European Chemicals Bureau

Institute for Health and Consumer Protection

European Chemicals Bureau

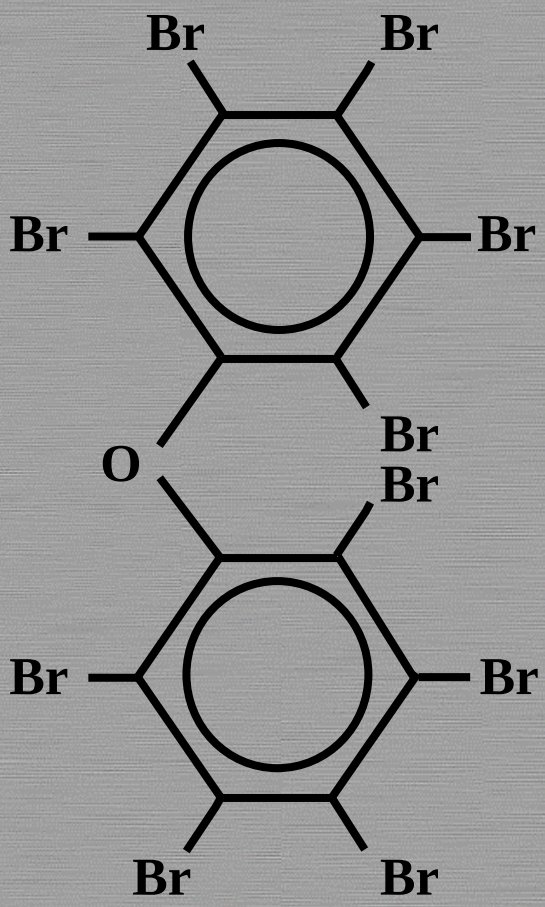
Existing Substances

European Union Risk Assessment Report

CAS No: 1163-19-5

EINECS No: 214-604-9

bis(pentabromophenyl) ether



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RISK ASSESSMENT

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RISK ASSESSMENT

Final Report, 2002

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

Foreword

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

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

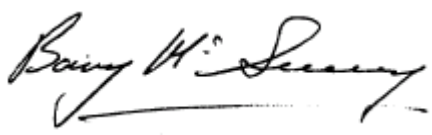
There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each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

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

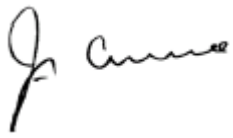
If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the "Rapporteur" to develop a proposal for a strategy to limit those risks.

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

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



Barry Mc Sweeney
Director-General
Joint Research Centre



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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: 1163-19-5
EINECS Number: 214-604-9
IUPAC Name Bis(pentabromophenyl) ether

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 decabromodiphenyl ether. The current PEC/PNEC approach indicates that there is no risk of secondary poisoning. The PEC/PNEC ratios are much less than 1 (in fact below 10^{-5}) for the commercial decabromodiphenyl ether product. 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 can not 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 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 decabromodiphenyl ether itself from all sources.

Human health

Human health toxicity

Workers

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.

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.

Humans exposed via the environment

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.

Combined exposure

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 (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.

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). 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. Furthermore, increasing levels in the environment and the possible formation of more bioaccumulative and toxic compounds via degradation could occur while the data were being gathered. Consequently Member States agreed that emission reduction measures should be considered without delay for the sources of this exposure. In the light of this agreement, a risk reduction strategy for this substance will be developed in parallel to the performance of the proposed testing listed under the conclusion (i) in Section 3.3.4. Depending on the strategy adopted, the further testing might have to 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.

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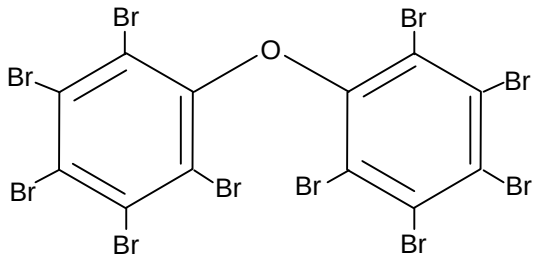
1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

This assessment considers the following commercial flame retardant product:

CAS Number: 1163-19-5
EINECS Number: 214-604-9
IUPAC Name: Bis(pentabromophenyl)ether
(decabromodiphenyl ether)
Molecular formula: $C_{12}Br_{10}O$
Molecular weight: 959.2
Structural formula:



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

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

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

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

The synonyms for decabromodiphenyl ether include: DBDPE; DBBE; DBBO; DBDPO; decabromo biphenyl oxide; decabromo phenoxybenzene; benzene 1,1' oxybis-, decabromo derivative. The abbreviation DBDPO 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 the products from different producers/suppliers is regarded as confidential information. WHO (1994) reported that a typical composition for modern products would be 97-98% decabromodiphenyl ether with 0.3-3.0% of other brominated diphenyl ethers, mainly nonabromodiphenyl ether, and the composition of products supplied in the EU is consistent with these figures. The composition of older products or products from other sources may be different from the figures above, for instance a composition of 77.4% decabromodiphenyl ether, 21.8% nonabromodiphenyl ether and 0.85 octabromodiphenyl ether has been reported for an older product (no longer supplied in the EU).

Timmons and Brown (1988) analysed a commercial decabromodiphenyl ether product for possible impurities using a high resolution gas chromatography - mass spectrometry (GC-MS) method. The major component identified was decabromodiphenyl ether, but three nonabromodiphenyl ether isomers and three octabromodiphenyl ether isomers were also present. Trace amounts of other compounds, thought to be hydroxybrominated diphenyl compounds were also tentatively identified as impurities. 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

The physico-chemical properties of decabromodiphenyl ether are summarised in **Table 1.1**.

1.3.1 Physical state (at ntp)

Decabromodiphenyl ether is a fine, white to off-white crystalline powder, depending on the manufacturer.

1.3.2 Melting point

The material has a melting range of around 300-305^{o}C (Dead Sea Bromine Group, 1993), with a range of 300-310^{o}C being quoted in IUCLID. There will be some variation depending on the manufacturer.

1.3.3 Boiling point

This material decomposes at elevated temperatures and therefore does not have a boiling point. At 343^{o}C, a 1% weight loss is experienced, with up to 50% weight loss at 446^{o}C (Dead Sea Bromine Group, 1993). This is in line with the substance's use as a flame retardant.

Table 1.1 Physico-chemical properties of decabromodiphenyl ethers

Property	Value
Chemical formula	$C_{12}Br_{10}O$
Molecular weight	959.2
Melting point	300-310°C
Boiling point	decomposes at >320°C
Particle size	typically <5 µm
Vapour pressure (at 21°C)	$4.63 \cdot 10^{-6}$ Pa
Log Kow	6.27 (measured - generator column method; GLP study)
Relative density	3.0
Flammability	not applicable
Autoflammability	not applicable
Explosive properties	none
Oxidising properties	none
Water solubility (at 25°C)	<0.1 µg/l (column elution method; GLP study)
Bromine content	about 83%

1.3.4 Relative density

The specific gravity has been measured as 3.0 at 20°C (Dead Sea Bromine Group, 1993).

1.3.5 Vapour pressure

The vapour pressure has been measured using a spinning rotor method in a study carried out according to the principles of Good Laboratory Practice (GLP) (Wildlife International Ltd, 1997). The substance tested was a composite sample from three manufacturers and had the following composition: octabromodiphenyl ether 0.04%; nonabromodiphenyl ether 2.5%; decabromodiphenyl ether 97.4%. The value obtained for the vapour pressure was 4.63×10^{-6} Pa at 21°C. The technical specification of the instrument used indicated that the low end for the recommended measurement range was 1×10^{-5} Pa and so the value measured was just outside the recommended range. The method used is not able to separate the contributions of the individual components present to the total vapour pressure and so the measured value is likely to represent the vapour pressure of the most volatile components present. Thus the value can be considered to represent the upper limit to the vapour pressure for decabromodiphenyl ether. This value will be used in the environmental assessment.

1.3.6 Solubility

1.3.6.1 Water solubility

The solubility of the substance in water was reported to be around 20-30 µg/l (Norris et al., 1973 and 1974). No details of how this value was obtained are available.

The water solubility of decabromodiphenyl ether has recently been determined using a generator column method carried out to GLP. In this study a composite sample of decabromodiphenyl ether from three producers was used (composition was 97.4% decabromodiphenyl ether, 2.5% nonabromodiphenyl ether and 0.04% octabromodiphenyl ether) and the water solubility was found to be very low at <0.1 µg/l at 25°C (Stenzel and Markley, 1997). The analytical method used was gas chromatography with electron capture detection (GC-ECD). Quantification was by comparison of the sum of the peak areas for the two major peaks (presumably corresponding to the decabromodiphenyl ether and nonabromodiphenyl ether components of the commercial product) with those obtained for standard solutions of the commercial product. Samples were collected until five consecutive samples gave similar results and this was considered to be the solubility plateau. The detection limit for the method used was 0.1 µg/l, and so the water solubility value obtained probably represents the upper limit of the true value. This value will be used in the assessment.

1.3.6.2 Solubility in other solvents

Norris et al. (1973) reported the following solubilities (as weight percentages) for decabromodiphenyl ether in various organic solvents: acetone 0.05%; benzene 0.48%; methylene bromide 0.42%; xylene 0.87%. A solubility in toluene of ~0.2% has also been reported (unpublished data). Decabromodiphenyl ether therefore shows limited solubility in common organic solvents.

1.3.7 Partition coefficient

The log Kow value for decabromodiphenyl ether has recently been determined using a generator column method (MacGregor and Nixon, 1997). The substance tested was a composite sample from three manufacturers and consisted of 97.4% decabromodiphenyl ether, 2.5% nonabromodiphenyl ether and 0.04% octabromodiphenyl ether. The log Kow value was determined as 6.265 at 25°C. The experiment was conducted to GLP and the experimental details are available. Briefly, stock solutions of the decabromodiphenyl ether were prepared in octanol (approximate concentration 0.1 mg/g), and, after centrifuging and filtering to remove any undissolved test substance, this was used to charge the generator column. The water used in the study was saturated with octanol prior to being pumped through the column (0.5 ml/minute overnight to equilibrate the system and then 1.0 ml/minute). Once equilibrated, three consecutive aqueous samples were collected from the column at four hour intervals (volumes collected 255-270 ml) and analysed for the presence of decabromodiphenyl ether. The analytical method used was GC-ECD. Quantification was by comparison of the sum of the peak areas for the two major peaks (presumably corresponding to the decabromodiphenyl ether and nonabromodiphenyl ether components of the commercial product) with those obtained for standard solutions of the commercial product. Using this method, the mean concentration measured in the aqueous effluent was 0.040 µg/l and the mean concentration measured in the octanol stock solution was 0.0738 g/l; thus the Kow value was $7.38\times10^{4}/0.040 = 1.845\times10^{6}$ (log Kow = 6.265). This value is lower, but similar to the values obtained for pentabromodiphenyl ether (log Kow = 6.59) and octabromodiphenyl ether (log Kow = 6.29) using the same procedure (further details are given in the individual assessments for those substances). From structural considerations, the log Kow would be expected to increase with increasing bromination. The fact that this pattern in log Kow is not seen in these experiments is probably the result of the difficulties inherent in measuring the log Kow value for this type of substance. For instance, since the substance is of very low water solubility, the presence of trace amounts of octanol in

the water phase may have an effect on the apparent water concentration and hence Kow value determined. The result probably represents the lower limit for the log Kow value.

Other reported values are log Kow = 9.97 using a HPLC technique (using this technique an increase in log Kow with increasing bromination was seen with a series of brominated diphenyl ethers; Watanabe and Tatsukawa, 1990) and log Kow = 5.24 (no details of the method used are available; Norris et al., 1973 and 1974).

The measured log Kow of 6.27 will be used for the environmental risk assessment. This value probably represents the lower limit for the log Kow value. The effect of uncertainties in this value on the subsequent environmental modelling are addressed in Appendix E.

1.3.8 Flash point

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

1.3.9 Autoignition

This material does not undergo autoignition but decomposes 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 the substance. Commercial decabromodiphenyl ether does not contain any substance with structural alerts for oxidising effects. Decabromodiphenyl ether is not considered therefore to be an oxidiser.

1.4 CLASSIFICATION

1.4.1 Current classification

Decabromodiphenyl ether is not currently classified for environmental or health effects.

1.4.2 Proposal of rapporteur

No classification proposed.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

There are three importers of decabromodiphenyl ether in the EU. One company did produce decabromodiphenyl ether recently in the EU, but only intermittently and in small quantities. It is understood that production at this site has now ceased (as of 1999).

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). In the early 1990s there were thought to be eight producers of polybrominated diphenyl ethers in total world-wide (although industry indicated that there were nine), with one in the Netherlands, one in France, two in the United States, three in Japan and one in the United Kingdom (WHO, 1994). 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 manufacture decabromodiphenyl ether.

Arias (2001) reported that world-wide demand for decabromodiphenyl ether was 54,800 tonnes/year in 1999.

2.1.1 Production processes

This information is included for completeness. The polybrominated diphenyl ethers are produced by direct bromination of diphenyl ether using a Friedel-Crafts catalyst. Information reported in EEC (1993) indicates that production of decabromodiphenyl ether is carried out by using bromine as both the reactant and reaction medium. Diphenyl ether is added to the bromine in the presence of a catalyst and the rate of addition of diphenyl ether effectively controls the rate of reaction. The reaction is a batch process and the temperature of the reaction is around the boiling point of the bromine solvent (~59^{o}C).

2.2 USE

2.2.1 Quantities used

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

Table 2.1 Production and import figures for total polybrominated diphenyl ethers into the EU (WHO, 1994)

Year	Production (tonnes)	Imports (tonnes)	Total (tonnes)
1986	4,276	4,310	8,586
1987	3,624	3,492	7,116
1988	4,066	4,955	9,021
1989	3,843	7,103	10,946

An industry source (personal communication) gave a very similar figure for EU usage of all brominated diphenyl ethers as 10,000-11,000 tonnes/year in the mid to late 1990's. A more recent estimate from industry (personal communication) indicates that the 1999 market demand for decabromodiphenyl ether in Europe was 7,500 tonnes/year. Similarly the 1999 market demand for octabromodiphenyl ether and pentabromodiphenyl ether in Europe was 450 tonnes/year and 210 tonnes/year respectively. Therefore the total 1999 market demand for the three commercial polybrominated diphenyl ether products in Europe was 8,160 tonnes/year, with decabromodiphenyl ether accounting for around 92% of the total usage of polybrominated diphenyl ether products.

Assuming that decabromodiphenyl ether accounted for 75% of the total EU usage of brominated diphenyl ether flame retardants in the mid 1990's, it can be estimated that up to 8,210 tonnes of decabromodiphenyl ether are used in the EU. This figure is reasonably consistent with the import data reported in IUCLID for decabromodiphenyl ether and also the known amount supplied to the EU in 1999 (7,500 tonnes/year) and so will be used as the EU usage figure in the rest of this report. This figure assumes that there is no export of decabromodiphenyl ether out of the EU. No export figures have been provided, although as decabromodiphenyl ether itself is now only imported into, rather than manufactured in, the EU, the amounts subsequently exported are likely to be small. In addition, it is possible that decabromodiphenyl ether may be imported into or exported from the EU in finished articles or masterbatch (compounded plastic pellets containing the flame retardant additive). It is not currently possible to estimate the size of these imports or exports. However, given that the estimated amount of decabromodiphenyl ether used world-wide is around 30,000-54,800 tonnes/year (see Section 2.1), then the above estimates for usage of decabromodiphenyl ether within the EU would account for around 15-30% of the total world-wide production (the 1999 data indicate the usage within the EU was around 13.7% of the total world-wide production), and hence use of, articles containing decabromodiphenyl ether. Based on these figures, the net import of decabromodiphenyl ether into the EU in finished articles and masterbatch could be considered to be small compared with the total amounts estimated to be used, although this may not necessarily be the case based on the 1999 data, which indicate that the relative amount of decabromodiphenyl ether used directly in the EU compared to the total used world-wide may have fallen slightly recently. Actual figures on the amounts of decabromodiphenyl ether imported to and exported from the EU in articles or masterbatch would be useful to confirm this hypothesis, although it is recognised that it is very difficult to obtain such data.

WHO (1994) gave figures for the use of polybrominated diphenyl ethers in several European countries. These figures are reproduced in **Table 2.2** and refer to total polybrominated diphenyl ethers.

Table 2.2 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

Note: a) Figures refer to total brominated flame retardants.

Klingenberg (1990) reported consumption figures for decabromodiphenyl ether in the Netherlands as 1,100-1,300 tonnes/year.

KEMI (1994) estimated the quantities of decabromodiphenyl ether imported into Sweden in 1993. It was thought that 17 tonnes of decabromodiphenyl ether were imported as the substance, with a further 20 tonnes imported present in plastic compound for use in production of printer housings, plastic foils, cable and electrical components. It was also estimated that around a further 400 tonnes/year of decabromodiphenyl ether could be imported into the country in pre-formed plastic goods such as televisions and computer casings.

Watanabe and Tatsukawa (1990) reported that around 4,000 tonnes of decabromodiphenyl ether were used in Japan in 1987. The consumption of decabromodiphenyl ether in Japan was reported to have reached a peak level of around 10,000 tonnes/year in 1990-1991, and then fallen back to the same level as the late 1980s by 1994 (Sellström, 1996).

As can be seen from the **Table 2.2**, up to 5,000 tonnes/year of polybrominated diphenyl ethers are used in any one EU country. Assuming that 75% of this use is made up of decabromodiphenyl ether, then a usage figure for an EU country can be estimated at up to 3,750 tonnes/year decabromodiphenyl ether.

2.2.2 Uses

Decabromodiphenyl ether is used as a flame retardant. It is mostly used in applications in the plastics and textile industries. It is an additive flame retardant, i.e. it is physically combined with the material being treated rather than chemically combined (as in reactive flame retardants). This means that there is the possibility that the flame retardant may diffuse out of the treated material to some extent (see Section 3.1.1.2).

2.2.2.1 Polymers

Decabromodiphenyl ether is a general purpose flame retardant and is used in a variety of polymer applications.

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.

Industry information indicates that decabromodiphenyl ether is used at loadings of 10-15% weight in polymers and is always used in conjunction with antimony trioxide. The major application for decabromodiphenyl ether is in high impact polystyrene (HIPS) which is used in the television industry for cabinet backs. It is also used in a large number of other polymers with end-uses in electrical and electronic equipment (e.g. computers, connectors, electrical boxes, wire and cable etc.). Examples include polypropylene (for electronics), acetate copolymers (EVA (ethylene-vinyl acetate) and other ethylene copolymers for wire and cable), EPDM (ethylene-propylene-diene terpolymer) and thermoplastic elastomers (for wire and cable) and polyester resins (for electronics). Other minor uses include styrenic rubbers, polycarbonates, polyamides and terphthalates, and small amounts are also reported to be used in hotmelt adhesives (see Section 4.1.1.2.4). It was not possible to obtain a breakdown of the amounts of decabromodiphenyl ether used in each application and so it is assumed that the emissions from these other polymer uses will be similar to those estimated for HIPS later in this report.

Based on the estimates for the total amount of decabromodiphenyl ether used in the EU of 8,210 tonnes/year and assuming that around 1,500 tonnes/year of this are used in textile

applications (see Section 2.2.2.2), then the amount of decabromodiphenyl ether used in polymer applications would be around 6,710 tonnes/year in the EU. The available figures for 1999 indicate that the total EU usage was 7,500 tonnes/year, with 1,125 tonnes/year used in textile applications and 6,375 tonnes/year used in polymer applications. These figures are in broad agreement with the estimates above. An unknown amount could also be imported into or exported from the EU in plastic articles or as masterbatch (compounded plastic pellets containing the flame retardant additive) ready for further processing, e.g. extrusion.

2.2.2.2 Textiles

Industry information indicates that decabromodiphenyl ether is widely used for flame retarding polypropylene drapery and upholstery fabric. The flame retardant is back coated onto the textiles in a latex binder. Decabromodiphenyl ether may also be used in some synthetic carpets, where it is encapsulated within the polymer fibres. It is not used as a flame retardant in textiles used for clothing.

In the United Kingdom it is thought that around 95% of all upholstery materials are flame retarded in order to comply with the United Kingdom Furniture and Furnishing (Fire) (Safety) Regulations 1988, which require furniture fillings and covers to meet specified performance requirements for ignition. Further, it has been estimated that over 50% of the total polybrominated diphenyl ether used in the United Kingdom is used in the textile industry, whereas in most other countries the amounts used in this application would be much lower. Around 1,000-1,200 tonnes/year of decabromodiphenyl ether are thought to be used in textile applications in the United Kingdom (WHO, 1994).

The only countries within the EU that have regulations specifying a level of flame retardancy for domestic upholstery fabrics are the United Kingdom and Eire. As a result, the vast majority of upholstered fabrics containing flame retardants are supplied to these markets. Discussions with industry indicated that a large fraction of the fabric that is used in the United Kingdom is produced in other countries and so application of the flame retardant treatment to the fabric could occur in countries other than the United Kingdom. It is estimated that around 80% of the decabromodiphenyl ether is applied to fabrics by companies in the United Kingdom, and 20% by companies in the rest of Europe. The industry source estimated that around 1,000-1,500 tonnes/year of decabromodiphenyl ether are used in domestic upholstery. They were not able to supply information on the amounts used in non-domestic upholstery etc. The vast majority of this flame retarded fabric, whether the coating is applied in the United Kingdom or not, is used in upholstery supplied to the United Kingdom market.

The industry can be split into three areas: compounders (formulators), who mix and manufacture the flame retardant formulation; finishers, who apply the flame retardant coating to the fabric; and self compounders, who both mix their own flame retardant formulation and apply it to the fabric.

In the United Kingdom, it is thought that there are three or four major compounders/self compounders and three or four smaller ones. It is also thought that there are two major compounders in Germany and three or four importers of flame retardant formulations into the United Kingdom. For the finishers, it is though that there are four large contract coaters and around six smaller ones in the United Kingdom. These facilities buy in textiles and apply flame retardant treatments as required. In addition, it was thought that there are two in-house weaver/coaters operating in the United Kingdom. In the rest of the EU, it was thought that there are 20-30 textile finishers dealing with flame retardant coatings.

In a typical compounding (formulation) process, antimony trioxide and decabromodiphenyl ether are pre-mixed as a dispersion in water. The dispersion contains around 70% solids and is made up in batches, with a batch being prepared typically every other day. The dispersion is stored in a large storage tank and is then piped directly into the mixing vessel to produce the final formulation. In these vessels, the water dispersion is added to emulsion polymers and mixed. Once mixed, the final product is discharged into drums, kegs, tanks etc., depending on customer requirements.

The flame retardant formulations are applied to fabrics by backcoating. In this process, the formulation is applied to the back of the textile by a running roll. The textile then passes through an oven at a temperature of 130-140^{o}C for a few seconds to drive off the water. The equipment is able to coat around 20 linear metres/minute (most fabric in the United Kingdom is 1.4 metres width).

The following loadings were thought to be typical for backcoating of textiles (the figures refer to g of dry coating/m^2 of fabric; decabromodiphenyl ether makes up around 30-40% of the dry coating weight):

velour pile fabrics	70-80 g/m^2
cotton	30-40 g/m^2
flat wovens (other types)	somewhere in between the two above (probably nearer to 40-50 g/m^2)

It was thought that decabromodiphenyl ether is used in the United States for backcoating of carpets. However, it was thought that this was not a big use in the EU since the much heavier weights of backing on carpets allows other types of flame retardant (e.g. aluminium hydroxide) to be used.

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

The following figures are derived from Sections 2.1 and 2.2 and will be used later in this assessment as the basis of the PEC calculations. The figures provided by industry for use of decabromodiphenyl ether in the EU in 1999 are slightly lower than, but in broad agreement with, these figures, and would lead to similar, but slightly lower, release estimates and predicted environmental concentrations.

Total usage within EU = 8,210 tonnes/year
Use in polymers (Industry Category 11, Use Category 22 (flame retardant)) in EU = 6,710 tonnes/year (81.7% of total)
Use in textile applications (Industry Category 13, Use Category 22 (flame retardant)) in EU = 1,500 tonnes/year (18.3% of total)

The regional use figure will be taken as 10% of these figures (i.e. 671 tonnes/year used in polymers and 150 tonnes/year used in textile applications).

In addition to these usage figures, decabromodiphenyl ether could be imported into (or exported from) the EU in finished products or as masterbatch (compounded plastic pellets containing the flame retardant additive). It is not possible to quantify these amounts. However, given that the estimated amount of decabromodiphenyl ether used world-wide is around 30,000-54,800 tonnes/year (see Section 2.1), then the above estimates for usage of decabromodiphenyl ether within the EU would account for 15-30% of the total world-wide production (the 1999 data indicate that this had fallen to around 13.7% of the total), and hence use, of articles containing decabromodiphenyl ether. Based on these figures, the net import of decabromodiphenyl ether into the EU in finished articles and masterbatch could be considered to be small compared with the total amounts estimated to be used. In the risk assessment, the possibility of release from finished articles is considered, taking into account the lifetime of the products. Thus the approach taken in this risk assessment, although not specifically identifying the decabromodiphenyl ether imported into the EU in finished products, would cover, to some extent, the releases from such products.

2.4 BREAKDOWN/TRANSFORMATION PRODUCTS

There is a large body of literature that shows that, under certain combustion/pyrolysis conditions, decabromodiphenyl 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. Generally, the amounts of brominated dibenzofurans and dibenzo-*p*-dioxins formed from decabromodiphenyl ether appear to be less than from other brominated diphenyl ether compounds tested. 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 decabromodiphenyl ether and any possible breakdown products appears to occur at temperatures of 800^{o}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 decabromodiphenyl ether and during accidental fires involving articles containing decabromodiphenyl 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 decabromodiphenyl ether is unlikely to significantly affect the total release of toxic products from fires as, in most cases, decabromodiphenyl 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^{o}C for 2 seconds (EEC, 1989a and 1989b). Draft proposals for hazardous waste incinerators require a minimum temperature of 1,000^{o}C. From the information reported in Appendix A, it can be seen that a combustion temperature of 850^{o}C is adequate to prevent the formation of brominated dibenzofurans and dibenzo-*p*-dioxins during incineration/pyrolysis of decabromodiphenyl ether in the laboratory.

