponding I-TEF, it is possible to estimate the range of the concentration in "2,3,7,8-Tetrachlorodibenzodioxin Toxic Equivalents" (TEQ) inhaled by a worker in such a situation. These are shown in **Table D2**.

Table D2   Estimated exposure (TEQ) during manufacturing in the chemical industry

	ng/g in OBDPO		ng/m^3 in a 5 mg/m^3 dust		I-TEF	TEQ (pg/m^3)	
	min	max	min	max		min	max
DIOXINS							
2,3,7,8 Tetra BDD	0.1	0.7	0.5.10^{-3}	3.5.10^{-3}	x 1	0.5	3.5
FURANS							
2,3,7,8 Tetra BDF	1	12.3	5.10^{-3}	61.5.10^{-3}	x 0.1	0.5	6.1
1,2,3,7,8 Penta BDF	5	6.3	25.10^{-3}	31.5.10^{-3}	x 0.05	1.25	1.6
2,3,4,7,8 " BDF	5	83.1	25.10^{-3}	415.5.10^{-3}	x 0.5	12.5	207.7
1,2,3,4,7,8 Hexa BDF	25	67.8	125.10^{-3}	339.10^{-3}	x 0.1	12.5	33.9
1,2,3,6,7,8 " BDF	25	50.6	125.10^{-3}	253.10^{-3}	x 0.1	12.5	25.3

Σ TEQ : 40 to 280 pg/m^3

Exposure during use in plastics industry

Considering the detailed static atmospheric measurements by Brenner and Knies (1990 and 1993) given earlier and applying the corresponding I-TEF, it is also possible to estimate the concentration in "2,3,7,8 Tetrachlorodibenzodioxin Equivalents" (TEQ) in the workplace area. These are shown in **Table D3**.

Table D3 Estimated exposure (TEQ) during use in the plastics industry

	ng/m^3 at the workplace	I-TEF	TEQ (ng/m^3)
DIOXINS			
2,3,7,8 Penta BDD	1.3	x 0.5	0.65
1,2,3,6,7,8 Hexa BDD	1.0	x 0.1	0.10
1,2,3,7,8,9 Hexa BDD	1.6	x 0.1	0.16
FURANS			
Penta BDF (isomer with 2,3,7,8 substitution)	1.3	x 0.05 (or x 0.5)	0.065 (or 0.65)
Hexa BDF (isomer with 2,3,7,8 substitution)	2.6	x 0.1	0.26
			Σ TEQ: 1.2 or 1.8 ng/m^3

Another similar calculation has been reported in BFRIP and IPCS documents from Hoechst-Celanese (USA) personal measurements concerning three extrusion workers. Values expressed in Σ TEQ are 0.04, 0.01 and 0.55 ng/m^3 (40, 10 and 550 pg/m^3).

An estimate of probable workplace concentration carried out by Battelle Laboratories (Columbus-USA) from experimental measurements of fume collected during extrusion of a commercial blend of polybutyleneterephtalate and DBDPO was 0.76 ng/m^3 as Σ TEQ (Vinci and Craig, 1988; Craig and al., 1989).

Parameters of biological monitoring of extrusion workers (Σ 2,3,7,8-TBDD and 2,3,7,8-TBDF ranging from 0 to 478 ppt) described by Zober et al. (1992) can be compared with the following indicative benchmark values from the TCDD literature:

- Human adipose tissue level linked to chloracne: >5000 ppt (Patterson and al., 1986).
- Adipose tissue level for workers directly exposed to TCDD in a factory's incident (estimated): 4000 ppt (Schecter and al., 1994).
- Adipose tissue level resulting from a daily occupational exposure to 200 pg/m^3 (calculated): 180 ppt (Leung and al., 1988).
- Maximum adipose tissue level of non-occupationally exposed persons in the USA: 20 ppt (Sielken, 1987).
- Mean adipose tissue level of non-occupationally exposed persons in the USA (control level): 5 ppt (Sielken, 1987).

There is an evidence of an higher internal load for these workers than for non-occupationally exposed subjects. However, according to the Zober et al. (1992) observations, exposure-related significative changes in immunological parameters (as complement C4, total lymphocyte,

T-Cell, T-helper Cell and natural killer Cell) do not appear, except for the one worker having a blood lipid TBDD concentration of 478 ppt. But no clinical signs of immune system deficiency were seen.

Conclusions on risk assessment for workers

There are several convincing data to put forward that packaging OBDPO in manufacturing plants or blending polymers with DBDPO by hot-processing results in human exposures to brominated dibenzofurans and dibenzodioxins in the chemical industry or in processing workshops. Levels of atmospheric concentrations are low, but sufficient to generate measurable body burdens in some occupationally exposed people.

Considering the high experimental toxicity of some of the congeners of the polyhalogenated dioxins or furans which justifies an additive acceptable daily intake of 10 pg/kg/day as "dioxin toxic equivalent" (TEQ) proposed by international experts as a general limit for human exposure, a national body has proposed an occupational threshold limit value of 50 pg TEQ/m^3 for chlorinated - dibenzodioxins and furans at work (German TRK, 1993). In the hypothesis of an overall equivalency of toxicity for brominated as for chlorinated compounds of this family, it appears that the 50 pg/m^3 limit can be exceeded during handling of pure flame retardants in powder form or during extrusion of some flame retarded plastics, since measurements and estimates range from 10 to 1800 pg/m^3.

These conclusions could be mitigated if industry could provide additional exposure data based on actual circumstances of use in real situations. The gaps that need filling are in particular atmospheric levels in "dioxin toxic equivalents" (TEQ) during industrial operations of "extrusion - blending" of other polymer/flame-retardant couples than polybutyleneterephtalate/DBDPO, such as:

- Acrylonitrile - Butadiene - Styrene (ABS)/OBDPO, which deals for a high proportion of the market,
- High Impact Poly Styrene (HIPS)/OBDPO or DBDPO,
- Polyurethane/DBDPO.

As a matter of fact, the value of exposure levels to halogenated (in this case brominated) dibenzofurans and - dioxins remains the major point of concern to decide if these exposures may or may not pose a human health threat, whatever the toxicity of these poorly investigated chemicals.

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Appendix E   Environmental 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	Tetra bromo	2,2',4,4'5-Penta	2,2'4,4',6-Penta	Commercial penta	Hexa	Hepta	Octa	Commercial octa	Nona	Deca	Commercial deca
Log Kow												
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	Tetra bromo	2,2',4,4'5-Penta	2,2'4,4',6-Penta	Commerc. penta	Hexa	Hepta	Octa	Commerc. octa	Nona	Deca	Commerc. deca
Henry's law constant (Pa m^3/mol)												
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 Kow 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$_{sed-water}$ (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 Kow 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	1.54×10^9	150,900; $1.50 \cdot 10^8$; $8.11 \cdot 10^9$	150,300

a) For log Kow<6: log BCF = 0.85 log Kow - 0.70; For log Kow>6: log BCF = -0.20 (log Kow)^2 + 2.74 log Kow - 4.72
b) log Koc = 0.81 log Kow + 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 Kow, 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 Kow 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 Kow 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 Kow 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 Koc 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 Kow (from the EPI programme) against measured log Kow, water solubility, vapour pressure, $Kp_{sed-water}$ (and Koc) and BCF were constructed.

Based on the plots below, the following relationships were found:

$$\log Kow_{measure,HPLC} = 0.718 \cdot \log Kow_{estimated} + 1.236 \quad [N=6, R^2=0.99]$$

$$\log (\text{water solubility } \{\mu g/l\}) = -0.611 \cdot \log Kow_{estimated} + 5.896 \quad [N=5, R^2 = 0.87]$$

$$\log (\text{vapour pressure } \{Pa\}) = -1.109 \cdot \log Kow_{estimated} + 4.225 \quad [N=5, R^2 = 0.92]$$

$$\log (Kp_{sed-water} \{l/kg\}) = 8,505 \cdot \log Kow_{estimated} - 19,709 \quad [N=4, R^2 = 0.85]$$

$$\log (Koc \{l/kg\}) = 170,108 \cdot \log Kow_{estimated} - 394,177 \quad [N=4, R^2 = 0.85]$$