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^oC 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, incinerator design and 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 decabromodiphenyl ether 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 decabromodiphenyl ether and processing of polymers containing decabromodiphenyl 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 heavy metals and certain brominated flame retardants, including polybrominated diphenyl ethers, in new electrical and electronic equipment in order to prevent problems during the waste management phase. Decabromodiphenyl 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 decabromodiphenyl ether is no longer used in electrical and electronic equipment. The proposals for WEEE also have some indirect implications for the use of decabromodiphenyl ether in electrical and electronic equipment.

3 ENVIRONMENT

3.1 EXPOSURE ASSESSMENT

3.1.1 General discussion

3.1.1.1 Emissions from production

Until recently, decabromodiphenyl ether was produced at one site in the EU, but only intermittently and not in large quantities. This site as since ceased production altogether (as of 1999). Information is available on releases to the environment from this site and these are detailed below for information. A generic assessment will also be carried out using a production plant of 1,000 tonnes/year for information.

3.1.1.1.1 Generic site

Proposals for emission factors from production are given in Appendix I of the Technical Guidance Document (TGD). 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).

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 published data on chemicals produced by similar methods, for example polybrominated diphenyls.

The estimated releases of decabromodiphenyl ether vapour to air from the reactor vessel are low, typically $1.1 \cdot 10^{-5}$ mg/tonne. The major source 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 (EEC, 1993). Thus the emissions to air of decabromodiphenyl ether vapour from production can be considered to be negligible.

The most likely way in which decabromodiphenyl ether may reach water from its production is due to washing out of equipment or washing down of floors etc. after the bagging operation etc. It is not clear how often this process would be carried out. EEC (1993) estimated that the emission of decabromodiphenyl ether from washing out the reactor after every batch would be unlikely to exceed 0.5 kg/tonne.

Using the worst-case emission factor from the Technical Guidance Document of 3 kg/tonne to wastewater, the predicted losses from a production site of 1,000 tonnes/year 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.

3.1.1.1.2 Site specific

Information on releases to the environment has been provided for a site producing decabromodiphenyl ether in the EU. The site produced the substance only intermittently and only in small amounts up until around 1999, when production ceased altogether. The amount of decabromodiphenyl ether released in effluent from the plant was estimated to be <0.8 kg/year based on monitoring data for a similar substance produced using the same reaction equipment. If it is assumed that production at the plant occurred over 100 days, then based on the relative amounts of decabromodiphenyl ether and the other substances produced at the plant, production of decabromodiphenyl ether would have occurred over 17 days/year. The effluent from the plant (50-100 m^3/day) went through a settling pond and was then released into a channel which leads to the sea. Sludges from the pond were regularly dredged, dried and incinerated.

3.1.1.2 Emissions from use in polymer applications

There are various stages in polymer processing such as compounding (blending of the polymer 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 to produce master batches (plastic compounds that contain high concentrations of additives which are subsequently mixed in 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 is 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 HIPS, assuming a decabromodiphenyl ether consumption of 671 tonnes/year in a region and 6,710 tonnes/year in the EU as a whole. Although the example is for use in HIPS, it should be noted that the actual release estimates are independent of the type of polymer, 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 150,000 tonnes/year of polystyrene are processed in the United Kingdom. Of this 62% (93,000 tonnes/year) is processed in closed systems and around 22% of this (20,460 tonnes/year) is used to make brown goods (e.g. TVs, videos etc.) which may contain around 20% by weight of flame retardant. According to the Use Category Document, polystyrene processed in partially open and open systems generally does not contain flame retardants.

3.1.1.2.1 Release during handling of raw material

Losses of powders during the handling of raw materials have been estimated as 1.6% for powders of particle size <40 μm (UCD, 1994). These losses will initially be to the atmosphere, but it is expected that the dust will rapidly settle within the facility and so the losses will be mainly to solid waste, which may be recycled or disposed of, or to wastewater (by washing down of floors, equipment etc.).

The release figure of 1.6% is made up of 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 <40 μm and such particles will not empty cleanly from a bag. For particles <40 μm, the worst-case loss could be as much as 1%. The third source of release during handling is from dust generation. This is estimated to be around 0.5% for substances with particle size <40 μm (UCD, 1994).

For decabromodiphenyl ether the losses from handling of the raw material will be 10.7 tonnes/year in a region and 107 tonnes/year in the EU. 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 floors and equipment. It is assumed that such releases to wastewater are accounted for in the emission factors from the Technical Guidance Document 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 the 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 around 0.05% for <40 μm particles (UCD, 1994). Release will again be initially to the atmosphere but the particles would be expected to settle within the facility and so losses will 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 at the elevated processing temperatures used (giving a total loss of 0.06%).

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

For decabromodiphenyl ether the losses from compounding will be 0.41 tonnes/year (0.34 tonnes/year as dust and 0.07 tonnes/year as vapour) in a region and 4.1 tonnes/year (3.4 tonnes/year as dust and 0.7 tonnes/year as vapour) in the EU. In addition, the estimated release during conversion will be around 0.07 tonnes/year (as vapour) in any one country and 0.7 tonnes/year (as vapour) in the EU.

Table A3.11 of Appendix 1 of the Technical Guidance Document also gives estimates for the releases of additives such as flame retardants during processing of thermoplastic polymers. For decabromodiphenyl ether the release fractions (based on a vapour pressure of <1 Pa and a boiling point of >300^{o}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 for decabromodiphenyl ether of 671 tonnes/year in a region and 6,710 tonnes/year in the EU as a whole, the estimated releases of decabromodiphenyl ether are 0.34 tonnes/year to air and 0.34 tonnes/year to wastewater in a region and 3.4 tonnes/year to air and 3.4 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, but of a similar order of magnitude, to those estimated using the Use Category Document. However, for the worst-case assessment, these higher figures will be used for the releases to water, as there is the possibility of 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 estimates are in fact similar. Thus releases of decabromodiphenyl ether to wastewater from processing of plastics are taken as 0.34 tonnes/year in a region and 3.4 tonnes/year in the EU as a whole. The estimated releases to air will be taken to be similar (i.e. 0.34 tonnes/year in a region and 3.4 tonnes/year in the EU as a whole) for the purposes of the worst-case assessment.

3.1.1.2.3 Releases at a polymer processing site

In order to estimate a PEC for a typical processing site, knowledge is needed of the size distribution of processing plants in a country/EU. As a worst-case approach, it could be assumed that all the decabromodiphenyl ether used in a region is on one site. However, for decabromodiphenyl 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 polystyrene containing flame retardants is carried out in closed systems only. It is thought that around 2,400 companies are using closed systems in the United Kingdom.

From the Use Category Document, the largest estimated usage per site is obtained for large sites 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 polystyrene processed in closed systems in the United Kingdom is 93,000 tonnes/year, thus the amount processed at a large site is 577 tonnes/year. If it is assumed that decabromodiphenyl ether is used in all this plastic at 15% concentration, the amount of decabromodiphenyl ether used at a site would be 87 tonnes/year. This usage figure is in line with information obtained from a plastic pellets manufacturer in the United Kingdom, who are thought to use around 23-45 tonnes/year of decabromodiphenyl ether.

Appendix 1 of the Technical Guidance Document also gives estimates of the likely amount of substance used at a given site. If it is assumed that the regional use of decabromodiphenyl ether in plastics is 671 tonnes/year and that it is typically present at a concentration of 15% by weight in the plastic, the amount of plastic containing decabromodiphenyl ether processed in a region is 4,473 tonnes/year. From Table B3.9 of that Appendix, for a polymer processed in amounts of 4,473 tonnes/year in a region, it is suggested that 15% (i.e. 671 tonnes/year of polymer or 100.7 tonnes/year of decabromodiphenyl ether) is used on a worst-case site over 268 days. This is slightly higher than the site usage figures estimated above. Based on the total emission of 0.34 tonnes/year of decabromodiphenyl ether estimated to be released in a region, the amount of decabromodiphenyl ether released to wastewater at a plant of this size would be 51 kg/year over 268 days. This figure will be used for the worst-case assessment.

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):

Loss due to volatilisation from plastic = $1.1 \cdot 10^{6} \cdot P \cdot N$ %
where P = vapour pressure of flame retardant (mmHg at 20°C)
N = service life of product (for brown goods N = 5-10 years)

For decabromodiphenyl ether the vapour pressure has been measured as $4.63 \cdot 10^{-6}$ Pa ($3.47 \cdot 10^{-8}$ mmHg) at 21°C and so the loss during the service life of a product (assuming a life of 10 years) will be 0.38% over 10 years, or 0.038% per year.

The total EU amount of decabromodiphenyl ether estimated to be used in plastics is 6,710 tonnes/year. Based on this quantity, the estimated losses during the service life of the product are likely to be 0.255 tonnes/year in a region and 2.55 tonnes/year in the EU as a whole. 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 decabromodiphenyl ether are likely to enter into use during this time, the actual amount of decabromodiphenyl present in plastic products, and hence potentially released, could be around 10 times the amount estimated above (i.e. the estimated releases would be 2.55 tonnes/year in a region and 25.5 tonnes/year in the EU as a whole). It is also possible that decabromodiphenyl ether may be imported into or exported from the EU in finished articles and/or masterbatch. If there is a net import in these products, this could also add to the amount of decabromodiphenyl ether present in, and hence released from, products.

Leaching

Given that the major use of plastics containing decabromodiphenyl ether appears to be in electrical/electronic applications and that the substance has a very low water solubility, the potential for leaching of decabromodiphenyl ether from plastics products during use appears to be small. The leaching of decabromodiphenyl ether from textile applications is considered later.

"Waste remaining in the environment"

"Waste remaining in the environment" can be considered to be small particles of polymer product, or dust generated from polymer products, containing decabromodiphenyl ether. These particles are primarily released to the industrial/urban soil compartment, but they may also end up in sediment or air. End-products with outdoor uses are most likely to be sources of this waste, where releases can occur over the lifetime of the product due to weathering and wear etc. This type of waste can also be generated during disposal of all types of plastic products, particularly where articles are dismantled or subject to other mechanical processes.

At present there is no agreed methodology given in the Technical Guidance Document for assessing the risks from this type of waste. However, a methodology was outlined in the draft risk assessment report for di-(2-ethylhexyl) phthalate (DEHP) (RAR, 2000) and a similar approach is taken here. The estimates obtained are open to a high degree of uncertainty. Recently, measurements of decabromodiphenyl ether in air and dust have been reported at several electronic equipment dismantling facilities. These data are shown in Section 3.1.3.2. Although it is not possible to use these data directly to estimate the amounts of decabromodiphenyl ether released from this source, they do indicate that this may be a source of environmental release.

Details of the approach used previously for other plastics' additives

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

Car undercoating;
Roofing material;
Coil coating;
Fabric coating;
Cables and wires;
Hoses and profiles; and
Shoe soles.

The emission factors used for these types of losses in the draft DEHP risk assessment were around 2-10% over the lifetime of the product, with the higher factor being applied to articles subject to high wear rates (such as car underbodies and shoe soles), and 2% during disposal operations. The assumptions behind the derivation of these factors were not given in the report. These releases were thought to occur mainly to industrial/urban 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 decabromodiphenyl ether

A similar approach to that used for DEHP is used here as a worst-case, using the same emission factors as used for DEHP. Only outdoor applications are considered to contribute significantly to the waste over the lifetime of the articles, but all applications are considered to contribute at disposal. The actual amount of decabromodiphenyl 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 to occur from this source. Given that the known applications of plastic containing decabromodiphenyl 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 estimate is also considered in the calculation.

The approach taken assumes the following:

- The quantity of articles/products containing decabromodiphenyl ether disposed of each year is equal to the quantity of new articles/products containing decabromodiphenyl 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 decabromodiphenyl 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 decabromodiphenyl 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. Furthermore, since this waste is essentially polymeric particles containing decabromodiphenyl ether, it is no known if this is in a form that is "available" in the environment and so would lead to actual exposure of organisms to decabromodiphenyl ether.

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

Total amount of decabromodiphenyl ether present in polymers = 6,710 tonnes/year
Amount of lost through volatilisation over service life = 25.5 tonnes/year
Total amount remaining in plastics = 6,685 tonnes/year
Fraction of plastics used for outdoor applications = 10% or 0.1% (estimate)
Total amount in plastics for outdoor applications = 669 or 6.69 tonnes/year
Amount lost as "waste remaining in the environment" = 2% over lifetime (estimate)
Emission of decabromodiphenyl ether over lifetime of product = 13.4 or 0.13 tonnes/year
Total amount remaining in plastics at disposal = 6,672 or 6,685 tonnes/year
Loss as "waste remaining in the environment" at disposal = 2% (estimate)
Emission at disposal = 133.4 or 133.7 tonnes/year
Amount in plastics for disposal = 6,539 or 6,551 tonnes/year

The estimated amount of "waste remaining in the environment" is therefore 147.8 or 133.8 tonnes/year for the EU as a whole. The regional amount will be taken as 10% of these figures. It will be assumed that this is released to industrial/urban soil, air and surface water as follows:

	Total EU	Region
75% to industrial/urban soil	110.9 or 100.4 tonnes/year	11.1 or 10.0 tonnes/year
0.1% to air	0.148 or 0.13 tonnes/year	0.015 or 0.013 tonnes/year
24.9% to surface water	36.8 or 33.3 tonnes/year	3.68 or 3.33 tonnes/year

3.1.1.2.5 Losses from landfill and incineration

Using the assumption that the amount of plastic containing decabromodiphenyl ether produced each year replaces that disposed of each year then the amount of decabromodiphenyl ether disposed of in plastic articles in the EU could be around 6,539-6,551 tonnes/year (or 654-656 tonnes/year in a region), based on the calculations in the previous Section.

Peltola (2002) has recently determined the concentration of decabromodiphenyl ether in bottom ash from two municipal incinerators in Finland. The detection limit of the method use was 0.02-0.6 μg/kg and decabromodiphenyl ether was not detected in either sample.

Plastics containing decabromodiphenyl ether will usually be disposed of either to landfill or by incineration. It is expected that emissions from controlled 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 decabromodiphenyl ether in plastics is disposed of to landfill, in theory it could leach out of the plastic and into groundwater or volatilise to the atmosphere. However, several experiments have shown that leaching of decabromodiphenyl ether from polymers is minimal (see below) and it would not be expected to leach to a significant extent from polymers

in landfill, unless the polymer itself undergoes some form of degradation, thus releasing the decabromodiphenyl ether. Any released decabromodiphenyl ether is likely to adsorb strongly onto soil, thus minimising the possibility of reaching groundwater (see also Section 3.1.1.6.2). Similarly, the low vapour pressure of the substance would limit its volatility to the atmosphere.

A study of the leaching of decabromodiphenyl ether (Dow FR-300-BA; 77.4% deca-, 21.8% nona- and 0.8% octabromodiphenyl ether) from pellets of acrylonitrile-butadiene-styrene (ABS) polymer and polystyrene (both containing 10% decabromodiphenyl ether) has been undertaken. The polymers were placed in 2 l of water and shaken mechanically. The results, expressed as the concentration of bromine in water, are shown in **Table 3.1**. The lack of increase of the bromine concentration with time and the erratic results are best explained by assuming that extraction of decabromodiphenyl ether was mainly due to erosion of surface particles (Norris et al., 1973 and 1974).

Table 3.1 Leaching of decabromodiphenyl ether from polymers

Time (hours)	Concentration in water (expressed as mg bromine/l)	
	ABS	Polystyrene
3	1.8	<1
19	1.3	<1
27	1.0	<1
43	3.7	<1
51	<0.5 (not detected)	<0.5 (not detected)
187	<0.5 (not detected)	<0.5 (not detected)

In static extractions of ABS containing 4.25% decabromodiphenyl ether (Dow FR-300-BA) with water, acetic acid and cottonseed oil at elevated temperatures, little or no leaching of the decabromodiphenyl ether was seen. The results are shown in **Table 3.2**.

No decabromodiphenyl ether was detected in the water and acetic acid and only about 0.03% of the total decabromodiphenyl ether was extracted by cottonseed oil over 7 days at elevated temperatures (Norris et al., 1973 and 1974).

Table 3.2 Solvent extraction of decabromodiphenyl ether from ABS

Solvent	Time (days)	Temperature (°C)	Concentration of decabromodiphenyl ether in solvent (mg/l)
Water	1	48.9	<0.075 (not detected)
3% Acetic acid	1	48.9	<0.075 (not detected)
3% Acetic acid	7	48.9	<0.075 (not detected)
Cottonseed oil	7	57.2	1

Although the available information indicates that leaching of decabromodiphenyl ether from landfills will be minimal, movement of polymer particles containing decabromodiphenyl ether within the landfill could provide a transport mechanism leading to entry into leachate water or groundwater. However, it is not currently possible to assess the significance of this type of process. Well designed landfills already include measures to minimise leaching in general and these measures would also be effective in minimising the leaching of any decabromodiphenyl ether present.

3.1.1.2.6 Possibilities for recycling

It has been reported (EEC, 1993) that off-cuts and off-specification plastic material 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 decabromodiphenyl ether losses from any recycling of off-cuts etc. could be similar to the losses described above for the individual steps in plastics processing.

3.1.1.3 Emissions from use in textiles

3.1.1.3.1 Formulation and application to textiles

Information on releases to the environment from use in textiles has been provided by an industry source with a detailed knowledge of the textiles coating industry in the EU. The major source of release during the compounding of flame retardant formulations for textile treatments are thought to be due to dust formation during the emptying of the flame retardant powder into the pre-mixer and due to washing out of the final formulation mixing tanks. At a major compounding site, the flame retardant powder is handled under LEV (the controls in place are generally there to limit exposure to antimony compounds). Any loose dust is vacuumed up and the area is then washed down with water. Thus a small amount of the flame retardant may reach the wastewater. The vast majority of the dust (>99%) that is collected is re-used. With regard to washing out of vessels, around 0.5% of the formulation is estimated to be lost, of which the flame retardant will make up a percentage (typically 15-20% of the wet formulation), and so the loss of the flame retardant is up to 0.1%. Based on the monthly amount of flame retardant used at a large formulation site, the losses of decabromodiphenyl ether due to washing out of vessels can be estimated to be around 38-50 kg/month (450-600 kg/year). The release from EU as a whole is expected to be around twice this figure (1,000-1,500 kg/year), based on an EU consumption of 1,000-1,500 tonnes/year in this application. The regional release would normally be taken as 10% of this figure i.e. 150 kg/year, however as a worst-case approach the release from a large site, as this is higher, will be taken as the regional release i.e. 600 kg/year. All the wastewater at the large site goes to an on-site wastewater treatment plant which has a solids extraction system, before being discharge to local sewer. The actual form of the flame retardant formulation at this stage is as a viscous mixture with the polymer. The solid extraction system at the wastewater treatment plant removes this as a "paint-like" film, and so the actual releases of decabromodiphenyl ether to sewer are likely to be very small. The solid residue is disposed of to landfill. The actual efficiency of such a solid extraction system for the removal of decabromodiphenyl ether is unknown, and it is not known if such a system will be fitted at all sites in the EU. As a worst-case approach it will be assumed that all the release at the generic large site is direct to a standard wastewater treatment plant as defined in the Technical Guidance Document. This approach will overestimate the resulting concentrations in the environment from sites where a solids extraction system is present.

Release of flame retardant formulation could also occur during the backcoating operation. The losses are as a result of initial set-up and washing down of the coating equipment between batches. An industry source estimated the likely loss as being around 1 kg of formulation between each batch. This equates to a loss of around 0.15-0.2 kg of decabromodiphenyl ether,

assuming that it makes up 15-20% of the wet formulation. The frequency of washing is dependent on the length of run, but could vary between a few hours and a few days. The waste is usually collected for suitable disposal but could be disposed of to drain. The amount of decabromodiphenyl ether released at a given site will depend on the number of coating machines at the site and the frequency of washing of equipment and so is not easy to quantify in general terms. However, if a figure of 1 kg/day (i.e. washing occurs 5 times/day) of decabromodiphenyl ether is taken to represent the daily loss (to within an order of magnitude) at a facility, this would give a yearly estimated loss of 300 kg, possibly to landfill or wastewater. Similarly, on an EU basis, there are thought to be around 40 textile finishers of various sizes using flame retardant coatings. Assuming that on average 0.2 kg of decabromodiphenyl ether are lost/site every other day, this would give an estimated EU wide release of 1,200 kg/year from this source. The regional release would normally be taken as 10% of this figure i.e. 120 kg/year, but in this case, as the amount released at a large site is higher (300 kg/year) this will be taken as the regional release. It is thought that around 80% of the backcoating of decabromodiphenyl ether onto textiles occurs in the United Kingdom (see Section 2.2.2.2).

The use of textiles treated with decabromodiphenyl ether in most EU countries, particularly for upholstery, is only relatively minor compared to the amounts used in the United Kingdom. The formulation and application of flame retardants for textile applications does take place in countries other than the United Kingdom but the information used above for these lifestages are thought to be representative of the situation throughout Europe.

3.1.1.3.2 Losses during service life of product

Washing of textiles

A possible source of release of decabromodiphenyl ether from fabrics is during the washing of the fabric itself. This is expected to be low for several reasons. Firstly, in order for the fabric to be acceptable for domestic upholstery use in the United Kingdom, it has to pass either a match or cigarette test. Both of these tests include washing of the fabric as part of the protocol. Thus the finish has to be reasonably durable in order to comply with the United Kingdom regulations. Secondly, the flame retardant is physically incorporated into a polymer on the back of the fabric and so this would be expected to minimise the loss of decabromodiphenyl ether during washing. The third point to consider is that the types of fabrics that decabromodiphenyl ether is used in, upholstery fabrics, are unlikely to be washed frequently. Indeed, for many items of furniture, no washing is envisaged as the covers are not removable. Even for furniture with removable covers, it would be expected that washing would be infrequent, perhaps of the order of once per year.

It has been reported that fabrics (100% cotton warp sateen) treated with decabromodiphenyl oxide and antimony trioxide decreased significantly in oxygen index (a method for measuring fire resistance of textiles) beyond 15 launderings (Crouch et al., 1985). Although this is an indirect measure of the leaching of decabromodiphenyl ether from textiles, it does give an indication that decabromodiphenyl ether may be lost during repeated washing of treated fabrics. This also does not distinguish between loss through leaching and loss through wear of the flame retardant coating on the fabric, leading to particulate loss. In terms of the risk assessment, both processes could lead to emissions to wastewater and so it is not necessary to identify the exact loss mechanism.

Given that the majority of fabrics treated with decabromodiphenyl ether are unlikely to be washed frequently (used mainly in drapery and upholstery fabrics), a loss rate of 3% of that

applied per year will be assumed in the absence of any data. This assumption is based on a washing rate of once per year and assuming that 45% of the flame retardant is removed after 15 washes. This would give an estimated release of 36 tonnes/year in a country such as the United Kingdom. This figure is based on the yearly usage rate of decabromodiphenyl ether in textiles (estimated at around 1,200 tonnes/year (WHO, 1994)). However, it should be borne in mind that finished articles will have quite a long usage life, probably 10 years or more. Thus, the actual amount of decabromodiphenyl ether present in textiles in the United Kingdom could be around 10 times the yearly usage figure and so the upper limit of the release from washing textiles could be 360 tonnes/year. Based on this figure, the release to a local wastewater treatment plant (population equivalent 10,000) can be estimated as 0.06 tonnes/year and the release in the regional environment (population equivalent 20,000,000) can be estimated as 120 tonnes/year (assuming population of UK is around 60,000,000). This approach to estimation of the regional release takes into account the fact that the use in this application is not evenly spread across the EU. The overall EU emissions from this source can be estimated at around 450 tonnes/year, assuming the total consumption is around 1,500 tonnes/year in this application. These figures are likely to overestimate the actual release since, as stated above, it is unlikely that all textiles treated with decabromodiphenyl ether will be washed each year.

"Waste remaining in the environment"

As discussed in Section 3.1.1.2.4, "waste remaining in the environment" can be considered to be particles of polymer product that contain decabromodiphenyl ether. Since in textiles, decabromodiphenyl ether is backcoated onto the textile in a polymeric matrix, this also has the potential to generate "waste remaining in the environment" over the service life of the textile.

As no agreed methodology is available in the Technical Guidance Document for this endpoint, a similar approach to that used for textiles in the draft risk assessment of DEHP (RAR, 2000) is used here. The method assumed a 4% loss during the lifetime of the textile for textiles used in outdoor applications, and a 2% loss from all textiles at disposal. It was also assumed that 75% of the emissions would be to industrial/urban soil and 0.1% would be to air, with the remainder being to surface water (and hence sediment). These figures are open to a high degree of uncertainty.

For decabromodiphenyl ether, most of the coated textiles will be used in indoor applications (e.g. furniture), which may not lead directly to release to the external environment. Possible particulate losses from laundering etc. are considered in the previous Section.

There is a possibility for generation of "waste remaining in the environment" at the final disposal of articles. Here a 2% loss could be assumed as used in the draft DEHP risk assessment. The estimated amount of waste remaining in the environment can therefore tentatively be estimated as follows:

Total amount of decabromodiphenyl ether present in textiles in EU = 1,500 tonnes/year
Amount lost over service life = 450 tonnes/year
Total amount remaining in textiles at disposal = 1,050 tonnes/year
Loss at disposal = 2%
Emission at disposal = 21 tonnes/year
Amount remaining in textiles for disposal = 1,029 tonnes/year

The estimated amount of "waste remaining in the environment" is 21 tonnes/year for the EU as a whole. Using the same approach as used above for the loss from washing to take into account the fact that the use of decabromodiphenyl ether in this application is not evenly spread across the

EU, the loss in the United Kingdom would be 16.8 tonnes/year, and the regional loss would be estimated as 5.6 tonnes/year (based on the relative population of the region (20,000,000) and the United Kingdom (~60,000,000)). It will be assumed that this is released to industrial/urban soil, air and surface water as follows:

	Total EU	Region
75% to industrial/urban soil	15.75 tonnes/year	4.2 tonnes/year
0.1% to air	0.021 tonnes/year	0.0056 tonnes/year
24.9% to surface water	5.23 tonnes/year	1.39 tonnes/year

3.1.1.3.3 Losses from landfill and incineration

It would be expected that textile articles containing decabromodiphenyl ether will be either disposed of to landfill or incinerated. When decabromodiphenyl ether in textiles is disposed of to landfill, in theory it could leach out of the textile and into groundwater or volatilise to the atmosphere. However, decabromodiphenyl ether has a very low water solubility and is likely to adsorb strongly onto soil. This will significantly lower its leaching potential (see Section 3.1.1.6.2). Similarly, the low vapour pressure of decabromodiphenyl ether should limit its volatility.

Using the assumption that the amount of decabromodiphenyl ether used each year in textile applications replaces that disposed of each year, then the amount of decabromodiphenyl ether disposed of each year in textile products in the EU could be around 1,029 tonnes taking into account the losses over the service life of the product discussed in Section 3.1.1.3.2. Again, taking into account the fact that the use in this application is not spread evenly across the whole EU, the amount disposed of in a large user country (e.g. the United Kingdom) can be estimated as approximately 823 tonnes/year, and the amount disposed of in a region is estimated at around 274 tonnes/year.

3.1.1.4 Summary of environmental releases

Table 3.3 summarises the estimated releases of decabromodiphenyl ether to the environment.

Table 3.3 Summary of estimated releases of decabromodiphenyl ether to the environment

Use	Release at a site (tonnes/year)	Release in regional model (tonnes/year)	Release in continental model* (tonnes/year)
Production (default)	0.5 (to wastewater) {or 3 (to wastewater)}	0.5 (to wastewater) {or 3 (to wastewater)}	0 (to wastewater)
Production (site specific)	0.0008 (to wastewater)	0.0008 (to wastewater)	0
Polymers: handling of raw materials	1.6 (as dust to landfill/incineration)	10.7 (as dust to landfill/incineration)	96.3 (as dust to landfill/incineration)
Polymers: compounding and conversion	0.051 (to air dust/vapour) 0.051 (to wastewater)	0.34 (to air dust/vapour) 0.34 (to wastewater)[b]	3.06 (to air as dust/vapour) 3.06 (to wastewater)[b]
Polymers: service life		2.55 (to air as vapour)	22.95 (to air as vapour)
Polymers: "waste remaining in the environment"		10.0-11.1 (to industrial/urban soil) 0.013-0.015 (to air as dust) 3.33-3.68 (to surface water)	90.4-99.8 (to industrial/urban soil) 0.117-0.133 (to air as dust) 30.0-33.1 (to surface water)
Polymers: disposal		654-656 (to landfill/incineration)	5,885-5,896 (to landfill/incineration)
Textiles: compounding	0.6 (to landfill/wastewater)[a]	0.6 (to landfill/wastewater)[a, b]	0.9 (to landfill/wastewater)[a, b]
Textiles: application	0.3 (to landfill/wastewater)[a]	0.3 (to landfill/wastewater)[a, b]	0.9 (to landfill/wastewater)[a, b]
Textiles: washing	up to 0.06 (to wastewater)	up to 120 (to wastewater)[b]	up to 330 (to wastewater)[b]
Textiles: "waste remaining in the environment"		4.2 (to industrial/urban soil) 0.0056 (to air as dust) 1.39 (to surface water)	11.5 (to industrial/urban soil) 0.0154 (to air as dust) 3.84 (to surface water)
Textiles: disposal		274 (to landfill/incineration)	755 (to landfill/incineration)
Maximum total emission figure for regional and continental modelling (excluding release from production)		2.9 (to air as dust/vapour) 84.9 (to wastewater via WWTP) 41.1-41.4 (direct to surface water) 14.2-15.3 (to industrial/urban soil) 939-941 (to landfill/incineration)	26.2 (to air as dust/vapour) 234.4 (to wastewater via WWTP) 134.3-137.4 (direct to surface water) 101.9-111.3 (to industrial/urban soil) 6,736-6,747 (to landfill/incineration)

Note: *Release in continental model = total estimated release in EU - estimated release in regional model.

a) The actual split between wastewater and landfill is unknown. As a worst case it will be assumed that all the release is to wastewater - this is likely to overestimate the release to surface water.

b) In the regional and continental model, a 70% connection rate to the wastewater treatment plant (WWTP) is assumed. Therefore 30% of these releases are taken as going direct to surface water.

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 swept up or washed away within the factory. Thus this release can be considered as being to solid waste or wastewater. It would be expected that only a very small fraction of this dust will enter the atmosphere outside the factory. Releases estimated for the regional model are taken as either 10% of the total release in the EU or, in most cases, the estimated release from a large site if this is larger. This reflects the fact that

much of the processing and use of decabromodiphenyl ether, particularly in textile applications, occurs in the United Kingdom.

In the United States, the releases to the environment of decabromodiphenyl ether from some facilities (production and use) are reported in the Toxic Releases Inventory database. In 1996, the total amount of decabromodiphenyl ether released or disposed of from these facilities was reported to be around 173 tonnes. Of this the around 14.2 tonnes where reported to be released to air, 2.7 tonnes released to water (either directly or via a municipal wastewater treatment plant), with the remainder disposed of by other methods (e.g. landfill, incineration). These figures do not take into account the amount of decabromodiphenyl ether disposed of each year in finished articles. However, it can be seen that the figures reported are of a similar order to the releases estimated for air and water for Europe as a whole from the production, polymer processing and textile compounding and application stages (**Table 3.3**).

Palm et al. (2001) determined emission factors for decabromodiphenyl ether of 46.1 mg/person/year to air, 2.02 mg/person/year to water and 8.64 mg/person/year to soil. These values were extrapolated from a study undertaken in Denmark using a substance-flow analysis to estimate the emissions of total brominated flame retardants in the Danish environment. Assuming a continental population of $3.7 \cdot 10^8$ (taken from the Technical Guidance Document), the estimated continental emissions of decabromodiphenyl ether using these factors would be 17.1 tonnes/year to air, 0.75 tonnes/year to water and 3.2 tonnes/year to soil. With the exception of the emissions to air, these estimates are much lower than those obtained in **Table 3.3**. However, the exact release sources covered by these emission factors is unclear.

3.1.1.5 Degradation

3.1.1.5.1 Abiotic degradation

Photolysis

Watanabe and Tatsukawa (1987) carried out photolysis experiments with decabromodiphenyl ether (97% deca, 3% nona) in a mixture of hexane, benzene and acetone (8:1:1). The concentration of decabromodiphenyl ether in the initial solution was 100 µg/ml and 50 ml of this solution was placed in a quartz tube and irradiated by either UV light using a mercury lamp (254 nm) or natural sunlight. The exposed solution was analysed for the presence of the parent diphenyl ether (by GC-electron capture detector) and brominated furans (by GC-MS using 2,3,7,8-tetrabromo dibenzofuran as reference). Semi-quantitation of other brominated diphenyl ethers was also carried out by GC-MS by assuming equal detector response with 4,4'-dibromodiphenyl ether standard. After 16 hours UV irradiation with the mercury lamp, decabromodiphenyl ether was found to debrominate mainly to tri- to octabromodiphenyl ethers. Formation of brominated furans with between 1 and 6 bromine atoms was also noted. Tetrabromodibenzofurans were found but the mass spectrum was different from that of the 2,3,7,8-tetrabromo dibenzofuran reference. No brominated dioxins were detected. The total yield of brominated dibenzofurans was around 20% after 16 hours. A similar formation and distribution of products was seen for the sunlight exposures (see Appendix A for possible problems in the identification of brominated dibenzofurans in the presence of brominated diphenyl ethers).

Watanabe et al. (1986) reported that in a preliminary test, decabromodiphenyl ether was quickly decomposed into nona-, octa-, hepta- and hexabrominated compounds on exposure to sunlight. No information on the solvent used was given.

Norris et al. (1973 and 1974) studied the photodegradation of decabromodiphenyl ether using a variety of solvents. A preliminary study was carried out using octanol as solvent. Decabromodiphenyl ether (possibly FR-300-BA) at a concentration of 0.00728 mg/ml in octanol was exposed to simulated sunlight via a sunlamp for 4 hours. The UV/visible spectrum of the solution in the 210-350 nm range was run at hourly intervals. A rapid decrease in the absorbance of the solution at 230 nm and an increase in absorbance at 280-285 nm and below 230 nm was seen during the experiment and a half-life of 4 hours was estimated for decabromodiphenyl ether from the results (Norris et al., 1973 and 1974).

Another study by Norris et al. (1973 and 1974) exposed decabromodiphenyl ether (5 g/l) to UV light (125 Watt Hg lamp) in xylene solution. The solution was constantly stirred and maintained at 25±5°C. Samples were periodically removed from the system and analysed for brominated diphenyl ethers by gas chromatography using a flame ionisation detector (identification was confirmed by mass spectrometry). The samples were also extracted with water and the extracts were analysed for the presence of bromide ion. Decabromodiphenyl ether was found to degrade by reductive debromination with a half-life of 15 hours. Lower brominated diphenyl ethers were thought to be formed.

The final study by Norris et al. (1973 and 1974) exposed decabromodiphenyl ether (98% deca- and 2% nonabromodiphenyl ether) in water to natural sunlight. Exposure was carried out in a large desiccator fitted with a polyethylene film lid (a similar desiccator covered with foil was used as a control). Each desiccator contained 10 g of decabromodiphenyl ether and 8 l of water and were placed side by side on the roof of a building. Samples were removed after 31, 66 and 98 days exposure and analysed for the presence of bromine by neutron activation analysis or were extracted with xylene and analysed by gas chromatography with electron capture detector. Over the 98 day exposure period, the total bromine content in water of the exposed sample was found to increase from 2.6 mg/l at 31 days, to 5.6 mg/l at 66 days to 7.3 mg/l at 98 days (this could be due to solubilising of decabromodiphenyl ether but is higher than the quoted solubility). The level of bromine in the water from the unexposed control was 0.2 mg/l after 98 days. GC analysis of the xylene extracts showed that lower brominated diphenyl ethers (by comparison with the following standards: 4-bromo-, 4,4'-dibromo- and mixed tribromodiphenyl ethers) were not formed as a result of the degradation. Several new unidentified peaks were seen in the GC trace after 98 days exposure but these were more volatile (i.e. had shorter GC retention times) than the 4-bromodiphenyl ether standard and so were not due to other brominated diphenyl ethers. However, given that the decabromodiphenyl ether in this experiment was essentially in the solid phase, it is not possible to infer anything about the rate and extent of photolysis of decabromodiphenyl ether in the environment. This is because only a small fraction of the total decabromodiphenyl ether present is likely to have been exposed to sunlight under the conditions used (i.e. that substance in solution and/or the surface layer of the solid). Thus the apparent small extent of photodegradation could be a result of factors other than a very slow photolysis rate.

The degradation of decabromodiphenyl ether (composition not given, but contained nona- and traces of octabromodiphenyl ether) has recently been studied using a variety of media (dissolved in toluene, or as a thin layer on silica gel, sand, soil or sediment (Sellström et al., 1998a, Tysklind et al., 2001)). The solid matrix samples were prepared by adding a solution of decabromodiphenyl ether in toluene to the solid and then allowing the toluene to evaporate in the dark. The light sources used were four mercury UV-lamps fitted with filters to give a spectrum as close as possible to natural sunlight (irradiance intensity 1.6 mW/cm^2) or natural sunlight

(sand, soil and sediment only: irradiation intensity at mid-day 2.3 mW/cm^2). In the experiments, the irradiance from 24 hours sunlight corresponded to that of around 9 hours of artificial light. Experiments were performed in triplicate and each series consisted of blanks, dark controls and the samples. Sub-samples of the various matrices were placed in pyrex tubes and were irradiated for up to 32 hours (artificial light) or 96 hours (natural light). The sediment samples were reconstituted with water before irradiation. The analysis of degradation products formed was carried out by gas chromatography-mass spectrometry using negative chemical ionisation and monitoring for the bromine ions formed (m/z -79 and -81). Sample extraction and preparation was carried out in the dark.

The experiments carried out in toluene using artificial sunlight showed that degradation was occurring by reductive debromination as a build up and then decrease of firstly nona-, then octa-, then hepta and then hexabromodiphenyl ether was seen as the experiment proceeded. The half-life for decabromodiphenyl ether was estimated to be less than 15 minutes under the conditions used.

The experiments using the solid matrices also indicated that reductive debromination was occurring, although the increase in the amounts of nona-, octa- and hepta- bromodiphenyl ethers present was not nearly so pronounced as in the toluene experiments. This indicates that either a stepwise reductive debromination pathway is less significant in environmental media or that in these media the lower brominated products formed themselves degrade at faster rate than in toluene. The result of this was that, although small amounts of nonabromodiphenyl ether formed, the subsequent formation octabromodiphenyl ether in the next step was a small fraction of this and the subsequent formation of heptabromodiphenyl was a small fraction of this. Further, no 2,2',4,4'-tetrabromodiphenyl ether (one of the dominant isomers found in the environment) was seen in this study (Sellström et al., 1998c). Thus from the results of these experiments, although it appears possible for reductive debromination to occur, the amounts of the lower brominated (e.g. tetra, penta-, or hexabrominated diphenyl ethers) formed will be very small. Further, it would also be expected that the products formed would themselves undergo similar reductive debromination reactions. The half-life for decabromodiphenyl ether in the sand experiments was around 35-37 hours using natural sunlight (Sellström et al., 1998a; Tysklind et al., 2001). The corresponding half-lives in sediment and soil were estimated to be 100 and 200 hours respectively (Tysklind et al., 2001).

It has recently been reported that exposure of decabromodiphenyl ether, dispersed as a thin layer on sand, to sunlight (midsummer 1990) resulted in the formation of debrominated products. In a similar experiment when water was added to the sand, brominated phenols as well as debrominated diphenyl ethers were seen (Örn, 1997). Few details of these studies are currently available.

Eriksson et al. (2001) recently reported the results of photolysis studies with decabromodiphenyl ether (and tetra-, penta-, hexa-, hepta- and octabromodiphenyl 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 decabromodiphenyl ether used in the study was 0.4 μM. The rate of photodegradation was found to generally increase with increasing degree of bromination and decabromodiphenyl ether was found to degrade rapidly in the system with a half-life of around 30 minutes (the half-lives for the tetra-, penta-, hexa-, hepta- and octabromodiphenyl ethers tested were 12-16 days, 2.4 days, 1.2 days, 1.2 days and 5 hours respectively). A number of decomposition products from the photolysis of decabromodiphenyl ether were identified with lower degrees of bromination. These were mainly polybrominated

diphenyl ethers with >6 bromine atoms/molecule or polybrominated furans with <6 bromine atoms/molecule.

The Eriksson et al. (2001) study found that, under the conditions used, the photochemical stability of polybrominated diphenyl ethers increased with decreasing bromination. Thus degradation of decabromodiphenyl ether could potentially lead to a build up of these lower brominated diphenyl ethers if the degradation pathway in the environment was the same as in these experiments. The actual significance of the test system used to the environment is unclear, particularly the use of a methanol:water mixture as solvent.

Further photodegradation testing of decabromodiphenyl ether under environmentally relevant conditions has recently been carried out to assess the significance of the products formed in such reactions. These tests were requested as part of the EU risk assessment process, and the results from these tests are discussed in detail below.

The degradation of decabromodiphenyl ether has been studied on hydrated surfaces (quartz glass and silica particles (sand)), humic acid-coated silica particles and also adsorbed onto glass surfaces in contact with aqueous solutions (Jafvert and Hua, 2001a). Some indirect aqueous photolysis studies were also carried out using humic acid as a source of photolytically produced free radicals in solution. In addition several experiments were also carried out to investigate the stability of 2,2',4,4'-tetrabromodiphenyl ether. In the experiments, two different light sources were used: 3,000 Å lamps (giving light in the $\lambda = 280$-320 nm (UV-B) range); and natural sunlight (the location was 40^{o} 26' N, 86^{o} 55' W).

The natural sunlight exposures with decabromodiphenyl ether were carried out from the end of March to the beginning of May 2001 and the experiments with 2,2',4,4'-tetrabromobiphenyl ether were carried out from the end of May until mid June 2001. The samples were exposed to sunlight between 9 am and 5 pm each day in the experiments (except for one study with decabromodiphenyl ether adsorbed onto sand which was exposed between 10 a.m and 4 p.m. daily).

In the experiments, various analytical methods were used to determine the extent of degradation seen and any polybrominated diphenyl ether products formed. The main analytical method used was High Performance Liquid Chromatography (HPLC) with UV detection. This was used to determine the concentration of the parent decabromodiphenyl ether present at various times during the experiment, and was also used as a screen to determine if any other polybrominated diphenyl ethers were possibly present. The tentative identity of any lower brominated diphenyl ethers present was determined by comparison of the retention times of any peaks formed with those of hexa- to nonabromodiphenyl ethers present in some commercial polybrominated diphenyl products, but as the HPLC method used provides no structural information, and UV-detection is relatively non-specific, the actual identity of the products formed could not unambiguously be determined by this method. A more detailed GC-MS analytical method was used in some exposures to positively identify any lower polybrominated diphenyl ethers formed in these experiments and, where available, these results are included in the discussion below. In addition, the amount of free bromide ion produced during the photolysis was determined at various times during the exposure.

For each experiment, a bromine mass balance was determined at various times during the exposures based on the measured concentration of parent decabromodiphenyl ether and the measured concentration of bromide ion using the following equation:

$$\% \text{ Bromine recovery} = \left(\frac{10 \times [\text{DBDPE}]_t + [Br^-]_t}{10 \times [DBDPE]_0} \right) \times 100$$

where: $[DBDPE]_t$ = concentration of decabromodiphenyl ether at exposure time t.
$[Br^-]_t$ = bromide ion concentration at exposure time t.
$[DBDPE]_0$ = initial concentration of decabromodiphenyl ether.

This allowed the amount of bromine present (expressed as a percentage of the initial amount of bromine added as decabromodiphenyl ether) in products that was not either decabromodiphenyl ether or bromide ion to be determined during the exposures. The actual identity of these products is currently unknown, but would include any lower brominated diphenyl ether congeners.

The first part of the Jafvert and Hua (2001a) study was to determine the absorption spectra of decabromodiphenyl ether (>98% purity), and other brominated diphenyl ethers (including 4,4'-dibromodiphenyl ether (99.6% purity), 2,2',4,4'-tetrabromodiphenyl ether (99.8% purity), and a commercial polybrominated diphenyl ether product containing hexa- to decabromodiphenyl ether congeners (probably a commercial octabromodiphenyl ether product)) in order to evaluate the potential for photolytic degradation. The di- and tetrabromodiphenyl ethers were found to absorb minimal light at wavelengths >300 nm, whereas both decabromodiphenyl ether and the commercial octabromodiphenyl ether product absorbed light up to around 325 nm. At 280 nm, all the compounds investigated showed similar molar absorptivities (molar absorption coefficients (ε) were all in the range 2,000 to 3,000 M^{-1} cm^{-1}). The absorption spectrum for decabromodiphenyl ether indicated that it may be susceptible to photodegradation with light at environmentally relevant wavelengths.

The first series of photolysis experiments carried out by Jafvert and Hua (2001a) looked at the solar irradiation of decabromodiphenyl ether adsorbed onto sand (silica). The spiked sand was prepared by adding a total of 50 ml of a solution of decabromodiphenyl ether in toluene (concentration $2.0 \cdot 10^{-3}$ M) to 500 g of sand in 1 ml increments. After each 1 ml addition, the sand was mixed with a steel spatula under a stream of nitrogen gas (to volatilise the toluene solvent). Once all the toluene solution had been added in this way the spiked sand was placed in a vacuum desiccator for 24 hours. This gave a decabromodiphenyl ether concentration of 3.8 g/kg sand. The experiments were carried out using twenty petri dishes each containing 7.015 g of the spiked sand and 9 ml of water. The water was replenished by weight at the end of each day. In addition, six control sand samples were prepared in a similar way. The six control samples and ten of the spiked samples were then left uncovered and exposed to natural light daily between 10 am and 4 pm. The remaining ten spiked samples were placed in a dark container to act as the dark controls. At various times during the experiments two dark controls, two controls and two exposed samples were sacrificed for analysis for the presence of decabromodiphenyl ether.

The results from this study with spiked sand indicated that the amount of decabromodiphenyl ether present in the sand declined by around 10% during the first 12 hours of irradiation, with a slower disappearance occurring during longer exposure. After 84 hours irradiation approximately 80% of the initial decabromodiphenyl ether remained on the sand. However, a similar disappearance of decabromodiphenyl ether was seen from the dark controls (the concentrations in the exposed samples and the dark control samples were statistically similar at all time points over the 84-hour exposure period). Therefore it was concluded that no or insignificant photodegradation of decabromodiphenyl ether occurred over 84 hours in this experiment. No bromide analysis appears to have been carried out in this experiment. Given the disappearance seen in the dark control samples, the significance of these findings can be questioned. As this

experiment was carried out with sand particles, only the decabromodiphenyl ether on the top few millimetres of the sand would be expected to be exposed to light.

The second series of experiments looked at the solar irradiation of decabromodiphenyl ether adsorbed onto humic acid-coated sand (Jafvert and Hua, 2001a). The sand (-50 to +70 mesh) was coated with a commercial humic acid at a concentration of $2.57 \cdot 10^{-3}$ g humic acid/g sand. The humic acid-coated sand was then prepared in a similar fashion to the sand samples above (in this case 4.8 ml of a $1.0 \cdot 10^{-3}$ M solution of decabromodiphenyl ether in toluene was added to 30 g of sand in 0.5 ml increments) giving a final concentration of 0.15 g/kg sand ($1.6 \cdot 10^{-4}$ mol/kg sand). The exposures were carried out using sealed quartz cuvettes containing 0.5 g of the spiked humic acid-coated sand and 2 ml of water. The depth of sand was around 3 mm. The samples were exposed to sunlight from 9 am to 5 pm daily. Controls and dark controls were also run as before.

The experiments with humic acid-coated sand indicated that loss of decabromodiphenyl ether was slow. After 96 hours of exposure to sunlight, around 88% of the decabromodiphenyl ether still remained on the sand. The dark controls were found to exhibit slight fluctuations in the concentration of decabromodiphenyl ether but generally showed no loss. Some indications of the presence of transformation products were found by HPLC analysis of the exposed samples, and bromide ion was found to accumulate during the exposure, but none of these peaks corresponded to tetrabromodiphenyl ether or pentabromodiphenyl ether congeners. The bromine mass balance at all time points indicated that >95% of the bromine was present as either decabromodiphenyl ether or bromide ion, showing that the amounts of other organic bromine compounds present, if any, would be small under these conditions.

A more detailed GC-MS analysis was carried out on the possible brominated diphenyl ether products formed from the experiment using humic acid-coated sand (Jafvert and Hua, 2001b). Two replicate exposures were carried out using the same conditions as indicated above, and the concentrations of 43 individual polybrominated diphenyl ether isomers, as well as the total di- to octabromodiphenyl ether congeners, were determined. The results of the experiment are shown in **Table 3.4**. The concentrations refer to ng of the polybrominated diphenyl ether per kg of sand. The paper indicated that the results were inconclusive as to whether octa- and nonabromodiphenyl ether were being formed in this experiment, but did not comment as to whether other lower brominated congeners were being formed.

Table 3.4 Detailed analysis of the products for photolysis of decabromodiphenyl ether on humic acid-coated sand (Jafvert and Hua, 2001b)

PBDE congener	Method detection limit (ng/kg sand)	Level in laboratory blank (ng/kg sand)			Level in 0 hour samples (ng/kg sand)			Level in 72 hour samples (ng/kg sand)		
		Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Mean[a]	Rep. 1	Rep. 2	Mean[a]
2-MonoBDE	2,290	nd	nd	nd	nd	nd		nd	nd	
3-MonoBDE	1,610	nd	nd	nd	nd	nd		nd	nd	
4-MonoBDE	1,470	nd	nd	nd	nd	nd		nd	nd	
2,4-DiBDE	13.6	nd	nd	nd	nd	40.9	23.9±24.1	54.0	nd	30.4±33.4
2,4'DiBDE	10.7	16.2	50.8	50.9	127	153	140±18	148	106	127±30
2,6-DiBDE	12.5	nd	nd	nd	nd	nd		nd	nd	
3,3'-DiBDE	not given	nd	nd	nd	nd	nd		nd	nd	
3,4-DiBDE	8.82	nd	nd	nd	nd	nd		nd	nd	
3,4'-DiBDE	9.72	nd	nd	nd	nd	nd		31.6	nd	18.2±18.9
4,4'-DiBDE	8.16	nd	nd	nd	6,860	9,650	8,255±1,973	14,800	2,090	8,445±8,987
2,2',4'-TriBDE	27.3	79.0	42.3	79.4	223	191	207±23	276	nd	145±186
2,3',4-TriBDE	31.0	nd	nd	nd	nd	nd		nd	nd	
2,4,4'-TriBDE	32.9	133	109	141	423	367	395±40	644	283	463±255
2,4,6-TriBDE	29.4	nd	nd	nd	nd	nd		nd	nd	
2,4',6-TriBDE	27.2	nd	nd	nd	nd	nd		nd	nd	
2',3,4-TriBDE	not given	nd	nd	nd	nd	nd		nd	nd	
3,3',4-TriBDE	19.1	nd	nd	nd	nd	nd		nd	nd	
3,4,4'-TriBDE	25.7	nd	nd	nd	nd	nd		nd	nd	
2,2',4,4'-TetraBDE	19.2	403	394	467	65,000	64,500	64,750±354	53,500	7,630	30,565± 32,435
2,2',4,5'-TetraBDE	30.2	30.9	nd	nd	nd	nd		147	nd	81.0±93.3

Table 3.4 continued overleaf.

Table 3.4 continued.