For the measured bioconcentration factors, a simple linear relationship between the BCF and estimated log Kow 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 Kow is available from the EPI programme. This approach necessarily assumes that there is a (linear) relationship between the given property and the estimated log Kow 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
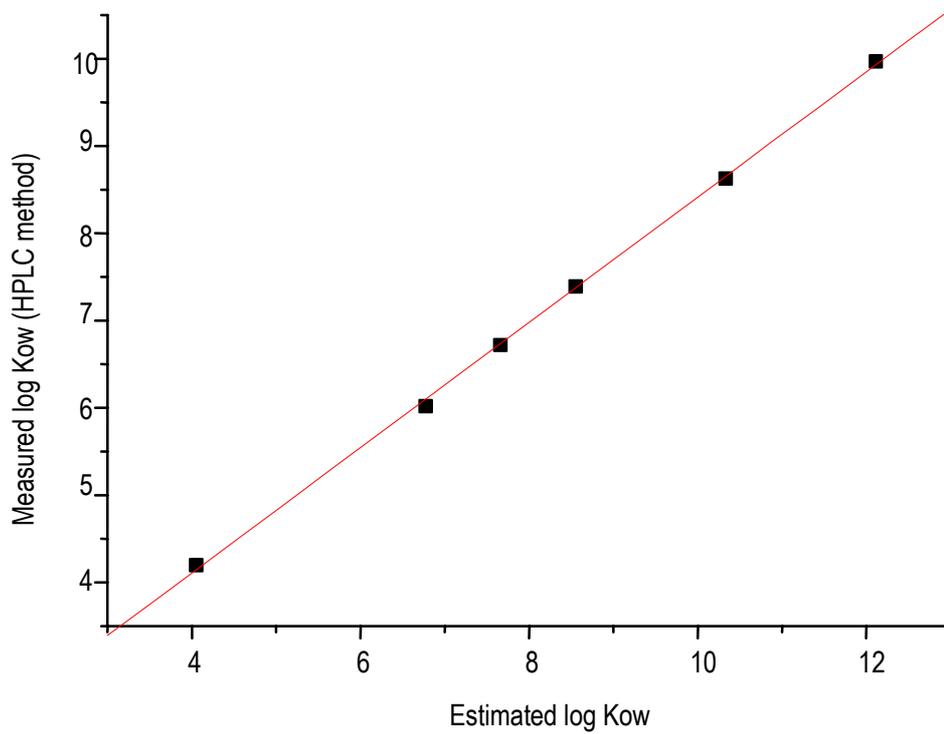
Plot 2: Relationship between log Kow and water solubility
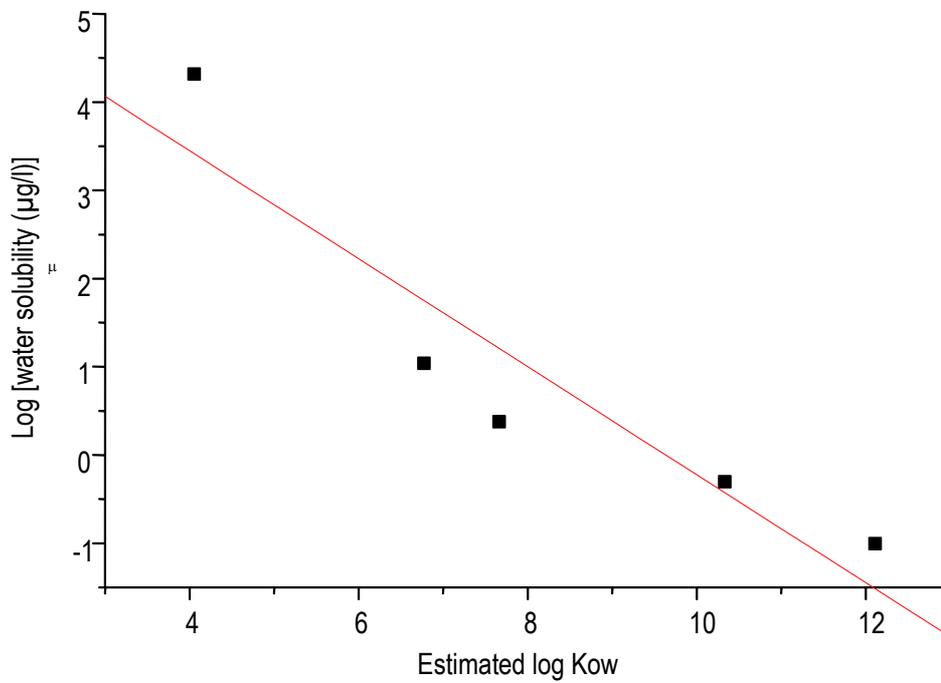
Plot 3: Relationship between estimated log Kow value and measured (GC method) vapour presure
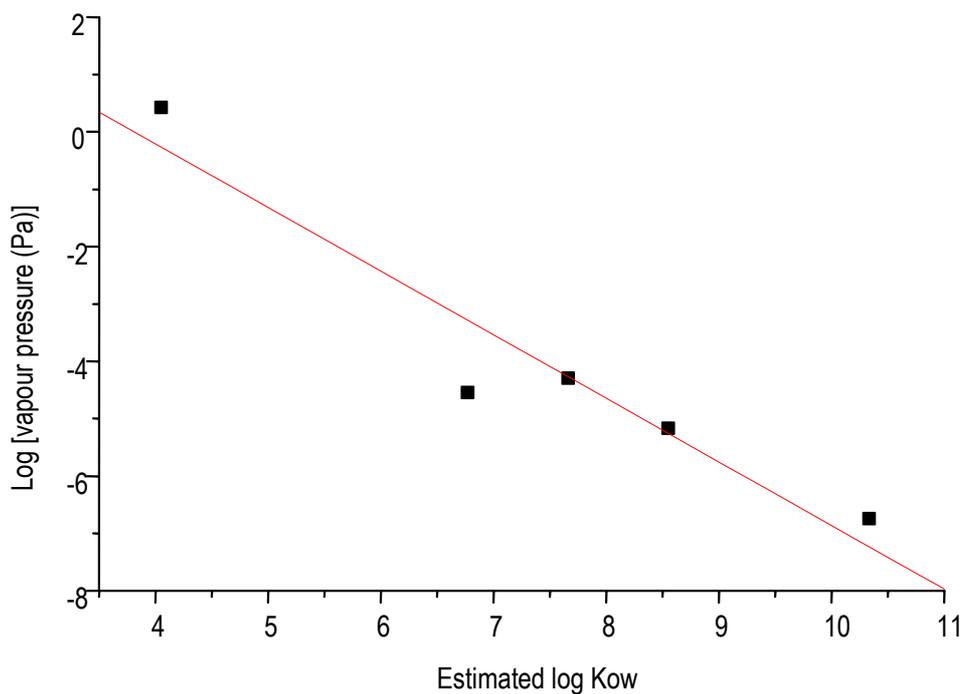
Plot 4: Relationship between bioconcentration factor and log Kow
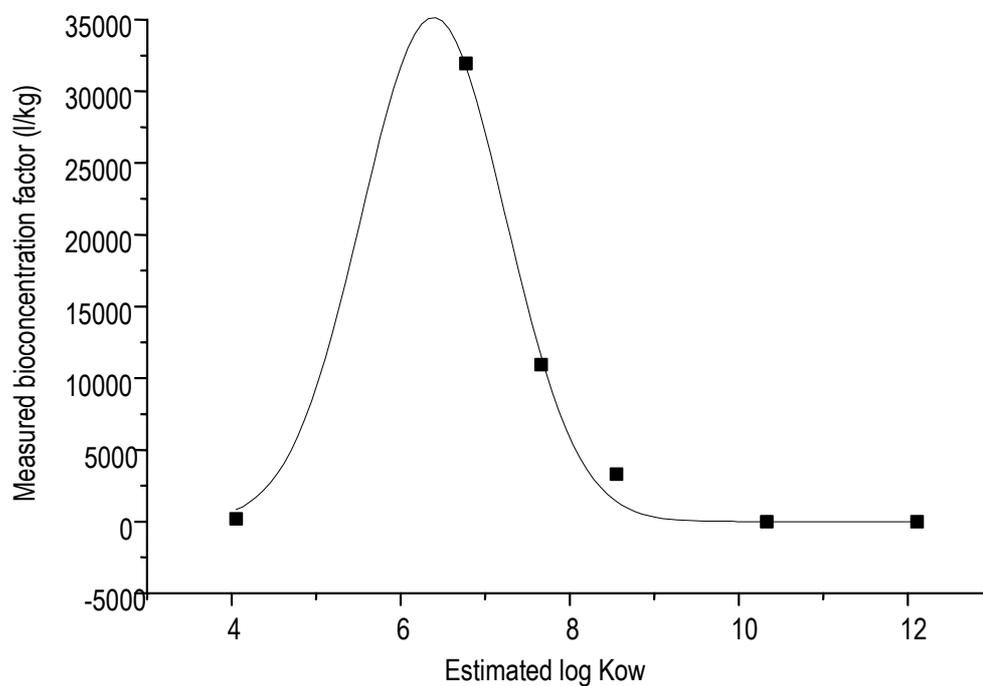
Plot 5: Relationship between estimated log Kow and measured sediment-water partition coefficient
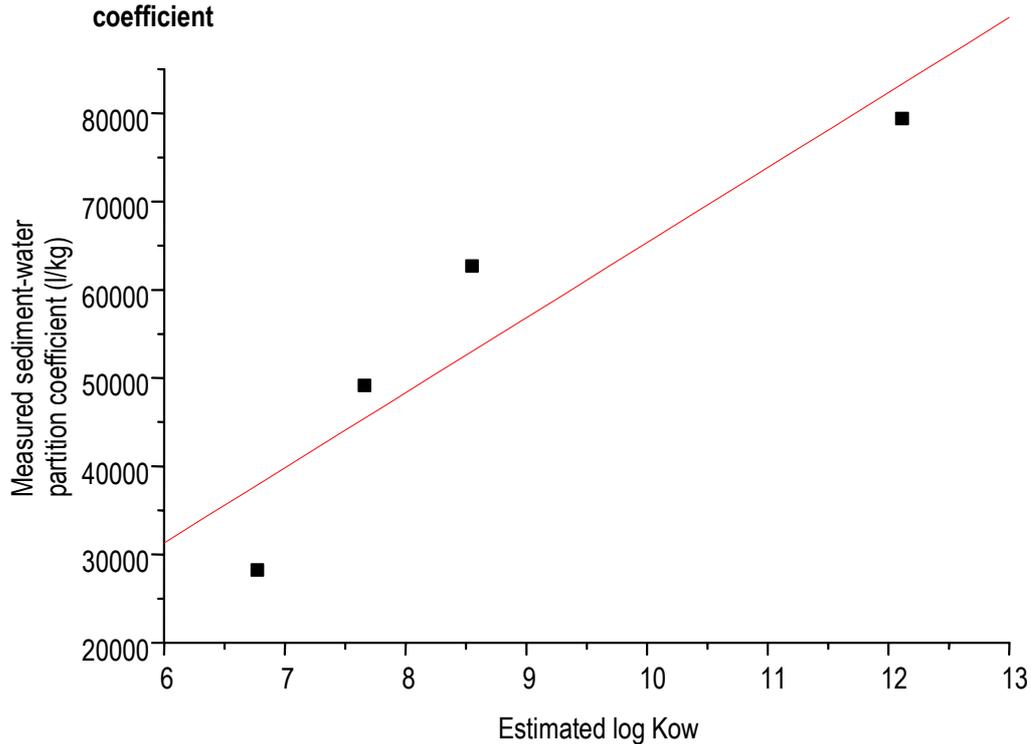
Estimated log Kow