PBDE congener	Method detection limit (ng/kg sand)	Level in laboratory blank (ng/kg sand)			Level in 0 hour samples (ng/kg sand)			Level in 72 hour samples (ng/kg sand)		
		Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Mean[a]	Rep. 1	Rep. 2	Mean[a]
2,3',4,4'-TetraBDE	39.2	113	74.8	114	1,100	1,070	1,085±21	905	377	641±373
2,3',4',6-TetraBDE	27.2	nd	nd	nd	nd	nd		nd	nd	
2,4,4',6-TetraBDE	22.5	91.1	26.2	99.6	279	214	247±46	165	156	161±6
3,3'4,4'-TetraBDE	22.1	nd	nd	nd	104	nd	57.5±65.7	nd	nd	
2,2',3,4,4'-PentaBDE	29.6	97.4	79.5	196	nd	406	210±277	nd	nd	
2,2',4,4',5-PentaBDE	25.4	417	331	482	1,570	1,160	1,365±290	4,170	923	2,547±2,296
2,2',4,4',6-PentaBDE	14.9	159	146	247	631	453	542±126	1,410	423	917±698
2,3,3',4,4'-PentaBDE	47.2	80.0	nd	nd	nd	nd		nd	nd	
2,3,4,5,6-PentaBDE	49.3	nd	nd	nd	nd	nd		nd	nd	
2,3',4,4',6-PentaBDE	24.7	nd	nd	nd	nd	nd		2,470	387	1,429±1,473
3,3',4,4',5-Penta	17.8	nd	nd	nd	nd	nd		nd	nd	
2,2',3,4,4',5'-Hexa	79.0	nd	nd	174	983	1,320	1,152±238	14,100	nd	7,070±9,942
2,2',3,4,4',6'-Hexa	47.7	nd	nd	nd	nd	nd		6,140	851	3,496±3,740
2,2',4,4',5,5'-Hexa	77.3	160	199	232	5,990	6,210	6,100±156	31,200	2,920	17,060± 19,997
2,2',4,4',5,6'-Hexa	37.5	159	91.7	169	1,320	1,000	1,160±226	26,700	2,960	14,830± 16,787
2,2',4,4',6,6'-Hexa	25.4	nd	nd	nd	nd	nd		1,570	429	1,000±807
2,3,4,4',5,6-Hexa	not given	nd	nd	nd	nd	nd		nd	nd	
2,2',3,4,4',5,6-Hepta	127	nd	nd	nd	nd	nd		26,600	nd	13,332± 18,764

Table 3.4 continued overleaf.

Table 3.4 continued.

PBDE congener	Method detection limit (ng/kg sand)	Level in laboratory blank (ng/kg sand)			Level in 0 hour samples (ng/kg sand)			Level in 72 hour samples (ng/kg sand)		
		Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Mean[a]	Rep. 1	Rep. 2	Mean[a]
2,2',3,4,4',5',6-Hepta	80.7	nd	nd	nd	22,100	20,800	21,450±919	140,000	16,700	78,350± 87,186
2,3,3',4,4',5,6-Hepta	165	nd	nd	nd	nd	nd		52,200	6,270	29,235± 32,477
2,2',3,3',4,4',5,5',6-Nona	188	nd	nd	nd	1,780,000	1,890,000	1,835,000± 77,782	2,400,000	149,000	1,274,500± 1,591,697
2,2',3,3',4,4',5,6,6'-Nona	188	nd	nd	nd	1,050,000	1,170,000	1,110,000± 84,853	2,130,000	175,000	1,152,500± 1,382,394
2,2',3,3',4,5,5',6,6'-Nona	188	nd	nd	nd	490,000	526,000	508,000± 25,456	1,710,000	143,000	926,500± 1,108,036
Total DiBDE		nd	nd	nd	9,570	12,900	11,235± 2,355	19,500	2,980	11,240± 11,681
Total TriBDE		1,510	1,690	50.9	7,560	7,280	7,420±140	7,560	3,980	5,770±2,531
Total TetraBDE		403	nd	1,800	66,100	64,500	65,300±1,13 1	53,700	7,910	30,805± 32,378
Total PentaBDE		673	146	467	2,200	1,160	1,680±735	6,910	1,190	4,050±4,045
Total HexaBDE		198	91.7	712	8,580	1,000	4,790±5,360	105,000	7,770	56,385± 68,752
Total HeptaBDE		nd	nd	nd	272,000	440,000	356,000± 118,794	1,830,000	121,000	975,500± 1,208,446
Total OctaBDE		nd	173	nd	1,240,000	1,140,000	1,190,000± 70,711	3,330,000	293,000	1,811,500± 2,147,483

Note: 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.

In order to analyse these data further, the rapporteur has carried out a relatively crude comparison of the mean and standard deviation of the concentrations of each isomer at the start and end of the experiment. These data are shown in **Table 3.4**. It is clear that there is considerable variation within the concentrations found in the two replicates, making it difficult to draw definite conclusions over whether there was a real increase in the concentrations of the lower congeners over the exposure period. However, there is some evidence that some lower brominated congeners, in particular 2,2'4,4',6,6-hexabromodiphenyl ether, were formed in the experiment (i.e. the mean concentration minus the standard deviation at 72 hours was higher than the mean concentration plus standard deviation at 0 hours), and for some congeners (for example several other hexa- and heptabromodiphenyl ether congeners) the mean concentration at 72 hours was higher than at 0 hour but there was overlap of the standard deviation ranges.

It is recognised that, due to the low sample size and high variability in the results, this comparison is relatively crude, but it does show that there are indications that several lower brominated congeners may have been formed, albeit at very low concentrations/yields, during this experiment.

The third series of experiments investigated the solar irradiation of decabromodiphenyl ether adsorbed onto quartz tubes containing humic acid solution (Jafvert and Hua, 2001a). The samples used were prepared by adding 1 ml of a $2 \cdot 10^{-5}$ M solution of decabromodiphenyl ether in toluene in a cylindrical quartz tube and then evaporating off the solvent under a stream of nitrogen gas. As the solvent was evaporated, the tubes were rotated at an angle of 45^{o} to ensure even coverage of the surface. The amount of decabromodiphenyl ether present in the tube was 0.019 mg. A solution of humic acid in water (2 ml of a 100 mg/l solution) was then added to each tube. Exposure was carried out using natural sunlight (9 am to 5 pm). Dark controls and control samples were also prepared.

The results from the experiments in quartz tubes showed a decrease in the decabromodiphenyl ether concentration and increase in bromide ion concentration with irradiation time. The decabromodiphenyl ether disappeared relatively quickly over the first 24 hours of exposure, after which the concentration remained relatively stable, whereas the accumulation of bromide ion showed an almost linear increase from 12 hours to the end of the 72-hour exposure period. Approximately 70% of the initial decabromodiphenyl ether remained after 72 hours exposure. The dark controls only showed a slight decrease in concentration over time (~1% decrease), and showed no detectable levels of bromide ion. The different pattern in the kinetics of disappearance of the decabromodiphenyl ether and the appearance of bromide ion indicated that the production of bromide ion continued after the loss of parent compound had slowed, i.e. bromide was being generated from the initial degradation products. The bromine mass balance for the system indicated that ~70% of the total bromine present was accounted for by decabromodiphenyl ether or bromide ion, with the remaining 30% being present as unidentified compounds. Analysis by HPLC did not indicate the presence of any lower brominated diphenyl ether congener, except possibly the nona- or octabromodiphenyl ethers.

The fourth series of experiments by Jafvert and Hua (2001a) investigated the solar irradiation of decabromodiphenyl ether in quartz tubes. These were prepared and tested in an identical way to the previous quartz tube experiments, except that no humic acid was present in the water added to the tube. The results of these tests showed a much more rapid loss of decabromodiphenyl ether than found with the analogous experiments with humic acid present. Approximately 29% of the initial decabromodiphenyl ether remained after 72 hours irradiation, and the rate of loss was relatively constant over the entire 72-hour period. Bromide ion was also shown to accumulate at a steady rate over the 72-hour period. Analysis of the dark controls showed that no bromide ion

was present and no significant loss of decabromodiphenyl ether had occurred. The mass balance indicated that approximately 50% of the total bromine was present as either decabromodiphenyl ether or bromide ion. The identity of the remaining 50% could not be determined with the analytical methods used. HPLC analysis did not indicate the presence of any lower brominated diphenyl ether congeners except possibly nona- or octabromodiphenyl ethers.

The difference between the experiments in quartz tubes with and without humic acids can be explained in terms of the humic acids themselves absorbing light and thus attenuating the degradation process.

The fifth set of experiments investigated the photolysis of decabromodiphenyl ether in a Rayonet Reactor using two 3,000 Å lamps (Jafvert and Hua, 2001a). The exposures were carried out in quartz tubes prepared in a similar way to the experiments above with natural sunlight. Each tube contained 0.019 mg of decabromodiphenyl ether and 2 ml of water. Exposure was via a merry-go-round system which rotated at 5 rpm. Controls and dark controls were also run.

The results from this series showed that decabromodiphenyl ether was rapidly degraded under the conditions used. Around 31% of the initial amount of decabromodiphenyl ether remained after 60 hours photolysis. A decline in the amount of decabromodiphenyl ether present in the dark control was also seen over the 60-hour period, but this decline was at a much slower rate than seen in the irradiated samples, and little or no bromide ion was detected in the dark controls. Bromide ion was found to rapidly accumulate in the irradiated samples, but the amount accumulated levelled off after 24 hours exposure. The bromine mass balance indicated that decabromodiphenyl ether and bromide ion accounted for a substantial proportion of the total bromine present and indicated that once decabromodiphenyl ether had degraded, any transformation by-products or intermediates also degraded quickly. The fraction of bromine as unidentified products was always <27%.

The sixth series of experiments essentially repeated the fifth series but used four instead of two 3,000 Å lamps as the irradiation source (Jafvert and Hua, 2001a). Each quartz tube contained 0.77 mg of decabromodiphenyl ether and 2 ml of water. The primary objective of this series of experiments was to identify any by-products formed by using a higher initial concentration of decabromodiphenyl ether. Under these conditions, decabromodiphenyl ether was found to degrade more slowly than in the previous series of experiments using the Rayonet Reactor, and a significant amount of decabromodiphenyl ether remained even after 240 hours irradiation. The accumulation of bromide ion followed a linear trend over the 240-hour exposure period. There was an apparent loss of decabromodiphenyl ether in the dark control samples over the same timeframe, however this loss was much less than seen in the irradiated samples. The bromine mass balance indicated that decabromodiphenyl ether and bromide ion accounted for a significant proportion of the total bromine present over the course of the experiment, indicating again that once formed, any intermediate degradation products from decabromodiphenyl ether themselves degraded quickly. The amount of unidentified bromine never exceeded ~20% of the total throughout the study. HPLC analysis indicated the presence of small amounts of substances with elution times shorter than the octabromodiphenyl ether congeners of a commercial octabromodiphenyl ether product, which may indicate the presence of lower brominated diphenyl ethers. Unfortunately, no GC-MS analysis of these products was undertaken.

Following on from the studies with decabromodiphenyl ether, 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, 2001c). Two replicate exposures were carried out using the same conditions as indicated above. The results of the experiment are shown in **Table 3.5**, 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 (in a similar way as was done in this assessment for the decabromodiphenyl ether data in **Table 3.4**), 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.

Table 3.5 Detailed analysis of the products for photolysis of tetrabromodiphenyl ether with natural sunlight (Jafvert and Hua, 2001c)

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 3.5 continued overleaf

Table 3.5 continued

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 3.5 continued overleaf

Table 3.5 continued

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	

Note: 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.

Summary of photodegradation

The available data on photodegradation of decabromodiphenyl ether clearly show that the substance photodegrades under a wide range of conditions.

Studies carried out using organic solvents indicate that products such as lower brominated diphenyl ether congeners (which are potentially more toxic and accumulative than the parent compound) and in some cases polybrominated dibenzofurans are formed using either UV and natural sunlight. However, as organic solvents can act as hydrogen donors in these reactions and so potentially affect the distribution of products formed, there is some uncertainty in extrapolation of these results to the likely products formed in the environment.

Several studies have also investigated the degradation of decabromodiphenyl ether under more environmentally relevant conditions using solid matrices in contact with water and either natural or artificial sunlight, for example Sellström et al. (1998a), Örn (1997), and Jafvert and Hua (2001a). These studies all show that decabromodiphenyl ether is likely to undergo photodegradation in the environment and that debromination to give lower brominated diphenyl ether congeners does occur, although these are not generally the major degradation products formed. It is also clear that the lower brominated congeners formed can also undergo photodegradation themselves, as seen in the study by Jafvert and Hua (2001c) with 2,2',4,4'-tetrabromodiphenyl ether.

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 formed in 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 decabromodiphenyl 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 decabromodiphenyl ether. There is insufficient information available to estimate the actual rates of photodegradation of decabromodiphenyl 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. Recent experiments 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 decabromodiphenyl ether into the system.

Many of the recent experiments have used solid decabromodiphenyl ether adsorbed onto surfaces. Although these systems may provide exposure conditions that may be relevant to the environment, it is not possible to infer from these studies the likely rate and extent of the degradation in the environment. This is because the exposure conditions in the laboratory studies are intended to maximise the exposure (e.g. by use of thin surface films of the substances). In the environment, where decabromodiphenyl 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 pathways must also be occurring by other pathways, although the products from these reactions are so far unknown.

Photodegradation of decabromodiphenyl ether is also likely occur in the atmosphere, where decabromodiphenyl ether is likely to be adsorbed onto atmospheric particulates.

Overall, although it is clear that photodegradation of decabromodiphenyl ether could occur in the environment, it is not possible to estimate the amount of lower brominated congeners that may be formed from this reaction. The available evidence indicates that the lower brominated congeners, if formed, will be only minor products, but there is uncertainty over the actual significance of the process in the environment, and not all products from the process are clear.

Atmospheric photooxidation

A second order rate constant for the reaction of decabromodiphenyl ether with atmospheric hydroxyl radicals has been calculated as $1.7 \cdot 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} from the chemical structure using the Syracuse Research Corporation AOP program. Assuming a hydroxyl radical concentration of $5 \cdot 10^5$ molecule/cm^3, an atmospheric half-life of 94 days can be estimated.

Hydrolysis

Gallet et al. (2001) reported that no major degradation products were found when 5 mg of decabromodiphenyl ether was placed in sealed vials containing 15 ml of water at pH 5 or pH 7 for six weeks at 100°C. Therefore decabromodiphenyl ether can be considered to be stable to hydrolysis.

3.1.1.5.2 Biodegradation

Aerobic conditions

The biodegradability of decabromodiphenyl ether has been studied under aerobic conditions using an activated sludge inoculum. Decabromodiphenyl ether (100 mg/l) was incubated with activated sludge (30 mg/l) from mixed sources in Japan over a 2-week period (equivalent to MITI I test). No degradation (as measured by BOD) was seen, therefore decabromodiphenyl ether is not readily biodegradable (CITI, 1992).

This result indicates that decabromodiphenyl ether is unlikely to biodegrade rapidly in the environment under aerobic conditions.

Anaerobic conditions

From the data generated for other halogenated aromatic substances (see Appendix F), there is a possibility for reductive dehalogenation to occur under some conditions. If such a process occurs for decabromodiphenyl ether, this could lead to the formation of more toxic and bioaccumulative congeners. An anaerobic degradation study has recently been undertaken with decabromodiphenyl ether and 2,2',4,4'-tetrabromodiphenyl ether in order to address these concerns.

KEMI (1994) and de Wit (2000) reported that no degradation/transformation of decabromodiphenyl ether was seen after four months incubation in sediment samples under anaerobic conditions. The inoculum used was an enrichment culture from a polybrominated diphenyl ether-contaminated sediment. The incubation of one of the anaerobic cultures was extended to two years, but no degradation of decabromodiphenyl ether was seen over this timeperiod. Unfortunately no further details of this test were reported.

The anaerobic biodegradation of ^{14}C-labelled decabromodiphenyl ether has been studied in a sediment-water system over 32 weeks (Schaefer and Flaggs, 2001a). A positive control (^{14}C-labelled glucose) was also tested in the same system. The decabromodiphenyl ether tested was a mixture of unlabelled substance (supplied as a composite sample from three manufacturers; purity 97.4% decabromodiphenyl ether, 2.5% nonabromodiphenyl ether and 0.04% octabromodiphenyl ether) with ^{14}C-labelled decabromodiphenyl ether (radiochemical purity 96.8%).

The sediment and accompanying overlying surface water used in the test was collected from the Schuykill River, Valley Forge, Pennsylvania, USA. The redox potential of the sediment was -284 mV. The sediment had an average moisture content of 26%, a pH of 6.3 and an organic matter content of 1.4%. A 0.2 mg/l resazurin solution was prepared using the collected overlying surface water.

The test chambers consisted of 500 ml bottles containing 300 ml of the sediment and were prepared in an anaerobic chamber. The sediment was carefully added to the bottles in order to maintain the sediment column structure. The decabromodiphenyl ether was tested at nominal concentrations of either 5 mg/kg or 500 mg/kg, and three replicate chambers were used at each concentration. In addition, a further six treatment groups at 5 mg/kg and 500 mg/kg were run to allow the concentrations of decabromodiphenyl ether and any metabolites to be determined at the start and end of the test. The ^{14}C-labelled test substance was added to dry sediment as a solution in tetrahydrofuran and allowed to stand for 24 hours for the solvent to evaporate. The unlabelled test substance was added by direct weight addition to give the desired nominal concentrations. The test substance was added to the surface of the sediment and mixed into the top 2.5 cm. Approximately 10 ml of the resazurin solution was then added to the sediment system. The positive glucose control was tested at a concentration of 5 mg/kg in duplicate chambers. The sediment used in these control chambers was treated with pure tetrahydrofuran in an identical way as for the decabromodiphenyl ether treatments before the glucose was added as a solution in pure water and mixed into the top 2.5 cm.

The test chambers were incubated at ambient room temperature (22^{o}C) in an anaerobic chamber. The test chambers were kept in the dark during the test. The headspaces in the chambers were continually purged with nitrogen and the production of $^{14}CO_2$ and $^{14}CH_4$ was determined over the 32-week incubation period. In addition, at the end of the incubation period, samples from each treatment group were analysed for decabromodiphenyl ether and the presence of any degradation products by a HPLC method using both UV and radiometric detection.

The mass balance results from the experiment are shown in **Table 3.6**.

Table 3.6 Anaerobic degradation of ^{14}C-labelled decabromodiphenyl ether

Nominal concentration	Mass balance at week 32			
	% as 14CO2	% as 14CH4	% 14C in solids	Total % recovery of 14C
5 mg/kg	0.4±0.04	0.4±0.04	129.9±24.1	130.9±24.1
500 mg/kg	0.4±0.03	0.4±0.06	122.5±7.9	123.3±7.9
Positive control (glucose at 5 mg/kg)	67.2±2.1	18.1±1.1	9.5±4.9	94.9±1.8

For the positive control, an average of 95% of the total radioactivity added as glucose was recovered from the system, with 85% being converted to $^{14}CO_2$ and $^{14}CH_4$ and 10% being associated with the sediment-phase. The degradation seen in the positive control indicates that the sample pre-treatment methods (e.g. use of tetrahydrofuran solvent) appeared to have had little effect on the viability of the microbial community present.

For decabromodiphenyl ether, <1% of the total radioactivity added was found as $^{14}CO_2$ and $^{14}CH_4$ indicating that essentially no mineralisation had occurred. Parent compound analysis (mean of seven replicate samples) indicated that the concentrations of decabromodiphenyl ether in the nominal 5 mg/kg treatment were 6.64±0.70 mg/kg at day 0 and 6.51±2.15 mg/kg at week 32. Similarly, the measured concentrations of decabromodiphenyl ether in the nominal 500 mg/kg treatment were 543±77 mg/kg at day 0 and 612±158 mg/kg at week 32. The differences in concentration between day 0 and week 32 were not statistically significant (the composition of the sediment cores were found to account for some of the variability seen in the measured concentrations, with sediments containing a greater number of stones leading to a higher variability between replicate measurements of concentration).

The HPLC chromatographic profiles also indicated that traces of some ^{14}C-labelled components with shorter retention times than decabromodiphenyl ether were present in some of the 32-week samples in the 5 mg/kg treatment group. Similar components also appeared to be present in the stock solution of the ^{14}C-labelled decabromodiphenyl ether test material used in the study. In addition to the HPLC analysis, a more detailed GC-MS analysis was carried out on several sediment samples at day 0 and week 32 of the experiment (the samples were randomly selected and so the replicates analysed at week 32 were not necessarily the same as those analysed at day 0) to see if trace amounts of lower brominated diphenyl ether congeners were formed (Schaefer and Flaggs, 2001b). The results are shown in **Table 3.7**.

Table 3.7 Results of trace analysis for polybrominated diphenyl ether products from the anaerobic degradation of decabromodiphenyl ether

Congeners	Concentration[b] in laboratory blanks (ng/kg dry weight)						Concentration[b] in experimental samples (ng/kg dry weight)					
	A	B	C	D	E	F	Control sediment sample	Day 0 sample (5 mg/kg treatment)	Day 0 sample (500 mg/kg treatment)	Week 32 sample[a] (5 mg/kg treatment)	Week 32 sample (5 mg/kg treatment)	Week 32 sample (500 mg/kg treatment)
2-MonoBDE	<2,470	<2,320	<2,290	<2,230	<3,050	<3,350	<1,480	<1,760	<1,900	<2,180 and <6,860	<2,550	<1,470
3-MonoBDE	<1,730	<1,630	<1,610	<1,470	<2,010	<2,200	<975	<1,160	<1,250	<1,530 and <4,810	<1,680	<971
4-MonoBDE	<1,590	<1,490	<1,470	<1,350	<1,850	<2,030	<899	<1,060	<1,150	<1,400 and <4,410	<1,550	<895
2,4-DiBDE	<15.3	<13.8	<13.6	<21.8	<19.4	<27.3	<36.6	<34.4	66.6	<16.1 and <21.8	262	267
2,4'DiBDE	50.8	50.9	16.2	<16.7	<14.9	<20.9	<28.0	<26.3	<18.4	49.4 and 24.2	87.1	80.3
2,6-DiBDE	<14.1	<12.7	<12.5	<20.5	<18.2	<25.6	<34.3	<32.3	<22.5	<14.8 and <20.1	<22.0	<18.7
3,3'-DiBDE												
3,4-DiBDE	<9.98	<8.96	<8.82	14.3	<11.5	<16.2	<21.7	<20.4	<14.2	<10.5 and <14.2	<13.9	22.9
3,4'-DiBDE	<11.0	<9.87	<9.72	<16.4	<14.6	<20.5	<27.5	<25.9	<18.0	<11.5 and <15.6	<17.6	46.0
4,4'-DiBDE	<9.23	<8.29	<8.16	<13.1	<11.7	<16.4	<22.0	<20.7	16.6	10.2 and 13.2	60.2	59.6
2,2',4-TriBDE	42.3	79.4	79.0	<45.9	<31.3	<39.8	119	47.4	74.7	88.8 and 114	398	404
2,3',4-TriBDE	<30.5	<44.1	<31.0	<56.7	<38.6	<49.0	<52.0	<45.2	<39.6	<51.5 and <63.4	60.6	36.3
2,4,4'-TriBDE	109	141	133	<57.8	45.8	<50.0	117	74.3	167	167 and 129	239	250
2,4,6-TriBDE	<28.9	<41.8	<29.4	<53.4	<36.4	<46.2	<49.0	<42.6	<37.3	<48.8 and <60.1	<40.8	<29.0
2,4',6-TriBDE	<26.7	<38.7	<27.2	<48.8	<33.3	<42.3	<44.8	<39.0	<34.1	<45.1 and <55.6	<37.3	<26.5
2',3,4-TriBDE												
3,3',4-TriBDE	<18.8	<27.2	<19.1	<34.1	<23.2	<29.5	<31.3	<27.2	<23.8	<31.7 and <39.1	<26.0	25.0
3,4,4'-TriBDE	<25.2	<36.5	<25.7	<44.6	<30.4	<38.6	<40.9	<35.6	<31.2	<42.7 and <52.5	<34.1	<24.2

Table 3.7 continued overleaf

Table 3.7 continued

Congeners	Concentration[b] in laboratory blanks (ng/kg dry weight)						Concentration[b] in experimental samples (ng/kg dry weight)					
	A	B	C	D	E	F	Control sediment sample	Day 0 sample (5 mg/kg treatment)	Day 0 sample (500 mg/kg treatment)	Week 32 sample[a] (5 mg/kg treatment)	Week 32 sample (5 mg/kg treatment)	Week 32 sample (500 mg/kg treatment)
2,2',4,4'-TetraBDE	394	467	403	259	209	224	3,690	1,380	1,600	996 and 1,200	5,290	4,080
2,2',4,5'-TetraBDE	<21.6	<33.7	30.9	<26.4	<27.4	<19.3	305	95.6	129	122 and 120	1,020	804
2,3',4,4'-TetraBDE	74.8	114	113	<32.9	<34.1	<24.0	<80.3	<107	<41.5	138 and 192	227	277
2,3',4',6-TetraBDE	<19.5	<30.5	<27.2	<26.1	<27.1	<19.1	<63.8	<84.8	<32.9	<24.8 and 31.9	85.3	139
2,4,4',6-TetraBDE	26.2	99.6	91.1	<21.5	<22.3	<15.7	<52.5	<69.8	<27.1	102 and 92.5	<19.4	33.1
3,3'4,4'-TetraBDE	<15.8	<24.7	<22.1	<18.3	<19.0	<13.4	<44.7	<59.4	<23.1	<20.1 and <23.5	<16.5	<11.3
2,2',3,4,4'-PentaBDE	79.5	196	97.4	<42.5	55.9	32.0	225	<141	<154	243 and 152	314	361
2,2',4,4',5-PentaBDE	331	482	417	188	135	233	4,650	1,910	2,460	1,470 and 1,120	6,760	5,130
2,2',4,4',6-PentaBDE	146	247	159	33.5	<21.9	51.0	1,000	342	363	372 and 294	1,270	992
2,3,3',4,4'-PentaBDE	<99.3	<91.1	80.0	<64.8	<72.2	<46.9	<343	<216	<235	<83.9 and <120	<19.1	459
2,3,4,5,6-PentaBDE	<104	<95.3	<49.3	<66.8	<74.4	<48.3	<353	<222	<242	<87.7 and <126	350	1,120
2,3',4,4',6-PentaBDE	<52.1	<47.8	<24.7	<33.6	<37.4	<24.3	<178	<112	<122	<44.0 and <63.2	<98.8	235
3,3',4,4',5-PentaBDE	<37.5	<34.4	<17.8	<25.9	<28.8	<18.7	<137	<86.1	<93.6	37.8 and <45.5	<76.1	<87.8
2,2',3,4,4',5'-HexaBDE	<114	174	<79.0	<122	<142	<114	<432	<426	1,620	244 and <153	<296	2,080

Table 3.7 continued overleaf

Table 3.7 continued

Congeners	Concentration[b] in laboratory blanks (ng/kg dry weight)						Concentration[b] in experimental samples (ng/kg dry weight)					
	A	B	C	D	E	F	Control sediment sample	Day 0 sample (5 mg/kg treatment)	Day 0 sample (500 mg/kg treatment)	Week 32 sample[a] (5 mg/kg treatment)	Week 32 sample (5 mg/kg treatment)	Week 32 sample (500 mg/kg treatment)
2,2',3,4,4',6'-HexaBDE	<68.9	<65.2	<47.7	<68.2	<79.2	<63.4	<241	<237	345	<78.4 and <92.7	<165	1,710
2,2',4,4',5,5'-HexaBDE	199	232	160	<110	<127	<102	834	616	11,100	622 and 859	1,530	15,900
2,2',4,4',5,6'-HexaBDE	91.7	169	159	75.5	<64.3	<51.4	483	250	1,670	471 and 670	824	2,790
2,2',4,4',6,6'-HexaBDE	<36.7	<34.7	<25.4	<39.0	<45.3	<36.3	<138	<136	<106	<41.8 and 80.5	124	<51.1
2,2',3,4,4',5,6-HeptaBDE	<98.2	<146	<127	<153	<107	<146	<381	<687	2,020	<517 and <511	<483	11,100
2,2',3,4,4',5',6-HeptaBDE	<62.2	<92.5	<80.7	<115	<128	<83.4	721	2,050	47,000	1,830 and 1,490	1,740	67,700
2,3,3',4,4',5,6-HeptaBDE	<127	<189	<165	<204	<143	<193	<506	917	7,530	<670 and <663	<642	31,900
2,2',3,3',4,4',5,5',6-NonaBDE	<173	<208	<188	<393	<384	<240	2,160	52,200	3,950,000	47,000 and 47,700	52,000	5,430,000
2,2',3,3',4,4',5,6,6'-NonaBDE	<173	<208	<188	<393	<384	<240	1,810	52,200	1,350,000	45,400 and 46,900	51,400	2,590,000
2,2',3,3',4,5,5',6,6'-NonaBDE	<173	<208	<188	<393	<384	<240	1,220	26,800	443,000	24,300 and 22,400	25,200	930,000
DecaBDE	<4,560	<3,860	<7,880	<16,100	<12,600	<13,500	142,000	not analysed	not analysed	not analysed	not analysed	not analysed

Notes: a) Duplicate analyses of the same sample.
b) Concentrations given as less than values indicate that the congener was not detected at the limit of detection.

The original paper indicated that these GC-MS results showed no evidence for the formation of lower brominated congeners from decabromodiphenyl ether under the conditions of the test. For the 5 mg/kg dry weight treatments, the levels measured in the week 32 samples are comparable with the levels measured in the day 0 samples or the laboratory blanks for all congeners. In the 500 mg/kg treatment, the levels of nona- to penta/hexabromodiphenyl ether congeners found in the week 32 sample appear to be similar but slightly higher than the concentrations found in the day 0 sample, but, owing to the small sample size, it is not possible to determine if these differences are significant. Given the variation seen in the results of the analysis of the week 32 samples from the 5 mg/kg treatment, it is most likely that any differences seen between the day 0 and week 32 samples from the 500 mg/kg treatments are due to the random errors inherent in the experimental methodology.

Overall, decabromodiphenyl ether was found to be stable under the conditions used in the test, and so this type of process is not expected to lead to the formation of significant amounts of lower brominated congeners.

de Boer et al. (2001) also concluded that it was unlikely that significant amounts of lower brominated diphenyl ethers were being formed from decabromodiphenyl ether in sediment, unless it was occurring at an extremely slow rate. This conclusion was based on the results of a detailed survey of the levels of polybrominated diphenyl ethers in various sediment cores which showed that although the concentration of decabromodiphenyl had increased in recent years there was generally no parallel increase in the concentrations of lower brominated diphenyl ethers (tetra- to penta- congeners) and no indication of increasing levels of nona- and octabromodiphenyl ethers.

A further similar anaerobic degradation study has been carried out with 2,2',4,4'-tetrabromodiphenyl ether (Schaefer and Flaggs, 2001c). 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 3.8**.

Table 3.8 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 seven 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 significant.

Therefore, based on the measured mass and concentrations of 2,2'4,4'-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 one and three 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 decabromodiphenyl ether directly, they do provide some evidence that other lower brominated diphenyl ethers may also have the potential to biodegrade under anaerobic conditions in the environment. These findings are considered further in the Risk Assessment Report for octabromodiphenyl ether (RAR, 2002).

3.1.1.5.3 Summary of degradation rates used for environmental modelling

From the preceding Sections there is some evidence that decabromodiphenyl ether may photodegrade in the environment under certain conditions, but it is not possible to estimate the rate or extent of this reaction. Decabromodiphenyl 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 decabromodiphenyl ether is a possibility, the rate of reaction will be assumed to be effectively zero for environmental modelling purposes.

The rate of degradation of decabromodiphenyl ether under aerobic and anaerobic conditions appears to be very low. The rate of biodegradation will be assumed to be effectively zero for environmental modelling purposes.

Decabromodiphenyl ether is predicted to react with atmospheric hydroxyl radicals, and a reaction rate constant of $1.7 \cdot 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} will be used for this reaction in the environmental modelling.

Decabromodiphenyl 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).

3.1.1.6 Distribution

Since decabromodiphenyl ether is a mixture of compounds of differing degrees of bromination (mainly nona- and 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 relevant degrees of bromination have to be considered 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 large 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 (the air compartment is of relatively minor importance to this assessment).

3.1.1.6.1 Volatilisation

The vapour pressure of commercial decabromodiphenyl ether has been determined as $4.63 \cdot 10^{-6}$ Pa at 21°C using a spinning rotor method. Since decabromodiphenyl ether is a mixture, the vapour pressure measured is likely to represent that of the most volatile components of the mixture. This value has been used in the EUSES modelling.

Brominated diphenyl ethers all have low vapour pressures, the vapour pressure tending to decrease with increasing bromination. Watanabe and Tatsukawa (1990) determined the vapour pressures for a range of brominated diphenyl ethers at 25°C using a gas chromatography (GC) technique. The results are shown in **Table 3.9**.

No information was given as to the actual composition of the substances tested. However, the method is based on determining the GC 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 vapour pressures will be obtained from the method. The results can thus be taken to represent the vapour pressures of the most and least volatile isomers in the products tested.

Table 3.9 Vapour pressures of polybrominated diphenyl ethers

Polybrominated diphenyl ether	Vapour pressure at 25°C (Pa)
Dibromodiphenyl ether	0.0127-0.0188
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	$4.2 \cdot 10^{-6}$-$9.5 \cdot 10^{-6}$
Octabromodiphenyl ether	$1.2 \cdot 10^{-7}$-$2.3 \cdot 10^{-7}$

The low vapour pressure for commercial decabromodiphenyl ether indicates that decabromodiphenyl ether is unlikely to volatilise from spillage to land. However, given the very low water solubility of this substance, volatilisation from surface water may still occur to a small extent, although adsorption onto sediment is likely to dominate and further reduce this tendency. Based on a vapour pressure of $4.63 \cdot 10^{-6}$ Pa and a water solubility of <0.1 µg/l, a Henry's Law constant of >44 Pa m^3/mol can be estimated (this value is uncertain due to difficulties in measuring reliable vapour pressures and water solubilities for this substance). Once in the atmosphere, it is likely to adsorb strongly onto atmospheric particles and subsequently be removed by wet or dry deposition. This may be a transport mechanism for decabromodiphenyl ether in the environment. However, the available monitoring data do not indicate widespread distribution of decabromodiphenyl ether in the environment away from sources of release.

3.1.1.6.2 Adsorption

Decabromodiphenyl ether is expected to adsorb strongly onto soil and sediment since it has a high octanol-water partition coefficient (log Kow = 5.24-9.97; see Section 1).

According to the Technical Guidance Document, soil organic carbon - water partition coefficients can be estimated for hydrophobic chemicals from log Koc = 0.81 · log Kow + 0.10. Thus Koc values of 22,100-$149 \cdot 10^6$ l/kg can be estimated. The value of Koc estimated using the measured log Kow value of 6.27 is 150,900 l/kg.

A soil organic carbon - water partition coefficient (Koc) value of 692,831 l/kg can be estimated for decabromodiphenyl ether based on a water solubility of 0.1 µg/l, using the relationship log Koc = -0.55 log S + 3.64, where s = solubility in mg/l (Lyman et al., 1982). A Koc value of 407,380 l/kg has been estimated for decabromodiphenyl ether using the EPI estimation program (see Section 3.1.1.6.4).

Watanabe (1988) measured a sediment - water partition coefficient for decabromodiphenyl ether. The partition coefficient was determined by adding sediment, to which decabromodiphenyl ether was already adsorbed, to clean water and a Kp(sed) of 79,433 l/kg was obtained. No information on the organic carbon content of the sediment was reported. If it is assumed that the sediment is 5% organic carbon (default from the Technical Guidance Document), then values of the partition coefficient for soil and suspended sediment can be estimated as Kp(soil) = 31,773 l/kg and Kp(susp) = 158,866 l/kg, assuming organic carbon contents of 2% and 10% for soil and suspended sediment respectively (i.e. Koc = $1.59 \cdot 10^6$ l/kg, which is in general agreement with the estimates given above). The equivalent values on a total compartment basis are $K_{soil\text{-}water}$

= 47,660 m^3/m^3, $K_{susp\text{-}water}$ = 39,717 m^3/m^3 and $K_{sed\text{-}water}$ = 39,800 m^3/m^3. These values will be used later in the assessment.

From the above information, it would be expected that decabromodiphenyl ether would be relatively immobile in soil and 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 decabromodiphenyl ether concentration of 1 kg/m^3 at a depth of 1 cm in the soil. No degradation in the soil was assumed and a value for Koc of $1.59 \cdot 10^6$ l/kg was used in the model. The model indicated that the majority of the decabromodiphenyl ether would occur in the top few centimetres of the soil, with an insignificant amount (zero) leaching into groundwater. The full output from the model can be found as Appendix C.

3.1.1.6.3 Accumulation

The bioconcentration of ^{14}C-labelled decabromodiphenyl ether (Dow FR-300-BA; 77.4% deca-, 21.8% nona- and 0.8% octabromodiphenyl ether) has been studied using rainbow trout under static conditions over a 48-hour period. A known bioaccumulative substance, 2,2',4,4'-tetrachlorobiphenyl (TCBP), at a concentration of 16 µg/l, was used as a positive control. During the experiment, little change in the concentration of the brominated diphenyl ether was seen in the water (initial concentration was 20 µg/l), indicating minimal uptake by the trout and insignificant losses by other means (e.g. volatilisation, adsorption onto surfaces etc.). The lack of bioconcentration of decabromodiphenyl ether was confirmed by analysis of flesh samples at intervals during the experiment. The results of the analysis are shown in **Table 3.10** and show little or no uptake of the test substance by the fish. The positive control, TCBP, was found to bioconcentrate at least 50 times over the initial exposure levels within 4 hours (Norris et al., 1973 and 1974). The concentrations of decabromodiphenyl ether used in this test are greater than the reported water solubility of the substance (<0.1 µg/l). No details are given in the paper on how the test solutions were made up in the study (i.e. if cosolvents/emulsifiers were used), and so the actual solubility of the substance in the test medium is unknown. Analysis of the concentration was carried out during the test and this indicated that the 20 µg/l exposure concentration was maintained, but no details of how these analyses were carried out were given. This study is also of only very short duration and may not have been long enough in order for the bioconcentration of decabromodiphenyl ether to reach equilibrium.

The bioconcentration of decabromodiphenyl ether has also been studied in carp over six weeks. Two exposure concentrations were used and the bioconcentration factors (BCFs) measured at the end of the experiment were <5 at an initial concentration of 60 µg/l and <50 at an initial concentration of 6 µg/l (the two values are consistent if no decabromodiphenyl ether was detected in the fish, and the detection limit in fish was around 300 µg/kg and indicate that little or no bioconcentration is occurring) (CITI, 1992). Few other details of this test are available, however, it is likely that a carrier solvent and emulsifier were used in the study, similar to the experiments with penta- and octabromodiphenyl ether carried out by the same institute (see the risk assessments of those two substances for further details). The water concentrations used in the study are greater than the known water solubility of decabromodiphenyl ether (<0.1 µg/l; see Section 1). The actual solubility of the substance in the test medium is unknown (a value of 20 µg/l is given in the CITI (1992) paper, but no details on how this was measured are given). It is possible that the actual dissolved concentration present in this test was less than indicated. If it is assumed that the substance was present at <0.1 µg/l, then the upper limit for the BCF would be <3,000 l/kg.

Based on its octanol-water partition coefficient (see **Table 1.2**), decabromodiphenyl ether would be expected to be bioaccumulative. However, experimental results indicate that commercial decabromodiphenyl ether does not appear to be taken up by fish in detectable amounts, probably due to its large size precluding crossing of cell walls in organisms and so it is considered to have a low bioaccumulation potential. It should be noted that the two bioconcentration studies were carried out at concentrations which exceed the water solubility of the substance, however in both cases, no detectable uptake of decabromodiphenyl ether was seen. Another possible criticism of the two fish bioconcentration studies, is that the duration of the study may not have been long enough for equilibrium to have been reached for a substance such as decabromodiphenyl ether. However, one of the studies was carried out for six weeks and, although this may still not have been long enough for equilibrium to have been reached, it was long enough to investigate if significant uptake would be expected.

Table 3.10 Results of bioconcentration studies of decabromodiphenyl ether in rainbow trout

Exposure time (hours)	Concentration of decabromodiphenyl ether in fish (µg/kg)[a]	Concentration of TCBP (positive control) in fish (µg/kg)
0	-	<100
0.5	-7	150
1	1	320
2	1	520
4	3	1,000
6	1	1,200
12	-2	1,300
24	3	1,200
48	6	1,000

Note: a) Concentrations based on ^{14}C measurements. Negative values indicate counting levels below the background radioactivity level.

A recent study has investigated the uptake of decabromodiphenyl ether by rainbow trout from food (Kierkegaard et al., 1997 and 1999). The substance used in the test was a commercial flame retardant (Dow FR-300-BA; the actual composition of this substance was not given in the paper but the composition of this product has been reported elsewhere as 77.4% deca-, 21.8% nona- and 0.8% octabromodiphenyl ether (Norris et al., 1973 and 1974) although it is recognised that the composition may have changed since this time), and the substance was purified on a charcoal column prior to use to remove planar compounds. The fish used in the test were juvenile rainbow trout which were kept in a continuous flow of charcoal-filtered brackish water at temperatures corresponding to those found outdoors in Sweden over the months June to September. The food used in the study was Barents Sea cod (*Gadus morhua*). The cod (excluding gonads, gall bladder and liver) was homogenised and mixed with an equal volume of 3% gelatine solution. The decabromodiphenyl ether was dissolved/suspended in corn oil and then mixed with the cod/gelatine solution. The mixture was then air dried and frozen until needed. The doses of decabromodiphenyl ether used in the experiment ranged between 7.5 and 10 mg/kg body weight/day. The fish were sampled for biological and chemical investigation after 16, 49 and 120 days. A further group were exposed for 49 days, followed by a 120-day depuration period. Fish were starved for 24-48 hours prior to sampling.

During the test, the lipid concentration in the rainbow trout muscle decreased from 3.3 to 1.3% in the exposed fish and 3.9 to 0.97% in the control fish and so the uptake of decabromodiphenyl ether in the fish was measured on a fresh weight basis. After 16 days exposure, the mean muscle

concentration of decabromodiphenyl ether was found to be 10 µg/kg fresh weight. The muscle concentration of decabromodiphenyl ether was found to increase with exposure time, reaching a level of 38 µg/kg fresh weight after 120 days. In the control fish, 4 out of the 34 muscle samples analysed showed traces of decabromodiphenyl ether (level <8% of the corresponding exposed fish). The concentration found in the livers of exposed fish exceeded those of the muscle (levels in liver were 560 µg/kg fresh weight after 16 days and 870 µg/kg fresh weight after 120 days). In the depuration phase of the experiment, the levels of decabromodiphenyl ether were found to decrease by a factor of 2 on a fresh weight basis after 71 days, but no decrease in the levels was observed when the results were expressed on a lipid basis. In both the liver and muscle, there was evidence that lower brominated diphenyl ethers were present (e.g. 2,2',4,4'-tetrabromodiphenyl ether; 2,2',4,4',5-pentabromodiphenyl ether; 2,2',4,4',6-pentabromodiphenyl ether), however, these compounds were also present at similar concentrations in control fish, and so were not related to the decabromodiphenyl ether treatment (i.e. were not metabolic products).

The concentrations of some hexa-, hepta-, octa- and nonabromodiphenyl ether congeners were also found to increase with exposure period in both muscle and liver. Some of these congeners were not detectable in the commercial decabromodiphenyl ether used in the study and it was thought that their presence was a result of either a) a metabolic process or b) an efficient absorption process of trace amounts initially present in the food/commercial product used. The study was not able to distinguish between these two possibilities (Kierkegaard et al., 1999).

The results indicated that only a very small proportion of the test material was taken up during the 120-day exposure phase of the experiment (uptake was estimated to be 0.02-0.13% based on the muscle concentrations of the total hexa- to decabromodiphenyl ethers present, or ~0.005% based on the decabromodiphenyl ether component only), although it is possible that steady state was not reached during the exposure part of this study.

A low bioaccumulation potential for decabromodiphenyl ether is shown in the results of metabolism studies in rats. Male and female rats were dosed with 1.0 mg of ^{14}C-labelled decabromodiphenyl ether as a suspension in corn oil. The composition of the commercial decabromodiphenyl ether used in the study was 77.4% deca-, 21.8% nona- and 0.8% octabromodiphenyl ether, but no details were given as to the position of the radio-label. The principle route of excretion of the dose was via the feces. Around 90.6% of the administered radioactivity was excreted in the feces within 24 hours and by 48 hours, all the administered radioactivity had been excreted (Norris et al. 1973 and 1974). Further, tissue accumulation studies of decabromodiphenyl ether in rats have also been reported. In these studies, rats were fed diets providing 0.1 mg/kg bw/day of decabromodiphenyl ether for 180 days. Various tissues (adipose tissue, liver, kidney, skeletal muscle, serum and testes) were analysed for bromine content by neutron activation analysis. The bromine contents of liver, kidney, skeletal muscle, serum and testes from the exposed animals were not significantly different from the levels found in unexposed controls. The bromine content of the adipose tissue of decabromodiphenyl ether dosed rats was found to be statistically increased at the $p<0.05$ level but not at the $p<0.01$ level when compared with controls (Norris et al. 1973 and 1974).

A similar low level of uptake of a decabromodiphenyl ether was seen in rat feeding studies reported by El Dareer et al. (1987). The decabromodiphenyl ether used was a mixture of unlabelled decabromodiphenyl ether (purity stated as 92%) and a ^{14}C-labelled decabromodiphenyl ether (radiochemical purity stated as 98.9%; no information on the congener distribution) and thus is not directly comparable with the commercial decabromodiphenyl ether products currently supplied. Male rats were given the decabromodiphenyl ether at levels of 0.025-5% of the diet (i.e. 0.25-50 g/kg food). After 24h, only trace amounts (<1% in total) of the radioactivity were found in organs or tissues (a maximum of 0.45% of the administered

radioactivity was found in liver and no other organ or tissue contained more than 0.26% of the radioactivity), and more than 99% of radioactivity was recovered in feces and gut content at 72h. In the feces of rat, three metabolites represented 1.5-27.9% of the radioactivity. Since absorption was minimal, most of the metabolism apparently took place in the intestinal tract.

Viberg et al. (2001) recently reported the findings of a study to investigate the uptake and retention of decabromodiphenyl ether in the brain of neonatal mice. The mice were given a single oral dose of ^{14}C-labelled decabromodiphenyl ether (purity >98%) on postnatal day 3, 10 or 19. The radioactivity in the brain was determined after 24 hours or 7 days after dosing. The results of the study showed that ^{14}C was taken up into the brain, but there were differences in the amount of radioactivity found in the different age mice. The mice exposed on postnatal day 3 or 10 had around 4‰ of the total administered dose of ^{14}C in the brain at 24-hours after dosing, whereas only 0.6‰ of the total administered dose was found at 24-hours in the brains of mice dosed on postnatal day 19. At day-7 after administration the amount of radioactivity in the brain had increased by around a factor of 2 in the mice exposed on postnatal days 3 or 10, whereas no noticeable increase in the amount of radioactivity present had occurred in brains of the mice dosed on postnatal day 19.

Mörck and Klasson Wehler (2001) have investigated the metabolism of ^{14}C-labelled decabromodiphenyl ether (purity not given) using conventional and bile duct-cannulated rats. The rats were given a single oral dose of 3 μmol/kg (~2.9 mg/kg) of the test material suspended in a vehicle (a mixture of Lutrol F127, soya phospholipid and water). Excreta were collected over the following 72 hours and analysed for ^{14}C content and phenolic metabolites. The results of the study showed that the major route of excretion (~90% of the dose within 3 days) was via the feces, with only minor amounts (<0.05% of the dose) being excreted via urine. Excretion via the bile accounted for ~9.5% of the dose within 3 days. Approximated 3% of the total administered radioactivity was present in tissues 3 days after dosing and was distributed mainly in liver (~0.9%), muscle (~0.7%), skin (~0.4%), adipose tissue (~0.3%), colon wall (~0.25%), jejunum wall (~0.05%), jejunum content (~0.05%), with minor amounts (<0.05%) in plasma, kidney, heart, lung, adrenals, testis, red blood cells, thymus and spleen. More detailed analysis of the feces showed that 22%, 42% and 45% of the radioactivity present at day 1, 2 and 3 respectively was present as phenolic metabolites. In all, 8 phenolic metabolites were identified as their corresponding methy derivatives. These were dimethoxylated derivatives of penta- to octabromodiphenyl ethers (the dihydroxyl groups were always on the same ring). The remaining radioactivity present in the feces was identified as unchanged decabromodiphenyl ether.

Summary of bioaccumulation

The available data indicates that little or no uptake of decabromodiphenyl ether occurs in aquatic organisms exposed via the water phase. Some limited uptake of decabromodiphenyl ether has been seen in experiments with fish exposed via food, but the tissue concentrations reached were much lower than those present in food (it is not clear if steady state had been reached during the 120-day exposure period and so it is possible that uptake could have increased further over extended timescales). Overall, it can be concluded that, although there is some experimental evidence that decabromodiphenyl ether can be taken up by aquatic organisms via food, only a very small proportion of the total dose was taken up (~0.02-0.13% over 120 days) and so the substance can be considered to have a low bioaccumulation potential.

Further evidence for this comes from the fact that there are very few reported occurrences of decabromodiphenyl ether in biota samples taken from the environment (see Section 3.1.5.2), which contrasts markedly with the situation with pentabromodiphenyl ether, which has been

shown to be bioaccumulative in laboratory studies and is widely found in measurable amounts in aquatic biota samples (see the risk assessment of pentabromodiphenyl ether for further details).

For mammalian systems, the available oral/feeding studies show that a small amount of the applied dose is taken up into, and distributed within, the various body tissues (the extent of uptake may be a function of the administration vehicle used), but depuration appears to be relatively rapid. Therefore, again the actual bioaccumulation potential for decabromodiphenyl ether, based on these studies, appears to be low. There is also evidence that decabromodiphenyl ether can be metabolised to form hydroxy derivatives.

There are generally few monitoring data available for decabromodiphenyl ether in mammalian species in the environment with which to compare with the laboratory findings. However, recently decabromodiphenyl ether has been found to be present in samples of eggs taken from wild bird populations and also some marine mammals and fish, indicating that uptake of decabromodiphenyl ether by organisms is occurring in the environment. These results are presented in Section 3.1.4.2 and are also considered in the risk characterisation section.

3.1.1.6.4 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 estimated 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 3.11**.

As can be seen from **Table 3.11**, 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.

Table 3.11 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 wastewater treatment plant:	76.21%	91.29%	91.57%	93.7%	93.99%	94.03%	94.04%	94.04%	94.04%	94.04%
Biodegraded:	0.65%	0.76%	0.76%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%
Adsorbed onto sludge:	74.41%	90.45%	90.78%	92.93%	93.22%	93.25%	93.26%	93.26%	93.26%	93.26%
To air:	1.15%	0.08%	0.03%	0%	0%	0%	0%	0%	0%	0%

Notes: 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.

Bioaccumulation potential would also be expected to increase with increasing bromination, however, the measured results given in Section 3.1.1.6.3 indicate that the decabromodiphenyl 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.

3.1.1.7 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 miss-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 decabromodiphenyl ether flame retardant.

3.1.2 Aquatic compartment

3.1.2.1 Calculation of PECs

3.1.2.1.1 Production

Production no longer occurs in the EU, but the calculations are included here for illustration. The release of decabromodiphenyl ether to wastewater from a generic 1,000 tonnes/year production site is estimated to be around 3 tonnes/year (default) or 0.5 tonnes/year (using general information on the production process). It will be assumed that all of this release occurs over 100 days (Table B1.1 of Appendix 1 of the Technical Guidance Document) to a wastewater treatment plant (wwtp).

Using the EU Guidance Document for Risk Assessment of Existing Substances, the size of the wwtp is 2,000 m^3/day and the overall removal of decabromodiphenyl ether is 91.7% (91.4% due to adsorption onto sewage sludge and 0.3% to air (as estimated by EUSES, assuming log Kow = 6.27, log H = 1.6 and no degradation 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 = 2000 m^3/day
Concentration in influent to wwtp = 15 or 2.5 mg/l
Removal in wwtp = 91.7%
Concentration in effluent = 1.25 or 0.21 mg/l
Dilution in receiving water = 10
Concentration in receiving water ($Clocal_{water}$) = 125 or 21 µg/l

Clearly the concentrations in receiving water estimated (particularly using the higher release factor) are above the water solubility of the substance and so are probably unreliable. The lower value will be used below to estimate the PEC_{local}.

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

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

where $Clocal_{water}$ = concentration of chemical from wastewater treatment plant
K_{susp} = suspended matter - water partition coefficient (l/kg) = 158,866 l/kg
C_{susp} = concentration of suspended matter in the river ($=1.5 \cdot 10^{-5}$ kg/l)
$PEC_{regional}$ = 0.094 µg/l (see Section 3.1.2.1.4)

PEC_{local}(water) from production (generic) = 6.3 µg/l

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 mater - water partition coefficient = 39,717 m^3/m^3
ρ_{susp} = bulk density of suspended matter = 1,150 kg/m^3

Thus for a PEC_{local}(water) of 6.3 µg/l, the PEC_{local}(sed) from a generic production site can be estimated as 218 mg/kg (wet weight).