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 Kow estimate, except where reliable measured data were 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 the following section.

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 Kow	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 G 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 E5**.

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-penta bromo diphenyl ether	Commercial product	2,2',4,4'5-penta bromo diphenyl ether	Commercial product	2,2',4,4'5-penta bromo 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-penta bromo diphenyl ether	Commercial product	2,2',4,4'6-penta bromo diphenyl ether	Commercial product	2,2',4,4'6-penta bromo 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 1.51 tonnes/year to air	54.1 kg/year to water and 638 kg/year to air	1.15 tonnes/ year to water and 13.6 tonnes/year to air	486 kg/year to water and 5.74 tonnes/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 wastewater 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.	0.048 tonnes/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 E4-11** as input data. In the model, all local releases to water were assumed to go to a wastewater treatment plant, but in the regional and continental model, a wastewater 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 by the two methods 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 to PNEC comparison 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 of 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 Koc value. The use of different Koc 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 Koc value, and so in terms of the actual risk assessment (PEC/PNEC ratio) the two modelling approaches should give similar overall results.

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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

Table E12 continued overleaf

Table E12 continued 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
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
	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

Table E12 continued overleaf

Table E12 continued 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
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

Table E12 continued overleaf

Table E12 continued 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
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

Table E13 continued overleaf

Table E13 continued 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)
Decabromo: production (generic)	Air concentration (emission episode)	n/a	n/a	n/a	n/a	$2.5 \cdot 10^{-3}$ ng/m³	4.2 ng/m³
	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/m³	52.2 ng/m³
	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 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)
Decabromo: textiles - compounding	Air concentration (emission episode)	n/a	n/a	n/a	n/a	$1 \cdot 10^{-3}$ ng/m^3	1.7 ng/m^3
	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/m^3	0.8 ng/m^3
	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/m^3	0.27 ng/m^3	0.26 ng/m^3	0.11 ng/m^3	0.015 ng/m^3	4.1 ng/m^3
	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

Notes: 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 used 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 Kow, and to a lesser extent vapour pressure, water solubility and Koc value. A similar effect would also be expected to occur in the local calculations (as was found earlier: see **Table E13**). This sensitivity to Kow 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 Kow	Koc (l/kg)	PEClocal				Regional				
				Air (mg/m^3)	Water (mg/l)	Sediment (mg/kg)	Agricultural soil (mg/kg)	Air (mg/m^3)	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	$1.8 \cdot 10^{-8}$	$2.2 \cdot 10^{-7}$	8.4×10^{-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 Kow and Henry's Law constant) is the behaviour during wastewater 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 wastewater 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 wastewater treatment as predicted using EUSES for octabromodiphenyl ether

log Kow	H (Pa m³/mol)	Koc (l/kg)	Predicted distribution during wastewater treatment		
			Air	Water	Solids
a) Fixed Koc 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) Koc estimated from Kow					
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 Kow. This is a particular problem for the congeners with very high log Kow 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   Debromination 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 are 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°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°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 have 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°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**.

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., 1991a
4-chlorobiphenyl and Aroclor 1254	alkaline 2-propanol	λ>300 nm	In presence of acetone, dechlorination to biphenyl occurred.	Hawari et al., 1991b
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$_2$O$_3$, 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$_2$O$_3$ 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 Summary of photolysis experiments for halogenated compounds

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 Summary of photolysis experiments for halogenated compounds

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	λ 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

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.

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 intermediate (radical cation intermediates species may be formed in water) 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 (as of 1999) 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, 1998 and 1999; 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; Andersson and Wartanian, 1992; Burreau et al., 1999; Strandman 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 F2**), 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). 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 (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)	Approx. total				
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	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 are	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 Levels of polybrominated diphenyl ethers in sediments

Location	Comments	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)	Approx. total				
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 IG
	Downstream	840	1,200		2,000				µg/kg IG
Lake Marsjön	Upstream from industry	<2	<1	<0.4	<3			<20	µg/kg IG
Lake Öresjö	Downstream from industry	7.4	3.5	1.2	12.1			<40	µg/kg IG
River Viskan	Downstream from town	12	12	3.5	27.5			150	µg/kg IG
River Viskan	At Moga	13	9.2	3.6	25.8			220	µg/kg IG
River Viskan	Upstream from Skene	23	43	8.9	74.9			3400	µg/kg IG
River Viskan	Downstream from Skene	50	53	19	122			12,000	µg/kg IG
River Häggån	Upstream from Fritsla	1.3	1.1	0.31	2.7			<20	µg/kg IG
River Häggån	Downstream from Fritsla	2	2.7	0.69	5.4			<20	µg/kg IG
Lake Skäresjön		<2	<2	0.63	<4.6			<30	µg/kg IG
Sediment core, Baltic Sea	0-5 mm depth	1.6	0.98	0.31	2.89				µg/kg IG
	5-10 mm depth	0.76	0.2	0.07	1.03				µg/kg IG
	10-15 mm depth	0.68	0.36	<0.04	1.04				µg/kg IG
	15-20 mm depth	0.5	0.13	<0.04	1.67				µg/kg IG
	80-90 mm depth	0.06	<0.04	<0.04	0.06				µg/kg IG
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
Forth		0.39	0.36					3.3	µg/kg dry wt
Seine		0.69	0.83					12.2	µg/kg dry wt