Some site-specific information has been reported for the (now closed) production site in the EU. The resulting PECs for this site can be estimated as follows:

Amount released to wwtp = 0.8 kg/year
No of days of operation = unknown – estimated at 17
Amount released daily = 0.047 kg/day
Flow of effluent from plant = 50 m^3/day
Concentration in plant effluent = 0.94 mg/l
Removal in settling pond = unknown

Here, the removal in the settling pond is unknown. However, it is clear that a substance such as decabromodiphenyl ether would adsorb onto particulate matter and be removed from solution. One way to estimate this is to use the equation given in the Technical Guidance Document for adsorption onto suspended matter i.e.

Concentration in settling pond = Plant effluent concentration/$(1+K_{susp} \cdot C_{susp})$

where K_{susp} = suspended matter - water partition coefficient (l/kg) = 158,866 l/kg
C_{susp} = concentration of suspended matter (e.g. $=1.5 \cdot 10^{-5}$ kg/l)

Dilution in settling pond = unknown – assume 10
Concentration in settling pond = 28 µg/l
Dilution in receiving water = unknown – assume 10 (eventually released to seawater)
Concentration in receiving water ($Clocal_{water}$) = 2.8 µg/l

Again, on release to the receiving water, adsorption onto suspended matter would be occurring, thus PEC_{local}(water) = 0.9 µg/l (annual average PEC_{local}) = 0.041 µg/l.

The site specific PEC_{local}(sed) is estimated to be 31 mg/kg wet wt.

The actual PECs at the site is likely to be much lower than this value. Further information on dilutions in the various receiving waters at the site would be useful to refine this value, but production at this site has now ceased.

3.1.2.1.2 Polymers

In Section 3.1.1.2.2 it was estimated that 0.34 tonnes/year in a region and 3.06 tonnes/year in the EU as a whole of decabromodiphenyl ether are released to wastewater during processing of (HIPS) plastics. The release to wastewater at a polymer processing site was estimated at 51 kg/year over 268 days.

The PECs below are calculated based on this 51 kg/year release figure. It is assumed that all of this release occurs to a wastewater treatment plant (wwtp). Using the Technical Guidance Document, the size of the wwtp is 2,000 m^3/day and the removal of decabromodiphenyl ether is 91.7%, mainly due to adsorption onto sewage sludge.

Amount released to wwtp = 51 kg/year
No of days of operation = 268
Amount released daily = 0.19 kg/day
Size of wwtp = 2,000 m^3/day
Concentration in influent to wwtp = 0.095 mg/l
Removal in wwtp = 91.7%
Concentration in effluent = 8.0 µg/l
Dilution in receiving water = 10
Concentration in receiving water ($Clocal_{water}$) = 0.8 µg/l

Using the same values for Koc as in Section 3.1.2.1.1, the PEC_{local}(water) and PEC_{local}(sediment) can be calculated as:

PEC_{local}(water) for polymer processing = 0.33 µg/l
PEC_{local}(sediment) for polymer processing = 10.8 mg/kg (wet weight)

Again, the PEC_{local}(water) is above the water solubility of the substance.

3.1.2.1.3 Textiles

In Section 3.1.1.2.7 it was estimated that up to 0.6 tonnes/year of decabromodiphenyl ether could be released at a compounding site and 0.3 tonnes/year at an application site. Much of the release is likely to be to landfill, although some could enter into wastewater. A worst-case scenario would be if compounding and application occurs on one site, and thus up to 0.9 tonnes/year could be released to wastewater.

Total amount released to wwtp = 0.9 tonnes/year
No. of days of operation = 300
Amount released daily/site = 3 kg/day
Size of wwtp = 2,000 m^3/day
Concentration in influent to wwtp = 1.5 mg/l
Removal in wwtp = 91.7%
Concentration in effluent = 126 µg/l
Dilution in receiving water = 10
Concentration in receiving water ($Clocal_{water}$) = 12.6 µg/l

Using the same value for Koc as in Section 3.1.2.1.1, the PEC_{local} (water) and PEC_{local} (sediment) can be calculated as:

PEC_{local} (water) for textile compounding and use = 3.8 µg/l
PEC_{local} (sediment) for textile compounding and use = 131 mg/kg wet weight

Based on the same figures, the worst-case PECs for a compounding site alone would be PEC_{local} (water) = 2.6 µg/l and PEC_{local} (sediment) = 89.0 mg/kg wet weight. Similarly the PECs for an application site alone would be PEC_{local} (water) = 1.3 µg/l and PEC_{local} (sediment) = 46.1 mg/kg wet weight.

The PEC_{local}(water) estimated are all above the water solubility of the substance.

3.1.2.1.4 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 decabromodiphenyl ether to industrial soil from "waste remaining in the environment" was assumed to occur in the model. A summary of the release estimates used in the model is given in **Table 3.3**.

The results of the model are shown in **Table 3.12**. No biodegradation was assumed in the model, but a rate constant for atmospheric reaction with hydroxyl radicals of $1.7 \cdot 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} was assumed. The following physical chemical properties were used: water solubility 0.1 µg/l, vapour pressure $4.63 \cdot 10^{-6}$ Pa, log Kow 6.27, Henry's law constant = 44.4 Pa m^3/mol (estimated from ratio of vapour pressure and water solubility). It should be noted that the actual values for these properties are uncertain as it is difficult to measure accurately very low vapour pressures and water solubilities and very high log Kow values. A full summary of the modelling results is given in Appendix B.

Table 3.12 Summary of Regional and Continental concentrations estimated using EUSES

Compartment	$PEC_{regional}$	$PEC_{continental}$
Concentration in surface water (dissolved)	0.093-0.094 µg/l	4.3-4.4 ng/l
Concentration in sediment	5.66-5.72 mg/kg wet weight	0.26-0.27 mg/kg wet weight

3.1.2.1.5 Summary of predicted levels for the aquatic compartment

Concentrations of decabromodiphenyl ether in the aquatic compartment have been estimated using a variety of methods. The concentrations are summarised in **Table 3.13**.

The predicted concentrations of decabromodiphenyl ether in water and biota are low for all of the scenarios considered. Adsorption onto sediment is predicted to be important and this is where the highest concentrations of decabromodiphenyl ether are predicted to occur in the aquatic environment.

It should be noted that all the PEC_{local} values for surface water are above the water solubility of the substance.

Table 3.13 Summary of predicted environmental concentrations for the aquatic compartment

Media	Source	Type	Concentration
Surface water	Production (generic)[a]	PEC_{local}	6.3 µg/l
	Production (site specific)[a]	PEC_{local}	0.9 µg/l
	Polymer processing	PEC_{local}	0.33 µg/l
	Textiles - compounding site	PEC_{local}	2.6 µg/l
	Textiles - application site	PEC_{local}	1.3 µg/l
	Textiles - combined compounding/application site	PEC_{local}	3.8 µg/l
	Regional scale	$PEC_{regional}$	0.093-0.094 µg/l
Sediment	Production (generic)[a]	PEC_{local}	218 mg/kg wet wt.
	Production (site specific)[a]	PEC_{local}	31 mg/kg wet wt.
	Polymer processing	PEC_{local}	10.8 mg/kg wet wt.
	Textiles - compounding site	PEC_{local}	89.0 mg/kg wet wt.
	Textiles - application site	PEC_{local}	46.1 mg/kg wet wt.
	Textiles - combined compounding/application site	PEC_{local}	131 mg/kg wet wt.
	Regional scale	$PEC_{regional}$	5.66-5.72 mg/kg wet weight

Note: a) Production of decabromodiphenyl ether no longer occurs in the EU.

3.1.2.2 Measured levels in water and sediment

This Section reports the levels of decabromodiphenyl ether measured in water, sediment and biota.

The analysis of decabromodiphenyl ether is complicated by the fact that the commercial product is a mixture and that there is a lack of analytical standards for individual congeners/isomers in the mixture. This is likely to be a particular problem with some of the older analyses, since modern commercial products consist of mainly decabromodiphenyl ether (typically >97%) but some older commercial products had much higher levels of other brominated diphenyl ethers. There are usually few experimental details as to how the analyses were carried out so it is often not clear if the levels refer to "pure" decabromodiphenyl ether or to a commercial product.

Since the commercial products also contain small amounts of lower brominated diphenyl ethers, it is also important to obtain some indication of the levels and distribution of the other components in the commercial product. These are summarised in the assessments of octabromodiphenyl ether (RAR, 2002) and pentabromodiphenyl ether (ECB, 2000).

3.1.2.2.1 Water

The levels of decabromodiphenyl ether measured in water are shown in **Table 3.14**.

Table 3.14 Levels of decabromodiphenyl ether in water

Location	Comments	Detection limit (μg/l)	Level (μg/l)	Reference
Aycliffe sewage treatment plant influent, United Kingdom, 2002	Receives wastewater from a supplier of decabromodiphenyl ether	0.005	Dissolved - not detected Suspended solids - 1.2[a]	Environment Agency, 2002
Sewage treatment plant effluent, United Kingdom, 2002	Receives wastewater from a supplier of decabromodiphenyl ether	0.005	Dissolved - not detected Suspended solids - not detected	Environment Agency, 2002
River Skerne United Kingdom, 2002	Upstream of effluent from Aycliffe sewage treatment plant.	0.005	Dissolved - 0.005 Suspended solids - not detected	Environment Agency, 2002
Demons Beck, United Kingdom, 2002	Upstream of effluent from Aycliffe sewage treatment plant.	0.005	Dissolved - 0.015 Suspended solids - not detected	Environment Agency, 2002
Howden Beck, United Kingdom, 2002	Upstream of effluent from Aycliffe sewage treatment plant.	0.005	Dissolved - not detected Suspended solids - not detected	Environment Agency, 2002
River Skerne, United Kingdom, 2002	Two locations downstream of effluent from Aycliffe sewage treatment plant.	0.005	Dissolved - not detected Suspended solids - not detected	Environment Agency, 2002
River Tees, United Kingdom, 2002	Downstream of effluent from Aycliffe sewage treatment plant.	0.005	Dissolved - not detected Suspended solids - not detected	Environment Agency, 2002
Finland, 2000	Creek receiving storm water from an urban area	0.02	0.4	Peltola, 2002
Landfill leachate, Finland, 2002	At Espoo	0.02	Not detected	Peltola, 2002
	Metal dismantling plant	0.02	Not detected	Peltola, 2002
Japan, 1977		0.2-2.5	Not detected in 15 samples	Environment Agency Japan, 1991
Japan, 1987		0.1	Not detected in 75 samples	Environment Agency Japan, 1991
Kino River, Japan		0.1	Not detected in 12 samples	Yamamoto et al., 1991
Japan, 1988		0.06	Not detected in 141 samples	Environment Agency Japan, 1991

Note: a) Estimated concentration.

The levels of decabromodiphenyl ether in surface water have recently been determined in samples taken from close to a former polybrominated diphenyl ether manufacturer (Environment Agency, 2002). The site manufactured penta- and octabromodiphenyl ether up until the late 1990s but never manufactured decabromodiphenyl ether, although this substance may have been imported to the site. It is possible that other sources of release of the substance may be present in the area sampled. The samples (two from each location) were filtered (0.45 μm) and both the

water (dissolved) phase and the suspended solid phase were analysed. The concentration of decabromodiphenyl ether found was close to or below the analytical detection limit of the method used (detection limit 0.005 μg/l).

Peltola (2002) has determined the total concentration of decabromodiphenyl ether in water from a creek in Finland that is fed by stormwater from a large urban area in Helsinki. The concentration of decabromodiphenyl ether found was 0.4 μg/l. In addition, the concentration of decabromodiphenyl ether was investigated in two samples of leachate from landfills. The concentration present was below the limit of detection in the samples from a landfill in Espoo and in leachate from a landfill at a metal dismantling plant.

As can be seen from **Table 3.14**, in most cases the levels in water are less than the detection limit (i.e. <0.06-<2.5 μg/l). There are data showing that low levels of decabromodiphenyl ether are present in urban stormwater. The samples are taken from several industrial, urban and rural areas of Japan and are thought to be representative of the country as a whole.

3.1.2.2.2 Sediment

The levels of decabromodiphenyl ether measured in sediments in three surveys carried out in the UK near to possible sources of release are shown in **Table 3.15**.

Table 3.15 Levels of decabromodiphenyl ether in sediment in the UK near to possible sources of release

Location	Comment	Level	Reference
River Tweed at Tweedmouth	Background site	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Tweed at Berwick upon Tweed bridges	Background site	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Nith, upstream of wwtp	Near rubber producer	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Nith, downstream of wwtp	Near rubber producer	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Nith at Glencaple	Near rubber producer	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Avonmouth	Near flame retardant producer/user (none brominated)	<0.6-7 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Demons Beck	Upstream of a supplier of decabromodiphenyl ether	5.8 μg/kg (dry wt.)	Environment Agency, 2002
River Skerne, upstream of Demons Beck	Upstream of a supplier of decabromodiphenyl ether	<5 μg/kg (dry wt.)	Environment Agency, 2002
River Tees at Croft-on-Tees	Near to a supplier of decabromodiphenyl ether	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Tees at Stockton	Near to a supplier of decabromodiphenyl ether	209 μg/kg (dry wt.)	Environment Agency, 2002
River Skerne at Croft-on-Tees	Near to a supplier of decabromodiphenyl ether	7 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999

Table 3.15 continued overleaf

Table 3.15 continued

Location	Comment	Level	Reference
River Skerne at Aycliffe Village	Near to a supplier of decabromodiphenyl ether	<5 μg/kg (dry wt.)	Environment Agency, 2002
River Skerne at Newton Aycliffe	Near to a supplier of decabromodiphenyl ether	64 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Skerne at Darlington	Near to a supplier of decabromodiphenyl ether	<5 μg/kg (dry wt.)	Environment Agency 2002
Howden Beck	Near to a supplier of decabromodiphenyl ether	23 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Howden Beck	Near supplier of decabromodiphenyl ether	60 μg/kg (dry wt.)	Environment Agency, 2002
River Skerne, upstream of Howden Beck	Near to a supplier of decabromodiphenyl ether	294 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Skerne, downstream of Howden Beck	Near to a supplier of decabromodiphenyl ether	95 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Calder	Near to a foam manufacturing site	399 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Hyndburn Brook, upstream of wwtp	Near to a foam manufacturing site	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Calder, downstream of wwtp	Near to a foam manufacturing site	3,190 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Elstow landfill	Landfill receiving brominated wastes	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Elstow Brook, downstream of landfill site	Landfill receiving brominated wastes	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Tees estuary, Portrack wwtp	Industrial area	5 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Tees estuary, Bamlett's Bight	Industrial area	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Tees estuary, No. 23 buoy	Industrial area	9 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Tees estuary, Philips approach buoy	Industrial area	8 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Great Ouse	Downstream of landfill site	<0.6 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Ribble	Near to a foam manufacturing site	111 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
River Humber, Paull		17 μg/kg (dry wt.)	Law et al., 1996; Allchin et al., 1999
Upstream of a plastics processor	Decabromodiphenyl ether used	<200 μg/kg (dry wt.)	Environment Agency, 1997
Downstream of a plastics processor	Decabromodiphenyl ether used	<200 μg/kg (dry wt.)	Environment Agency, 1997
Upstream of warehouse	Decabromodiphenyl ether stored	<500 μg/kg (dry wt.)	Environment Agency, 1997

Table 3.15 continued overleaf

Table 3.15 continued

Location	Comment	Level	Reference
Downstream of warehouse	Decabromodiphenyl ether stored	<500 µg/kg (dry wt.)	Environment Agency, 1997
Industrial area, Stockport	Upstream of site possibly using pentabromodiphenyl ether	<500 µg/kg (dry wt.)	Environment Agency, 1997
Industrial area, Stockport	Downstream of site possibly using pentabromodiphenyl ether	<500 µg/kg (dry wt.)	Environment Agency, 1997
Mersey estuary	Industrial area, upstream of polymer processing site	<500 µg/kg (dry wt.)	Environment Agency, 1997
Mersey estuary	Downstream of polymer processing site	<500 µg/kg (dry wt.)	Environment Agency, 1997
Wales, upstream of a plastic compounder	Decabromodiphenyl ether used	<200 µg/kg (dry wt.)	Environment Agency, 1997
Wales, downstream of a plastic compounder	Decabromodiphenyl ether used	may be present at around 850 µg/kg but interference was present in the analysis	Environment Agency, 1997
Landfill site	Pentabromodiphenyl ether waste disposed on-site	<500 µg/kg in sediment at the site and nearby stream	Environment Agency, 1997

A survey of marine sediments in estuaries discharging into the North Sea has been carried out and these results are shown in **Table 3.16**.

Table 3.16 Levels of decabromodiphenyl ether in sediments (<63 µm fraction) from estuaries (van Zeijl, 1997)

Estuary/location	% of sediment <63 µm	% organic carbon in <63 µm fraction	% organic carbon in whole sediment	Concentration in the <63 µm fraction
Liffey River	23.4	2.01	0.86	40.3 µg/kg (dry wt.)
Clyde	72.4	3.25	3.13	8.4 µg/kg (dry wt.)
Mersey	42.1	2.44	1.09	1,700 µg/kg (dry wt.)
Southampton	35.7	1.03	0.81	2.1 µg/kg (dry wt.)
Thames	10.0	1.90	0.3	18.3 µg/kg (dry wt.)
Humber	20.3	2.40	1.17	39 µg/kg (dry wt.)
Tyne	29.2	1.89	1.01	4.3 µg/kg (dry wt.)
Forth	19.8	2.41	0.78	3.3 µg/kg (dry wt.)
Seine	53.3	2.77	2.92	12.2 µg/kg (dry wt.)
North sea (off Belgium)	38.4	1.48	1.1	11.6 µg/kg (dry wt.)
Schelde	5.8	3.53		200 µg/kg (dry wt.)
Rijn	51.9	2.83	2.65	15.7 µg/kg (dry wt.)
Noordwijk	7.4	2.91		11.3 µg/kg (dry wt.)
Waddensee	10.2	2.27	0.33	1.1 µg/kg (dry wt.)
Ems	68.9	4.13	4.53	4.9 µg/kg (dry wt.)

Table 3.16 continued overleaf

Table 3.16 continued

Estuary/location	% of sediment <63 µm	% organic carbon in <63 µm fraction	% organic carbon in whole sediment	Concentration in the <63 µm fraction
Weser	54.7	2.73	2.46	3.4 µg/kg (dry wt.)
Elbe	49.9	1.79	1.59	0.83 µg/kg (dry wt.)
Goto	73.1	2.28	2.23	2.6 µg/kg (dry wt.)
Glomma	71.2	2.38	2.19	<0.52 µg/kg (dry wt.)
Skiens	70.3	3.30	3.02	1.0 µg/kg (dry wt.)
Otria	61.2	2.68	2.64	0.71 µg/kg (dry wt.)
100 km off Terschdling (reference site)	18.7	1.15	0.33	<0.51 µg/kg (dry wt.)

Levels measured in sediments from countries outside of Europe are summarised in **Table 3.17**.

Table 3.17 Levels of decabromodiphenyl ether in sediments from the rest of the world

Location	Comments	Level	Reference
Sediment near to a manufacturing site in the United States	Detection limit 100 µg/kg	Not detected-14,000 µg/kg*	Zweidinger et al., 1979
Sediment near to a manufacturing site in the United States	Detection limit unknown	Detected	DeCarlo, 1979
Surface sediment from Lake Ontario	Detection limit unknown	13 µg/kg dry weight	Alaee, 2001
Japan, 1977	Detection limit 25-870 µg/kg	Not detected in 15 samples	Environment Agency Japan, 1991
Japan, 1987	Detection limit 7 µg/kg	Detected in 16/60 samples at 10-1,370 µg/kg	Environment Agency Japan, 1991
Japan, 1988	Detection limit 4 µg/kg	Detected in 39/129 samples at 4-6,000 µg/kg	Environment Agency Japan, 1991
Sediment, Kino River, Japan, 1991	Detection limit unknown	Detected in 20 samples	Yamamoto et al., 1991
River sediment, Japan, 1981-1983	Detection limit 5 µg/kg dry weight	Detected in 6/6 samples at 33-375 µg/kg dry weight	Watanabe et al., 1987a
Estuary sediment, Japan, 1981-1983	Detection limit 5 µg/kg dry weight	Detected in 1/ 7 samples at 20 µg/kg dry weight	Watanabe et al., 1987a
Marine sediment, Japan, 1981-1983	Detection limit 5 µg/kg dry weight	Not detected in 2 samples	Watanabe et al., 1987a
River sediment, Osaka, Japan, 1983		200 µg/kg dry weight	Watanabe et al., 1986
3 River sediments, Osaka, Japan, 1983		120, 160 and 310 µg/kg dry weight	Watanabe et al., 1987b
3 Marine sediments, Osaka Bay, Japan, 1983	Detection limit ≈ 5 µg/kg dry weight	Not detected	Watanabe et al., 1987b

Note: *A sample was also screened by a Thin-layer chromatographic (TLC) method which gave a level of 1 g/kg.

As can be seen from **Tables 3.15** to **3.17**, decabromodiphenyl ether has been detected much more frequently in sediment than water. This is as expected from its physico-chemical properties. Levels of up to 6 mg/kg dry weight have been detected in Japan and levels up to 14 mg/kg (or 1 g/kg) have been detected near to a manufacturing site in the United States. In the United Kingdom, levels up to 3.2 mg/kg dry weight have been measured near to sites using decabromodiphenyl ether.

More recent data on levels of decabromodiphenyl ether in sediments from Sweden have been determined by Sellström (1998b). In this study, surface sediment (0-2 cm) was collected at eight locations in the River Viskan, its tributary (River Häggån) and other nearby water systems. Samples were collected up and downstream from a number of industries thought to be using flame retardants. The levels are measured ranged between <20-12,000 µg/kg IG (dry weight ignition loss basis), with the highest levels generally being found downstream from industry. The results are shown in **Table 3.18**.

Table 3.18 Levels of decabromodiphenyl ether measured in sediments from the River Viskan area (Sellström et al., 1998b)

Location	Dry weight (% wet solids)	Ignition loss (% dry solids)	Measured level (µg/kg ignition loss)	Measured level converted to µg/kg wet wt.
Lake Marsjön, upstream from industry	18	31	<20	<1.1
Lake Öresjö, downstream from industry	19	14	<40	<1.1
River Viskan downstream from town of Borås	18	32	150	8.6
River Viskan at Moga	23	37	220	18.7
River Viskan upstream from Skene	73	2	3,400	49.6
River Viskan downstream from Skene	67	3	12,000	241
River Häggån upstream from Fritsla	27	31	<20	<1.7
River Häggån downstream from Fritsla	49	12	<20	<1.2
Lake Skäresjön (a parallel water system)	12	37	<30	<1.3

In addition to these studies, a recent detailed investigation into the levels of decabromodiphenyl ether in sediment from the Western Scheldt, the Netherlands and River Tees, United Kingdom has been reported (de Boer et al., 2001). For the Western Scheldt, 19 samples (each sample was a composite of nine sub-samples) were collected. The mean level of decabromodiphenyl ether found was 172 µg/kg dry weight, and the highest level found was ~1,000 µg/kg dry weight. The higher levels were generally found in the eastern part of the Western Scheldt, but similar high levels were also found at Terneuzen and Vlissingen. 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 Barrage), lower Tees (Tees Barrage to Tees mouth) and Tees estuary (Tees mouth and Tees bay). Decabromodiphenyl ether was generally not found (<0.2 µg/kg dry weight) in samples from the upper Tees (it was present at 2 µg/kg dry weight at one site). The level in the middle Tees was generally around 1 µg/kg dry weight at sites upstream of the confluence with

the River Skerne at Croft on Tees, but was 107 µg/kg dry weight at the first sampling point downstream of the confluence with the River Skerne (near to the site of a supplier of decabromodiphenyl ether). The concentrations then generally decreased down stream of this site. In the lower Tees the mean concentration found was 140 µg/kg dry weight (highest value 378 µg/kg dry weight). The highest concentrations were found in the Tees estuary, where the mean and highest level measured were 240 µg/kg dry weight and 1,400 µg/kg dry weight respectively. The measured levels were generally found to decline with distance from the estuary. Based on these data it was estimated that the Tees estuary contained around 0.1 tonnes of decabromodiphenyl ether and that the overall input (by dredging and flushing/water exchange) of decabromodiphenyl ether from the estuary into the North Sea was estimated at 0.06-0.45 tonnes/year (mean 0.15 tonnes/year). The estimated input of decabromodiphenyl ether to the North Sea from all estuaries in the United Kingdom was estimated at 0.2-0.8 tonnes/year.

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 decabromodiphenyl 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 1960s, with decabromodiphenyl ether becoming present around a decade later.

A final part of the de Boer et al. (2001) study investigated recent trends in the levels of decabromodiphenyl ether in sediments by re-sampling sediments from locations used in earlier studies (such as some of the locations in the van Zeijl (1997) study). These results are shown in **Table 3.19**. The results show that although the concentration of decabromodiphenyl ether appears to have decreased at one location (Humber), the other sites for which information are available generally show that the concentration of decabromodiphenyl ether has increased by around 50-100% since 1995.

Table 3.19 Recent trends in levels of decabromodiphenyl ether in sediment

Location	Measured concentration (µg/kg organic carbon)	
	1995 (van Zeijl, 1997)	1999-2001 (de Boer et al., 2001)
Liffey	2,010	4,457
Clyde	259	1,260
Mersey	69,700	104,700[a]
Humber	1,630	160
Western Scheldt	5,670	5,670
Haringvliet-east		470-1,510
Nieuwe Merwede		910-8,040
Waal (Tiel)		760-2,310
Meuse (Keizersveer)		110-990

Note: a) The levels are reported on a µg/kg organic carbon basis for comparison with the earlier study. Using the TGD default values for the sediment properties, a concentration of 104,700 µg/kg organic carbon is equivalent to around 2 mg/kg wet weight.