Table F2 continued overleaf

Table F2 continued Levels of polybrominated diphenyl ethers in sediments

Location	Comments	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])	Approx. total				
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 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)]				
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
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
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
	Southern North Sea, 1984-1991	0.3-1	<0.1					µg/kg wet wt

Table F3 continued overleaf

Table F3 continued 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)				
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
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
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
Turbot liver	Southern North Sea, 1992	7	1					µg/kg wet wt

Table F3 continued overleaf

Table F3 continued 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]				
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
	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
	Linge (Rhenoij), 1991	12	0.6					µg/kg wet wt

Table F3 continued overleaf

Table F3 continued 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)				
Yellow eel (continued)	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
	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
	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
	Zuidlaardermeer, 1992	1.5	1.3					µg/kg wet wt

Table F3 continued overleaf

Table F3 continued 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)]				
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
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
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
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

Table F3 continued overleaf

Table F3 continued 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)				
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
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

Table F3 continued overleaf

Table F3 continued 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)				
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 are only suggestive and not conclusive. A 37 week anaerobic degradation study has been undertaken by Industry to address this point (the results are in the main Risk Assessment Report for decabromodiphenyl ether).

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Appendix G 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 G1**. 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 have 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. These data indicate 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 G1 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

Composition of Polybrominated diphenyl ethers
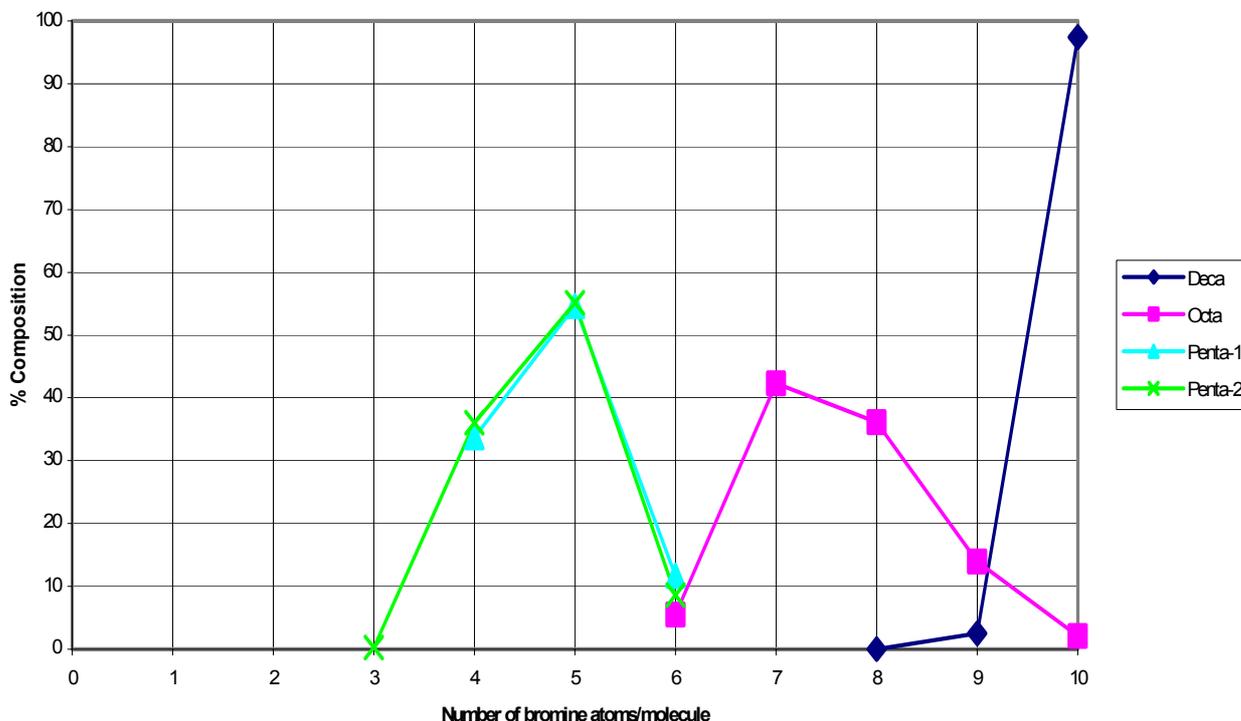
Note: Penta-1: 1997 figures   Penta-2: 2000 figures

Other information

Commercial decabromodiphenyl ether

Recently data have 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 G2**.

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 G2** 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 G2   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 G1**), 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 G1** 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). 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).

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Appendix H   Alternative nomenclature used for polybrominated diphenyl ethers

Table H1 gives identities of the common polybrominated diphenyl ether congeners using the numbering system based on the polychlorinated biphenyl system.

Table H1   Number system for polybrominated diphenyl ethers

Isomer	Congener	Identity
2	monobromodiphenyl ether	1
3	monobromodiphenyl ether	2
2,4	dibromodiphenyl ether	7
2,4'	dibromodiphenyl ether	8
2,6	dibromodiphenyl ether	10
3,4	dibromodiphenyl ether	
3,4'	dibromodiphenyl ether	13
4,4'	dibromodiphenyl ether	15
2,4,4'	tribromodiphenyl ether	28
2,4,6	tribromodiphenyl ether	30
2,4',6		32
2',3,4	tribromodiphenyl ether	33
3,3',4	tribromodiphenyl ether	35
3,4,4'	tribromodiphenyl ether	37
2,2',4,4'	tetrabromodiphenyl ether	47
2,2',4,6'		51
2,3',4,4'	tetrabromodiphenyl ether	66
2,3',4',6	tetrabromodiphenyl ether	71
2,4,4',6	tetrabromodiphenyl ether	75
3,3',4,4'	tetrabromodiphenyl ether	77
2,2',3,4,4'	pentabromodiphenyl ether	85
2,2',4,4',5	pentabromodiphenyl ether	99
2,2',4,4',6		100
2,2',4,5,5'	pentabromodiphenyl ether	101
2,3,3',4,4'	pentabromodiphenyl ether	105
2,3,4,5,6	pentabromodiphenyl ether	116
2,3',4,4',6	pentabromodiphenyl ether	119
2,2',3,4,4',5	hexabromodiphenyl ether	138
2,2',3,5,5',6	hexabromodiphenyl ether	151
2,2',4,4',5,5'	hexabromodiphenyl ether	153
2,2',4,4',5,6'	hexabromodiphenyl ether	154
2,3,4,4',5,6	hexabromodiphenyl ether	166

Table H1 continued overleaf

Table H1 continued Number system for polybrominated diphenyl ethers

Isomer	Congener	Identity
2,2',3,4,4',5',6	heptabromodiphenyl ether	183
2,3,3',4,4',5,5'	heptabromodiphenyl ether	189
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European Commission

**EUR 20403 EN - European Union Risk Assessment Report
diphenyl ether, octabromo derivative**

*Editors: S.J. Munn, R. Allanou, K. Aschberger, F. Berthault, J. de Bruijn, C. Musset,
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The report provides the comprehensive risk assessment of the substance diphenyl ether, octabromo derivative. It has been prepared by France and the UK 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, octabromo derivative concludes that there is concern for workers. There is at present no concern for consumers. For humans exposed via the environment and for infants exposed via breast milk, the risk assessment concludes that there is at present a need for further information in order to characterise the risks. The risk assessment for the environment concludes that there is concern for top predators via accumulation up the food chain (secondary poisoning) for at least one emission scenario. There is at present no concern for the atmosphere, aquatic ecosystem, terrestrial ecosystem or for microorganisms in the sewage treatment plant.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commission's Committee on risk reduction strategies set up in support of Council Regulation (EEC) 793/93.

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