Klamer et al. (2001) carried out a further survey of the levels of decabromodiphenyl ether in the <0.63 µm fraction of surface sediments (top 5 cm). In this study, ten samples from the southern part of the Dutch section of the North sea continental shelf were taken. The highest concentration measured was 32 µg/kg dry weight in a sample off the Western Scheldt. The concentrations

where found to generally decrease with increasing distance from the shore and were ~1 µg/kg dry weight in the remoter areas sampled.

Kemmlein (2000) analysed freshwater sediment samples from a number of locations around Berlin. At two sites, samples were taken from different depths corresponding to different ages of sediment. For one of these sites, decabromodiphenyl ether levels increased from 0.76 µg/kg dry weight in the 1960s to 46 µg/kg dry weight in the 1970s and 71 µg/kg dry weight after 1985. At the second site, the levels were 1.2 µg/kg dry weight in the 1970s and 66 µg/kg dry weight in the 1990s. Decabromodiphenyl ether was found in most of the samples from other sites, at levels from 0.16 µg/kg dry weight to 201 µg/kg dry weight.

Further recent data on levels of decabromodiphenyl ether in sediments from Hamburg Harbour and the Danube River has been presented by Sawal et al. (2002a and b). The first part of the study (Sawal et al., 2002a) investigated the levels of decabromodiphenyl ether in sediments from Hamburg Harbour as part of the analytical method development. In all, eight samples were analysed and decabromodiphenyl ether was found in all eight samples at a concentration of 0.7-7 µg/kg dry weight. The median level found was 3.7 µg/kg dry weight.

The second part of the study (Sawal et al., 2002b) determined the levels of decabromodiphenyl ether in sediments from the Danube River and its main tributaries. In all 26 samples were collected from sites in Germany, Austria, Slovakia, Hungary, Croatia, Yugoslavia, Bulgaria, Romania, Moldova and Ukrane during the summer of 2001. Decabromodiphenyl ether was found in all samples at a concentration of 0.032-83.8 µg/kg dry weight. The median level found was 3.30 µg/kg dry weight. The highest concentration of decabromodiphenyl ether found was at the Moson Danube arm which was near an industrialised region with textile, electronic and plastics industries. The study also found that high concentrations of decabromodiphenyl ether were not necessarily accompanied with high concentrations of lower brominated diphenyl ethers.

The results of a survey of levels of decabromodiphenyl ether in marine and freshwater sediments from Denmark have been reported (Platz and Christensen, 2001). In all, six marine and six freshwater samples were analysed and the level found was <0.9-21.5 µg/kg dry weight in the marine sediments and <1.3-8.1 µg/kg in the freshwater sediments.

Peltola (2002) has recently determined the levels of decabromodiphenyl ether in sediment samples from Finland. The samples were collected in the summer/autumn of 2000 and were taken from the aerobic surface layer of the sediments and the detection limit for the method was around 7-17 µg/kg dry weight. Decabromodiphenyl ether was not detected in three coastal samples taken around the Finish Gulf, but was present at a concentration of 7.4 µg/kg dry weight in sediment from an urban creek that collects stormwater from Helsinki. The highest level found in the study was 2,697 µg/kg dry weight in a sediment sample from a stormwater trench of a metal dismantling plant.

3.1.2.3 Comparison of measured and calculated levels

The levels of decabromodiphenyl ether measured in water are in most cases less than the detection limit (i.e. <0.06-<2.5 µg/l). The samples are taken from several industrial, urban and rural areas of Japan and are thought to be representative of the country as a whole. The measured results are reasonably consistent with the regional (0.093-0.094 µg/l) and continental (0.0043-0.0044 µg/l) surface water levels predicted using EUSES. It is not known if any of the sites sampled were near to a polybrominated diphenyl ether production site, a polymer processing site

or a textile finishing site so it is not possible to compare the levels with the PEC_{local} calculated at such sites.

Recent surveys carried out in the United Kingdom and Finland have indicated that decabromodiphenyl ether is present in sediments close to sites where decabromodiphenyl ether is used or stored, and sites where equipment is dismantled. However, the levels measured (up to around 3.2 mg/kg dry weight or approximately 1.2-2 mg/kg wet weight assuming sediment is typically 80% water by volume or 62% water by weight) are generally lower than those predicted in the local and regional scenarios. This indicates that the actual releases at sites using decabromodiphenyl ether are possibly lower than those estimated in Section 3.1.1. This measured value of 1.2-2 mg/kg wet weight will be used in the assessment along with the predicted values.

3.1.3 Terrestrial compartment

3.1.3.1 Predicted concentrations

No information is available about the direct application/disposal of decabromodiphenyl ether to soil as a result of polymer processing or use in textiles. It is likely that waste material may be disposed of to landfill.

It is possible that decabromodiphenyl ether may reach soil through the application of sewage sludge containing it or by wet/dry deposition of the substance from the atmosphere. These two processes are included in the EUSES model and this was used to estimate soil concentrations for decabromodiphenyl ether in the local, regional and continental scenarios. Further details of the model are given in Section 3.1.2.1.4 and Appendix B. The concentrations predicted in soils are shown in **Table 3.20.**

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

High levels of decabromodiphenyl ether are also predicted in agricultural soil at the regional level. Here the predicted concentrations are higher than found at the local level. This is because the major source of release at the regional level is predicted to be from leaching from washed textiles which dominates over the other industrial releases. A worst-case approach has been used for this area, but it should be noted that there is some uncertainty over the amounts of decabromodiphenyl ether released to the environment from washing textiles. Another reason why the concentrations predicted in soil at the regional level are higher than at the local level in some situations is that the regional concentration is the equilibrium concentration obtained over many years of application, whereas, the local concentration is obtained after 10 years application (it is estimated that the fraction of the equilibrium value obtained after 10 years application is around $6 \cdot 10^{-3}$-0.01 (0.6-1%)).

Atmospheric deposition of decabromodiphenyl ether appears to make only a small contribution to the regional concentration in soil, as the concentration predicted in natural soil (which receives atmospheric inputs only) is much lower than that predicted in agricultural soil.

It should be noted that in all of the PEC calculations, the pore water concentration is higher than the water solubility of the substance (<0.1 µg/l). This throws some doubt over the estimation methods used. The soil pore water concentration is used later in the assessment for estimation of the exposure of man via the environment, particularly from root crops and also the estimation of the concentrations in earthworms for the secondary poisoning assessment. One approach to this problem would be to limit the soil pore water concentration to the water solubility of the substance. This approach has been used later for the estimation of exposure of man via the environment, but for earthworms, the possibility of ingestion of soil-bound residue exists (although the Technical Guidance Document makes no allowance for this).

Table 3.20 Predicted concentrations in soil

Scenario	Soil type	PEC
Production (generic)[a]	Agricultural soil	PEC_{local} = 84.9 mg/kg wet wt.
	Grassland	PEC_{local} = 34.0 mg/kg wet wt.
	Pore water	PEC_{local} = 3.0 µg/l
Production (site specific)[a]	Soil	no sludge application
Polymer processing	Agricultural soil	PEC_{local} = 3.33 mg/kg wet wt.
	Grassland	PEC_{local} = 1.40 mg/kg wet wt.
	Pore water	PEC_{local} = 0.12 µg/l
Textiles - compounding	Agricultural soil	PEC_{local} = 34.0 mg/kg wet wt.
	Grassland	PEC_{local} = 13.6 mg/kg wet wt.
	Pore water	PEC_{local} = 1.2 µg/l
Textiles - application	Agricultural soil	PEC_{local} = 17.1 mg/kg wet wt.
	Grassland	PEC_{local} = 6.9 mg/kg wet wt.
	Pore water	PEC_{local} = 0.61 µg/l
Textiles - combined compounding/application site[b]	Agricultural soil	PEC_{local} = 51.0 mg/kg wet wt.
	Grass land	PEC_{local} = 20.4 mg/kg wet wt.
	Pore water	PEC_{local} = 1.82 µg/l
Regional scale	Agricultural soil	$PEC_{regional}$ = 27.0 mg/kg wet wt.
	Natural soil	$PEC_{regional}$ = 0.11 mg/kg wet wt.
	Pore water	$PEC_{regional}$ = 0.97 µg/l
	Industrial soil	$PEC_{regional}$ = 17.8-19.0 mg/kg wet wt.

Notes: a) Production has now ceased in the EU.
b) As a first approximation the PECs for the combined site are the sum of the values for separate compounding and application sites.

Since decabromodiphenyl ether is a persistent substance, the levels found in soil might be expected to build up with time. The regional concentration estimated above is a "steady state" concentration, and represents the concentration that would build up in the environment over many years assuming a constant input rate. At the local level, the concentrations are estimated after ten years input via sewage sludge and atmospheric deposition. For decabromodiphenyl ether it is estimated that, after ten years, the concentrations predicted represent around 1% 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 concentrations

No measured levels of decabromodiphenyl ether in soil have been reported. Levels of decabromodiphenyl ether in digested sludge from Sweden were reported by de Wit (1999). The samples were collected from Stockholm in 1998 and the levels found were in the range 140 to 350 µg/kg dry weight.

Weisser (1992) sampled sludges from ten treatment plants in Germany, covering rural plants, medium-sized town plants and large city plants. The larger plants received input from industry. Decabromodiphenyl ether levels ranged from <0.05 to 57.8 mg/kg dry weight, with a mean value of 6.62 mg/kg dry weight. The mean level in raw sludges was 14.4 mg/kg dry weight and that in digested sludges was 2.27 mg/kg dry weight.

Decabromodiphenyl ether has been found at a concentration of 3.52 mg/kg dry weight in sewage sludge from a treatment plant receiving effluent from a site where decabromodiphenyl ether may be imported (Environment Agency. 2002). It is also possible that other sources of release of this substance may be present in the area sampled.

Peltola (2002) has recently determined the concentrations of decabromodiphenyl ether in municipal sewage sludge samples from two sewage treatment plants in Finland. The samples were pooled samples of dried sludge collected over 15 days at each plant. The concentration of decabromodiphenyl ether was 83 and 584 µg/kg dry weight in the two samples respectively.

Hale et al. (2001) reported that decabromodiphenyl ether was measured at concentrations of <75-9,160 µg/kg dry weight in eleven sewage sludges collected from 4 different regions of the United States. All the sludges sampled were destined for land-application.

These data indicate that spreading of sewage sludge onto land is a route for decabromodiphenyl ether to soil.

3.1.4 Levels in air

3.1.4.1 Predicted concentrations

Using the EUSES program (see Appendix B), very low levels of decabromodiphenyl ether in air were predicted in the regional (5.4 ng/m^3) and continental (1.8 ng/m^3) scenarios. This is as expected, given the low vapour pressure of the substance and limited sources of release to air. In addition, very low levels were predicted in the local model. The results are summarised in **Table 3.21**.

Table 3.21 Predicted concentrations of decabromodiphenyl ether in air

Scenario	Concentration
Production (generic)[a]	4.2 ng/m^3 - emission episode 1.2 ng/m^3 - annual average $PEC_{local(air, ann.)}$ = 6.6 ng/m^3
Polymer processing	52.9 ng/m^3 - emission episode 38.8 ng/m^3 - annual average $PEC_{local(air, ann.)}$ = 44.2 ng/m^3
Textiles – compounding	1.7 ng/m^3 – emission episode 1.4 ng/m^3 - annual average $PEC_{local(air, ann.)}$ = 6.8 ng/m^3
Textiles – application	0.8 ng/m^3 – emission episode 0.7 ng/m^3 – annual average $PEC_{local(air, ann.)}$ = 6.1 ng/m^3
Textiles – combined compounding/application site[b]	2.5 ng/m^3 – emission episode 2.1 ng/m^3 – annual average $PEC_{local(air, ann.)}$ = 7.5 ng/m^3
Regional	$PEC_{regional}$ = 5.3-5.4 ng/m^3
Continental	$PEC_{continental}$ = 1.8 ng/m^3

Notes: a) Production has now ceased in the EU.
b) As a first approximation the PECs for the combined site are the sum of the values for separate compounding and application sites.

3.1.4.2 Measured concentrations

Decabromodiphenyl ether has been identified in ten samples of air collected in the vicinity of two manufacturing facilities in the United States. The concentrations measured were between 0.016 and 26 μg/m^3 and the decabromodiphenyl ether was present mainly in the particulate phase (Zweidinger et al., 1977). These figures are higher than the levels predicted for a typical processing plant and may reflect dust rather than vapour releases. Further, it is not clear if these levels were taken on the manufacturing site or outside the site. This is of importance for the risk assessment as on-site levels are more appropriate to occupational exposure than environmental exposure.

Bergander et al. (1995) analysed air samples from two areas of Sweden for the presence of decabromodiphenyl ether. The areas sampled were Ammarnäs (located on approximately N 65^o on the eastern rim of the mountain ridge separating Norway and Sweden) in January 1991, and Hoburgen (located on the southernmost tip of the island Gotland in the central Baltic) in July 1990. Both sampling sites are considered to be in areas remote from industry. In the sampling, the substances in the particulate phase were collected on glass fibre filters and substances in the gas-phase were adsorbed onto polyurethane foam plugs. No decabromodiphenyl ether was found in either the particulate or gas phase samples (the detection limit of the method given was not stated).

The concentration of decabromodiphenyl 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 have been reported (Strandberg et al., 2001). Air samples (both particulates and gas phase) were taken over 24 hours. The average temperature was 20±3°C at the time of sampling, and four samples each for the years 1997, 1998 and 1999 were analysed. The average concentration at the remote and rural locations was <0.10 pg/m^3 for each of the years investigated. The average concentration at the urban location was 0.35 pg/m^3 in 1997, 0.20 pg/m^3 in 1998 and 0.34 pg/m^3 in 1999. The decabromodiphenyl ether was found to be mainly in the particulate phase.

Pettersson et al. (2001) reported the levels of decabromodiphenyl ether in air samples and sedimentary dust samples at an electronics dismantling plants in Öbrebro, Sweden. Two air samples and two dust samples were collected daily over a two week period. The air samples were representative of the breathing zone of workers in the dust removal area and dismantling hall of the facility. The levels of decabromodiphenyl ether found were 7.9 ng/m^3 and 12 ng/m^3 in air from the dust removal area and dismantling hall respectively. The level present in dust in these two areas was 24,000 µg/kg and 8,100 µg/kg respectively.

The levels of decabromodiphenyl ether in air at another electronic equipment dismantling plant in Sweden were found to be 12-200 ng/m^3. The level present in office air was reported to be at most 0.08 ng/m^3 (Sjödin et al., 1999).

Decabromodiphenyl ether at concentrations of 260 to 6,900 µg/kg dust have been found in dust samples from Parliament buildings from 8 countries and the offices of an internet provider (Leonards et al., 2001; Santillo et al., 2001). The samples were collected in 2000.

The levels of 7 polybrominated diphenyl ethers in rain in southern Sweden have been reported (ter Schure and Larsson, 2001). 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 decabromodiphenyl ether. These were reported to be 321 pg/m^2.day for decabromodiphenyl ether in the particulate phase and 673 pg/m^2.day for decabromodiphenyl ether in the dissolved phase.

3.1.4.3 Comparison of measured and predicted levels

Most of the available information relates to the levels of decabromodiphenyl ether 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. Most of this information is most relevant to the human health assessment, but it does show that particulate or dust emissions of decabromodiphenyl ether do 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 decabromodiphenyl ether could reach the environment.

3.1.5 Non-compartment specific exposure relevant for the food chain (secondary poisoning)

3.1.5.1 Predicted concentrations

Predicted concentrations for decabromodiphenyl ether have been calculated in fish and earthworms using EUSES (see Appendix B) and are summarised in **Table 3.22**. The model assumes that 50% of the dose comes from local sources and 50% comes from regional sources.

However, this method is likely to grossly overestimate the concentration of decabromodiphenyl ether in earthworms. This is because the estimation method relies on the determination of bioconcentration factors and, in the absence of any data, these are estimated from the octanol - water partition coefficient. Since decabromodiphenyl ether has a very high octanol - water partition coefficient, this bioconcentration factor has been estimated to be very large and has probably lead to unrealistic predicted levels in earthworms (little or no uptake was seen over 28-days in an earthworm reproduction test; see Section 3.2.2.2). A low bioconcentration factor of 4 l/kg has been used for fish.

Table 3.22 Concentrations in fish and earthworms for secondary poisoning

Scenario	Concentration in fish	Concentration in earthworms
Production (generic)[a]	3.7-3.8 µg/kg	149 mg/kg
Production (site specific)[a]	0.27 µg/kg	no route to soil
Polymer processing	0.72 µg/kg	40.3 mg/kg
Textiles – compounding	4.4 µg/kg	81.0 mg/kg
Textiles – application	2.4 µg/kg	58.5 mg/kg
Textiles – combined compounding/application site[b]	6.4-6.5 µg/kg	103-104 mg/kg

Notes: a) Production has now ceased in the EU.
b) As a first approximation the PECs for the combined site are the sum of the values for separate compounding and application sites.

The concentrations of decabromodiphenyl ether in various parts of the human food chain have been estimated using EUSES. The results are shown in Section 4.1.1.4.

3.1.5.2 Measured concentrations

The measured levels of decabromodiphenyl ether in biota are shown in **Tables 3.23** (EU) and **3.24** (rest of world).

Samples of starfish pyloric caeca and hermit crab abdomen, whelks and shrimps collected from various locations in the North Sea during August and September 1999 have been analysed for the presence or decabromodiphenyl ether. The substance was sometimes found to be present in the samples at concentrations just above the detection limit, however, the samples analysed all contained parts of the digestive system and so the results do not necessarily reflect actual uptake of decabromodiphenyl ether by the organisms (de Boer et al., 2001; Zegers et al., 2001). However, de Boer et al. (2001) also found decabromodiphenyl ether to be present in harbour seals (blubber and liver), harbour porpoises (blubber and liver) and white beaked dolphin (liver) from the North Sea (see **Table 3.23**) at levels up to 318 µg/kg lipid, and some of these findings probably do reflect actual uptake of decabromodiphenyl ether by the organisms.

Table 3.23 Levels of decabromodiphenyl ether measured in biota in the EU

Species	Location	Level	Reference
Bream	River Elbe, Germany (22 samples)	Detected in 11 samples at up to 37.3 μg/kg lipid. Median level 0.97 μg/kg lipid	Karasyova et al., 2002
Eel	River Elbe, Germany (5 samples)	<0.1-<1.3 μg/kg lipid	Karasyova et al., 2002
Pike (muscle)	Lake Marsjön, Sweden 1995	nd-trace	Sellström et al., 1998b
	Lake Öresjö, Sweden 1995	nd	Sellström et al., 1998b
	River Viskan, downstream from Borås 1995	nd	Sellström et al., 1998b
	River Viskan at Moga, 1995	nd-trace	Sellström et al., 1998b
	Lake Skäresjön, 1995	nd	Sellström et al., 1998b
	Finland, 1997	nd-3.6 μg/kg wet weight (<52-1,700 μg/kg lipid)	Peltola, 2002
Baltic salmon (muscle)	River Kymijoki, Finland, 1997-1999	nd-0.72 μg/kg wet weight (<19-29 μg/kg lipid)	Peltola, 2002
	River Simojoki, Finland, 1993-1999	nd-1.2 μg/kg wet weight (<5-21 μg/kg lipid)	Peltola, 2002
Dab (liver)	Off River Tees, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Off the Wash, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Bideford Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Tees Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Dab (muscle)	Bideford Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Tees Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Whiting (liver)	Bristol Channel, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Flounder (liver)	Off Lune/Wyre, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Off River Humber, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Nith estuary, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Bideford Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Tees Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Flounder (muscle)	Nith estuary, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Bideford Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Tees Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Plaice (muscle)	Bideford Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Tees Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Plaice (liver)	Bideford Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
	Tees Bay, UK	<1.2 μg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999

Table 3.23 continued overleaf

Table 3.23 continued

Species	Location	Level	Reference
Herring liver	North Sea, 1999-2001	<4.6 - <11 µg/kg lipid	de Boer et al., 2001
Herring fillet	North Sea, 1999-2001	<1.4 - <2.6 µg/kg lipid	de Boer et al., 2001
Herring milt and eggs	North Sea, 1999-2001	<2.1 - <5.0 µg/kg lipid	de Boer et al., 2001
Mackerel	Muscle, Dutch coast, 1995	<2 µg/kg wet wt.	de Boer et al., 1998
Cod liver	North Sea, 1999-2001	<0.29 - 2.5 µg/kg lipid	de Boer et al., 2001
Cod fillet	North Sea, 1999-2001	<0.89 - <40 µg/kg lipid	de Boer et al., 2001
Whiting liver	North Sea, 1999-2001	<0.4 - <1.2 µg/kg lipid	de Boer et al., 2001
Whiting fillet	North Sea, 1999-2001	<6.5 - <11 µg/kg lipid	de Boer et al., 2001
Gudgeon	Western Scheldt, 1999-2001	<6.0 - <17 µg/kg lipid	de Boer et al., 2001
Greater Sandeel	Western Scheldt, 1999-2001	<18 - <22 µg/kg lipid	de Boer et al., 2001
Winkles	River Tweed	<1.2 µg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Mussels	The Wash, UK	<1.2 µg/kg wet weight	Law et al., 1996 ; Allchin et al., 1999
Star fish	North Sea, 1999-2001	<2-8.9 µg/kg lipid	de Boer et al., 2001; Zegers et al., 2001
Hermit crab	North Sea, 1999-2001	<1.1-7.0	de Boer et al., 2001; Zegers et al., 2001.
Whelk	North Sea, 1999-2001	<2.3 - <14 µg/kg lipid	de Boer et al., 2001
Shrimp	North Sea, 1999-2001	<2.5 - <5.6 µg/kg lipid	de Boer et al., 2001
Mysid shrimp	Western Scheldt, 1999-2001	<20 - 93 µg/kg lipid	de Boer et al., 2001
White beaked dolphin (liver)	Dutch coast, 1995	<1 µg/kg wet wt.	de Boer et al., 1998
	North Sea, 1999-2001	140-318 µg/kg lipid	de Boer et al., 2001
White beaked dolphin (blubber)	Dutch coast, 1995	<10 µg/kg wet wt.	de Boer et al., 1998
	North Sea, 1999-2001	<3.8 µg/kg lipid	de Boer et al., 2001
Bottlenose dolphin (liver)	North Sea, 1999-2001	<6.4 µg/kg lipid	de Boer et al., 2001
Bottlenose dolphin (blubber)	North Sea, 1999-2001	<2.5 µg/kg lipid	de Boer et al., 2001
Harbour porpoises (liver)	North Sea, 1999-2001	<1.4 - 1.2 µg/kg lipid	de Boer et al., 2001
Harbour porpoises (blubber)	North Sea, 1999-2001	<2.7 - 26 µg/kg lipid	de Boer et al., 2001
Minke whale	Blubber, Dutch coast, 1995	<1 µg/kg wet wt.	de Boer et al., 1998
Sperm whale (liver)	Dutch coast, 1995	<3 µg/kg wet wt.	de Boer et al., 1998
Sperm whale (blubber)	3 samples, Dutch coast, 1995	<3, <3 and <5 µg/kg wet wt.	de Boer et al., 1998

Table 3.23 continued overleaf.

Table 3.23 continued

Species	Location	Level	Reference
Harbour seal (liver)	3 samples, Dutch coast, 1995	<2, <1 and <2 μg/kg wet wt.	de Boer et al., 1998
	North Sea, 1999-2001	<6.5 - 160 μg/kg lipid	de Boer et al., 2001
Harbour seal (blubber)	3 Blubber samples, Dutch coast, 1995	<15, <10 and <10 μg/kg wet wt.	de Boer et al., 1998
	North Sea, 1999-2001	<2.1 - 16 μg/kg lipid	de Boer et al., 2001
Common tern eggs	Western Scheldt, 1999-2001	<5.0 - 27 μg/kg lipid	de Boer et al., 2001
Common tern eggs	Maasvlakte, 2001	<5.7 - 70 μg/kg lipid	de Boer et al., 2001
Cormorant livers	North Sea, 1999-2001	<0.5 μg/kg wet weight	de Boer et al., 2001
Peregrine falcon eggs	Sweden, 1988-1999	28-430 μg/kg lipid	de Wit (2001); Sellström et al., 2001

Note: nd - Not detected (detection limit 100 μg/kg lipid) - lipid concentration in these samples was between 0.46 and 1.09% body weight, so detection limit is equivalent to 0.46-1.1 μg/kg body weight

The levels of decabromodiphenyl ether have been determined in fish samples from Finland (Peltola, 2002). The samples analysed included Baltic salmon (*Salmo salar*) muscle from populations from the River Kymijoki and River Simojoki) and pike (*Esox lucius*) muscle samples. In all, three pike muscle samples from 1997 and ten salmon muscle samples covering the years 1993 to 1999 were analysed. The detection limit of the method was around 5-52 μg/kg lipid and decabromodiphenyl ether was found to be present in seven salmon samples at a concentration of 4.2-29 μg/kg lipid and two pike samples at 300-1,700 μg/kg lipid. These levels were equivalent to 0.23-1.2 μg/kg on a fresh weight basis in salmon (the salmon samples were collected immediately before spawning and so had a relatively low lipid concentration) and 0.93-3.6 μg/kg fresh weight in pike. Five of the samples (two pike and three salmon) in which decabromodiphenyl ether was found were also analysed by a second laboratory in order to confirm the results. The re-analyses failed to confirm the results as the decabromodiphenyl ether was not found in any of the samples at concentrations above the detection limit (reported to be 0.02 μg/kg fresh weight for the second laboratory). Therefore there is some uncertainty whether or not decabromodiphenyl ether was present or not in these samples.

A recent study has found decabromodiphenyl ether to be present in bream (*Abramis abrama*) but not eel (*Anguilla anguilla*) taken from the River Elbe upstream of Dresden in 2001 (Karasyova et al., 2002). The detection limit of the method was 0.1-1.3 μg/kg lipid and in all 22 samples of bream and five samples of eel were analysed. Decabromodiphenyl ether was found to be present in 11 out of 22 bream samples at a concentration of up to 37.3 μg/kg lipid. The median concentration found was 0.97 μg/kg lipid. In eel, the concentration decabromodiphenyl ether was below the detection limit of the method used. The presence of decabromodiphenyl ether in the bream samples was confirmed by the use of gas chromatography with high resolution mass spectrometry detection.

Sellström et al. (2001) determined the levels of decabromodiphenyl ether present in eggs of Peregrine Falcons (*Falco peregrinus*). The eggs were collected in 1988-1999 from breeding populations from northern Sweden (8 eggs), southern Sweden (9 eggs) and a captive breeding population from Sweden (4 eggs). Decabromodiphenyl ether was detected in 18 out of the 21

samples analysed and the level found in the egg contents was 28-430 µg/kg lipid. The levels in the wild populations were generally higher than in the captive-bred populations.

Levels of decabromodiphenyl ether of up to 70 µg/kg lipid in Common Tern (*Sterna hirundo*) eggs have been measured by de Boer et al. (2001). However, the authors noted that decabromodiphenyl ether was present in only 5 out of the 15 eggs analysed from the Western Scheldt and 1 out of 15 eggs analysed from the Maasvlakte, and the concentrations found were very close to the detection limit of the method used.

Table 3.24 Levels of decabromodiphenyl ether in biota in rest of 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 5 µg/kg	Not detected in 138 samples	Environment Agency Japan, 1991
Mussels, Japan, 1981-1985	Detection limit 0.5 µg/kg wet weight	Detected in 1 out of 5 samples at 1.4 µg/kg wet weight	Watanabe et al., 1987a
Mullet, Japan. 1981-1985	Detection limit 0.5 µg/kg wet weight	Not detected in 4 samples	Watanabe et al., 1987a
Goby, Japan, 1981-1985	Detection limit 0.5 µg/kg wet weight	Not detected in 2 samples	Watanabe et al., 1987a
Sardine, Japan, 1981-1985	Detection limit 0.5 µg/kg wet weight	Not detected in 2 samples	Watanabe et al., 1987a
Sea bass, Japan, 1981-1985	Detection limit 0.5 µg/kg wet weight	Not detected in 1 sample	Watanabe et al., 1987a
Horse mackerel, Japan, 1981-1985	Detection limit 0.5 µg/kg wet weight	Not detected in 1 sample	Watanabe et al., 1987a
Mackerel, Japan, 1981-1985	Detection limit 0.5 µg/kg wet weight	Not detected in 1 sample	Watanabe et al., 1987a
Hairtail, Japan, 1981-1985	Detection limit 0.5 µg/kg wet weight	Not detected in 1 sample	Watanabe et al., 1987a
Farmed Chinook Salmon, Canada, 1999-2000	Detection limit 0.65 ng/kg wet weight	Not detected in 2 samples	Easton et al., 2002
Wild Chinook Salmon, Alaska, 2000	Detection limit 0.65 ng/kg wet weight	Not detected in 1 sample	Easton et al., 2002
Wild Chum Salmon, Alaska, 2002	Detection limit 0.65 ng/kg wet weight	Not detected in 1 sample	Easton et al., 2002
Wild Sockeye Salmon, Canada, 2002	Detection limit 0.65 ng/kg wet weight	Not detected in 2 samples	Easton et al., 2002
Fish feed, Canada, 2000	Detection limit 0.65 ng/kg wet weight	Not detected in 2 samples	Easton et al., 2002

Decabromodiphenyl ether has also been investigated 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 found in adipose tissue were reported to be 0.44-1.19, not detected-3.35 and 0.47-1.02 µg/kg lipid in chickens from the dioxin contaminated sites, 0.63-2.91 µg/kg lipid in chickens from the uncontaminated site and 0.57 µg/kg lipid in chickens from the grocery. These levels have to be

put into context in that the reported level of decabromodiphenyl ether in the method blank samples was 0.74 µg/kg lipid, meaning that it is uncertain that decabromodiphenyl ether was present in the chicken samples analysed. The lipid content of the samples was reported to be around 86-96%.

In the United States, human fat tissue was monitored for the presence of decabromodiphenyl ether. In all, five samples were analysed. No decabromodiphenyl ether was found in two of the five samples, a weak decabromodiphenyl ether response was found in one of the samples and levels of decabromodiphenyl ether of 0.4 and 0.7 µg/kg were found in the other two samples (Cramer et al., 1990; Stanley et al., 1991). In another study from the United States, decabromodiphenyl ether was found at concentrations of 5 µg/kg in 2 out of 40 hair samples collected from barber shops near to sites where it is manufactured (DeCarlo, 1979).

The levels of decabromodiphenyl ether in blood plasma have been measured at <0.3-3.9 µg/kg lipid in hospital workers, <0.3-8.0 µg/kg in computer clerks and <0.3-9.9 µg/kg in electronic equipment dismantlers. Decabromodiphenyl ether was found in 45 out of the 59 samples analysed (Sjödin et al., 2001). Decabromodiphenyl ether levels of 2.3 µg/kg lipid and 1.5 µg/kg lipid have also been reported in the plasma from smelter workers and computer technicians respectively from Sweden (Hagmer and Bergman, 2001).

Decabromodiphenyl ether was not detected (detection limit 10 µg/kg fat weight) in samples of human adipose tissue from Japan in 1978 (Watanabe et al., 1987b).

Ryan and Patry (2001) reported the findings from a recent survey of the levels of decabromodiphenyl ether in human milk and commercial foods from Canada. The analysis of decabromodiphenyl ether in these samples was reported to be difficult, and the presence of decabromodiphenyl ether in laboratory blanks made quantification in the samples uncertain. However, little or no decabromodiphenyl ether could be detected in 72 human milk samples from 1992. In foods, no information on the levels of decabromodiphenyl ether was provided, but 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.

3.1.5.3 Comparison of measured and predicted levels

Decabromodiphenyl ether has not been detected or found only in trace amounts in fish, invertebrates, whale, dolphin and seal samples collected in the EU. Many of the samples were collected in areas near to potential sources of release of decabromodiphenyl ether. Of the many analyses carried out decabromodiphenyl ether was detected only occasionally, usually at a concentration close to the detection limit of the method used. However, decabromodiphenyl ether is found to be present more often in the more recent studies (such as de Boer, 2001, Karasyova et al. 2002 and Peltola, 2002) than in the earlier studies. Some of these positive determinations of decabromodiphenyl ether may be due to its presence in the gut contents of the organisms analysed (this may be true for the invertebrate analyses) or analytical artefacts for determinations very close to the detection limit of the method (where possible the detection limits of the methods used have been given; detection limit for results expressed on a lipid basis may depend on the actual lipid content of the sample used), for example the results of Peltola (2002) were not confirmed by another laboratory. Despite these uncertainties, in general it has to be concluded that decabromodiphenyl ether appears to now be present, albeit at low concentrations, in some types of marine mammals and possibly also other aquatic organisms. The apparent increasing incidence of the presence of decabromodiphenyl ether in the more recent studies compared with the earlier studies could be due to a number of possible reasons,

e.g. the increasing sensitivity of the analytical methods used, the increasing range of species tested and the fact that the levels of decabromodiphenyl ether in organisms are actually increasing with time (accumulation is very slow and/or the actual amount of decabromodiphenyl ether in the environment is increasing). It is not possible to distinguish between these possibilities with the currently available data.

Decabromodiphenyl ether has also been found in the contents of predatory birds' eggs. Although it has been found so far in eggs from only relatively few species (Peregrine Falcons and to a lesser extent Common Tern), it is also possible that decabromodiphenyl ether could be present in eggs of other species (for example Newton and Haas (1988) reported that, in general, Merlin *Falco columbarius* eggs had higher concentrations of certain persistent halogenated pollutants than Peregrine Falcon eggs). Based on the current information it is not possible to determine by which of the possible routes (e.g. via food, water or air) the uptake is occurring. Since the concentrations of decabromodiphenyl ether in food (e.g. fish), water (see Section 3.1.2.2.1) and air (see Section 3.1.4.1) are all generally low it has to be tentatively concluded that bioaccumulation of decabromodiphenyl ether may be taking place in these organisms, but it should be borne in mind that the concentrations of decabromodiphenyl ether in the media to which these specific birds were exposed is not known.

The recent monitoring data for the levels of decabromodiphenyl ether in human plasma are probably related to occupational exposure by inhalation.

In discussing these results it is important to bear in mind that the levels found in many organisms in the environment are at or near the detection limit or limit of quantification of the method used. This means that there is generally some uncertainty over a) whether decabromodiphenyl ether is present and b) the concentration that may be present. This can be seen in the study of levels in chickens, where the concentration found in the laboratory blank samples was around the same level found in the chickens. However, despite this, there are an increasing number of positive detections of decabromodiphenyl ether in environmental biota, and, as a precautionary approach, it cannot be assumed that all these are due to artefacts of the analytical methodology used.

Overall, the available results indicate that decabromodiphenyl ether may be present in certain organisms in the environment, particularly marine mammals and predatory birds' eggs, but only at relatively low concentrations. The exact route of decabromodiphenyl ether into these organisms is not clear, but uptake could be occurring via diet, water and/or air.

The predicted concentrations in fish are inconsistent with the mainly "not detected" levels in fish found in the environment. The predicted concentrations in earthworms are very high and probably unrealistic. There are no measured data with which to compare these levels, and so the earthworm concentrations will not be considered in the risk characterisation.

3.1.6 Summary of PECs for risk assessment

The following PECs have been estimated and will be used in the following Sections for the risk assessment. It should be noted that many of the surface and pore water concentrations are greater than the actual water solubility of the substance. This casts some doubt over the applicability of the estimation methods used in the Technical Guidance Document for this type of substance.

Surface water: PEC_{local}(production) = 0.9 µg/l
PEC_{local}(polymer processing) = 0.33 µg/l
PEC_{local}(textiles - compounding) = 2.6 µg/l
PEC_{local}(textiles - application) = 1.3 µg/l
PEC_{local}(textiles - combined compounding/application) = 3.8 µg/l
$PEC_{regional}$ = 0.093-0.094 µg/l

Sediment: PEC_{local}(production) = 31 mg/kg wet wt.
PEC_{local}(polymer processing) = 10.8 mg/kg wet wt.
PEC_{local}(textiles - compounding) = 89.0 mg/kg wet wt.
PEC_{local}(textiles - application) = 46.1 mg/kg wet wt.
PEC_{local}(textiles - combined compounding/application) = 131 mg/kg wet wt.
$PEC_{regional}$ = 5.66-5.72 mg/kg wet wt.
Measured data = 1.2-2 mg/kg wet wt.

Soil: PEC_{local}(production) = negligible
PEC_{local}(polymer processing) = 3.30 mg/kg wet wt.
PEC_{local}(textiles - compounding) = 34.0 mg/kg wet wt.
PEC_{local}(textiles - application) = 17.1 mg/kg wet wt.
PEC_{local}(textiles - combined compounding/application) = 51.0 mg/kg wet wt.
$PEC_{regional}$ = 27.0 mg/kg wet wt.

Air: $PEC_{local(air,\ ann.)}$(production) = 5.4 ng/m^3
$PEC_{local(air,\ ann.)}$(polymer processing) = 44.2 ng/m^3
$PEC_{local(air,\ ann.)}$(textiles - compounding) = 6.8 ng/m^3
$PEC_{local(air,\ ann.)}$(textiles - application) = 6.1 ng/m^3
$PEC_{local(air,\ ann.)}$(textiles - combined compounding/application) = 7.5 ng/m^3
$PEC_{regional}$ = 5.3-5.4 ng/m^3

Secondary poisoning: PEC (production)= 0.27 µg/kg
PEC (polymer processing) = 0.72 µg/kg
PEC (textiles - compounding) = 4.4 µg/kg
PEC (textiles - application) 2.4 µg/kg
PEC (textiles - combined compounding/application) = 6.4-6.5 µg/kg

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

3.2.1 Aquatic compartment

3.2.1.1 Toxicity to algae

Walsh et al. (1987) studied the toxicity of decabromodiphenyl ether to the marine unicellular algae *Skeletonema costatum*, *Thalassiosira pseudonana* and *Chlorella* sp. The tests were carried out at a salinity of 30$^{o}/_{oo}$ for either 72 hours (*S. costatum* and *T. pseudonana*) or 96 hours (*Chlorella* sp.). The end-point measured was the EC_{50} for growth based on cell numbers. The exposure concentrations in the test solutions were verified by analysis. In the tests, the decabromodiphenyl ether was added as a solution in acetone (final acetone concentration around 1 ml/l). Six different growth media were used in the test, one natural sea water and five synthetic sea water formulations. The natural sea water had a salinity of 32‰ and was diluted to give a final test salinity of 30‰ to be comparable with that of the synthetic media. The pHs of the various test media were in the range 7.6-8.2. At the highest concentration tested (1 mg/l) decabromodiphenyl ether reduced growth of all three species by <50% and so it was not possible to determine the EC_{50} (it is not clear if any toxic effect were seen at 1 mg/l). The toxicity limit reported is well in excess of the compound's water solubility.

3.2.1.2 Toxicity to aquatic invertebrates

No information is currently available for decabromodiphenyl ether.

A long-term *Daphnia* test has been carried out using octabromodiphenyl ether. No effects on survival, reproduction or growth were seen over 21 days at concentrations up to 2 µg/l (solubility limit) (see the assessment of that substance for further details). Taken as a whole, it is clear that the aquatic toxicity and bioaccumulation potential of the polybrominated diphenyl ethers (penta-, octa- and decabromodiphenyl ether) decreases with increasing bromination and therefore it is unlikely that decabromodiphenyl ether will show any toxic effects to invertebrates at concentrations below its solubility limit.

3.2.1.3 Toxicity to fish

A 48h-LC_{50} for orange-red killifish (*Oryzias latipes*) has been determined for decabromodiphenyl ether as part of a six week bioconcentration study. The LC_{50} was >500 mg/l (CITI, 1992). The reported toxicity limit is well in excess of the compound's solubility in water. Few other details of this study have been reported.

In a recent 120-day feeding experiment with rainbow trout (*Oncorhynchus mykiss*) (Kierkegaard et al., 1997 and 1999), decabromodiphenyl ether (DOW FR-300-BA; the actual composition of this substance was not given in the paper but the composition of this product has been reported elsewhere as 77.4% deca-, 21.8% nona- and 0.8% octabromodiphenyl ether (Norris et al., 1973 and 1974)) was reported to cause increased liver weights (after 120 days exposure, but not after 16 or 49 days exposure) and lactate levels in blood when administered in food at a dose of 7.5-10 mg/kg body weight/day. No significant effects were reported on the number of lymphocytes or blood haemoglobin levels (a significant decrease in haemoglobin levels occurred

at day 16, but this effect had disappeared by day 120) and no effects were seen on Ethoxyresorufin-O-deethylase (EROD), Ethoxycoumarin-O-deethylase (ECOD) or the transketolase activity. In addition no DNA adducts were seen. The effects on the liver occurred late in the exposure period (and also occurred in fish exposed for 49 days, followed by a 41-day depuration period) and may have been related to a build up of more toxic lower brominated congeners in the fish (see Section 3.1.1.5.3). The substance used in this test had a higher fraction of lower brominated congeners than found in current products, which consist of >97% decabromodiphenyl ether and <3% nonabromodiphenyl ether. Although the substance was purified on a charcoal column prior to use to remove planar compounds, the significance of these effects to the current commercial product is unknown.

3.2.1.4 QSAR data

The high octanol-water partition coefficient for decabromodiphenyl ether (log Kow = 6.27) 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 for non-polar narcosis in Appendix II of Chapter 4 in the Technical Guidance Document. The results are shown below:

96h-LC_{50} for fish = $1.91 \cdot 10^{-7}$ mol/l = 183 µg/l
28d-NOEC for fish = $1.14 \cdot 10^{-8}$ mol/l = 10.9 µg/l
48h-EC_{50} for *Daphnia* = $5.29 \cdot 10^{-8}$ mol/l = 50.7 µg/l
16d-NOEC for *Daphnia* = $3.69 \cdot 10^{-9}$ mol/l = 3.5 µg/l
72-96h-EC_{50} for algae = $3.16 \cdot 10^{-9}$ mol/l = 30.3 µg/l

The predicted NOECs and L(E)C_{50}s are all greater than the water solubility of decabromodiphenyl ether.

3.2.1.5 Toxicity to sediment organisms

Prolonged sediment toxicity tests using decabromodiphenyl 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 USEPA 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 a composite sample from three manufacturers and had a purity of 97.9%. The test substance was finely ground using a mortar and pestle prior to being 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 (129 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 44 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 6.6-7.9 cm. The total exposure period was 28 days.

The nominal concentrations tested in the studies were 313, 625, 1,250, 2,500 and 5,000 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^{o}C. The dissolved oxygen concentration fell below 60% of saturation on days 7 and 12 of the test with the 2.4% organic carbon sediment (the minimum dissolved oxygen concentration reached was 3.1 mg/l or 36% of saturation) and on day 7 of the test with the 5.9% organic carbon sediment (minimum dissolved oxygen concentration was 56% of saturation). Gentle aeration of the overlying water was then introduced for the remainder of the study.

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 decabromodiphenyl ether. The draft revised Technical Guidance Document indicates that for highly adsorptive substances such as decabromodiphenyl 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 decabromodiphenyl 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 decabromodiphenyl ether is unknown.

In the experiments with the 2.4% organic carbon content sediment the overlying water was clear and colourless at the start of the test, but at test termination the overlying water in all chambers was slightly cloudy, probably due to precipitation of the organic matter present in the sediment. In the test with the 5.9% organic carbon sediment the overlying water was reported to be clear and colourless at the start and end of the test.

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. Some oligochaetes were observed to leave the sediment throughout the test in both the control groups and the treatment groups but this effect was not thought to be treatment related. 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 3.25**. At the end of the test, except for two replicates in the 625 mg/kg dry wt. treatment, there was an increase in the number of worms present, indicating that reproduction had occurred. The reduction in the mean number of worms/replicate in the 625 mg/kg dry wt. treatment was statistically significant ($p=0.05$) when compared with controls. However, this reduction was considered slight, and no significant reduction was seen at any of the higher concentrations tested, and so it was considered in the test report that this effect was not treatment related. For the mean dry weight/worm, no statistically significant differences were found between the treatments and the control groups. The mean weight/worm in the 625 mg/kg dry weight treatment was slightly higher than the other treatment and control groups, but this was due mainly to the higher mean weight/worm present in the two replicates with lower survival (these would have received the same amount of food as the other replicates and so

potentially would have had more food/worm available). Based on these findings, the overall NOEC from the study was given as ≥5,000 mg/kg dry wt. based on nominal values.

In the test with the 5.9% organic carbon sediment some oligochaetes were observed leaving the sediment in both the control and treatment groups. This effects was therefore not treatment related. No other 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 3.25.** With the exception of one replicate in the 625 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 ≥5,000 mg/kg dry weight based on the nominal concentration.

Table 3.25 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	22.9	1.41	17.8	1.67[b]
313	20.4	1.50	22.0	1.17
625	14.3[a]	1.89	14.9	1.47
1,250	18.8	1.59	20.0	1.17
2,500	21.3	1.36	17.8	1.45
5,000	22.9	1.55	20.1	1.29

Note: a) Statistically significant difference from control group (p=0.05).
b) The mean dry weight/worm for the controls was 1.67±1.19 mg. This included one value of 4.61 mg which was considered as an outlier. When this value is excluded, the mean dry weight/worm for the control group is 1.26±mg, which is very similar to the values in the treatment groups.

During the studies, the concentration of decabromodiphenyl ether present in the sediment, overlying water and pore water phases of the test medium were determined analytically. These results are shown in **Table 3.26**. These show that the concentration of decabromodiphenyl ether in the sediment phase remained relatively constant throughout the test. The high concentration of decabromodiphenyl ether in the pore water probably reflects the fact that sediment-bound substance may also have been analysed in this fraction, along with decabromodiphenyl ether in the dissolved phased.

Based on the analytical results the NOECs from these studies based on measured concentrations are 4,536 mg/kg dry weight for the 2.4% organic carbon sediment and 3,841 mg/kg dry weight for the 5.9% organic carbon sediment.

Table 3.26 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	<1.16	2.89	13.1	<1.16	<2	<4
	Day 7	<1.16	<2	<6.67	<1.16		
	Day 28	<1.16	<0.80	4.96	<1.16	<0.8	<4
313	Day 0	318-365	12.8	158	242-305	11.9-12.9	1,360
	Day 7	289-291	<2	674	228-256		
	Day 28	234-246	0.82-1.2	1,140	242-274	0.58-13.3	2,340
	Mean	291	2.96	657	258	9.67	1,850
2,500	Day 0	2,486-2,505	65.9	2,477	1,997-2,163	24.0-39.9	1,240
	Day 7	2,378-2,488	4.16-7.05	1,073	2,006-2,032		
	Day 28	2,124	11.2-28.3	1,480	1,955-2,052	0.0737-0.147	4,640
	Mean	2,360	23.3	1,677	2,034	16.0	2,940
5,000	Day 0	4,602-4,904	74.3	639	4,393-4,469	15.8-43.2	1,090
	Day 7	4,631-4,822	24.2-26.4	3,688	3,399-3,763		
	Day 28	3,990-4,266	32.2-40.3	6,800	3,500-3,522	7.55-7.79	6,200
	Mean	4,536	39.5	3,709	3,841	18.6	3,650

3.2.1.6 Toxicity to microorganisms

An activated sludge respiration inhibition (OECD 209) test has been carried out with a composite sample of commercial decabromodiphenyl ether products from three manufacturers (Schaefer and Siddiqui, 2001). The purity of the test substance was given as 97.9% decabromodiphenyl ether. 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 20-22^{o}C and the respiration rate of the activated sludge over 3 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 both 41.6 mg O_2/l/hour. The mean respiration rate in the decabromodiphenyl ether treatments was 41.1 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 9.8 mg/l, which is within the normal range of 5 to 30 mg/l for this test. The NOEC for decabromodiphenyl ether from this test is therefore ≥15 mg/l.

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

Based on the available data for fish and algae, decabromodiphenyl ether appears to have a very low toxicity in acute tests, with no effects being seen up to the substances water solubility. Toxicity of decabromodiphenyl ether to *Daphnia* would also not be expected to occur at concentrations up to its water solubility, based on the lack of effects seen in long-term tests with another highly brominated diphenyl ether (octabromodiphenyl ether (RAR, 2002)). The lack of effects seen or predicted in aquatic toxicity tests means that it is not possible to derive a true PNEC for decabromodiphenyl ether. No effects on aquatic organisms are expected to occur at concentrations up to the substances water solubility.

In the absence of toxicity data suitable for derivation of a PNEC for decabromodiphenyl ether, two approaches could be used to derive tentative values.

Based in the EC_{50} from the algal studies being >1 mg/l, a tentative PNEC of >1 µg/l can be estimated using an assessment factor of 1,000 (i.e. decabromodiphenyl ether is not expected to cause adverse effects on aquatic organisms at concentrations up to its water solubility). This value should be treated as a minimum value for the PNEC since no clear effects of decabromodiphenyl ether have been demonstrated in any of the acute toxicity tests reported so far.

Another approach to the estimation of a tentative PNEC for decabromodiphenyl ether would be to assume that it has a similar toxicity to octabromodiphenyl ether in long-term tests. Thus a PNEC of >0.2 µg/l could be estimated based on the long-term *Daphnia* NOEC for octabromodiphenyl ether and an assessment factor of 10 (see octabromodiphenyl ether assessment). Again, this value should be treated as a minimum value for the PNEC since no effects of octabromodiphenyl ether was seen at the concentrations tested.

3.2.1.8 Predicted no effect concentration (PNEC) for microorganisms

For microorganisms, a NOEC of ≥15 mg/l has been determined for decabromodiphenyl 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 decabromodiphenyl ether.

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

Decabromodiphenyl 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 3,841 mg/kg dry weight. Studies on three sediment species with the substance pentabromodiphenyl ether (see the published EU risk assessment report (ECB, 2000)) suggest that other available test species are unlikely to be more sensitive to decabromodiphenyl 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 ≥384 mg/kg dry weight. Expressed on a wet weight basis (using the default sediment water contents from the Technical Guidance Document) the $PNEC_{sed}$ is ≥148 mg/kg wet weight.

The $PNEC_{sed}$ can usually also be calculated using the equilibrium partitioning method. However, for decabromodiphenyl ether no PNEC for aquatic organisms can be estimated. This is because

no toxic effects were seen in the aquatic tests at concentrations in excess of the substance's water solubility. In Section 3.2.1.5, two possible approaches for deriving a tentative PNEC for water were given. These are open to some uncertainty but could be used to derive a tentative PNEC for sediment using the equilibrium partitioning method.

$$PNEC_{sed} = \frac{K_{susp-water}}{RHO_{susp}} \times PNEC_{water} \times 1000$$

where $K_{susp\text{-}water}$ = suspended matter - water partition coefficient = 39,717 m^3/m^3
RHO_{susp} = bulk density of suspended matter = 1,150 kg/m^3

Thus $PNEC_{sed}$ = >34.5 mg/kg wet weight or >6.9 mg/kg wet weight could be derived. Again, these values should be treated as a minimum value for the PNEC since no effects of octabromodiphenyl ether was seen at the concentrations tested. These values are consistent with the $PNEC_{sed}$ of ≥148 mg/kg wet weight based on the sediment toxicity tests and this value will be used in the risk characterisation.

3.2.2 Terrestrial compartment

3.2.2.1 Toxicity to plants

The toxicity of decabromodiphenyl 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 84% sand, 8% silt and 8% clay, and the soil had a pH of 7.7 and an organic matter content of 2.8%.

The substance used in the test was a composite sample from three suppliers and was reported to have a purity of 97.9%.

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 60 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 391, 781, 1,563, 3,125 and 6,250 mg/kg dry soil. Analysis by HPLC with UV detection of gave the mean measured concentrations in these treatments as 292, 707, 1,177, 2,098 and 5,349 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 3.27**. 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 3.27**.

Table 3.27 Effects of decabromodiphenyl ether on seedling emergence, survival and growth

Plant	Endpoint		Nominal treatment level (mg/kg dry wt.)					
			Control	391	781	1,563	3,125	6,250
Corn	Number of emerged seedlings/ replicate	day 7	9.75	9.75	9.75	9.75	9.50	9.75
		day 14	9.75	9.75	9.75	9.75	9.50	9.75
		day 21	9.75	9.75	9.75	9.75	9.50	9.75
	Number of surviving seedlings/replicate		9.75	9.75	9.50	9.50	9.50	9.50
	Mean seedling dry wt.		0.5248 g	0.5433 g	0.5507 g	0.6994 g	0.6637 g	0.5707 g
	Seedling height		44.8 cm	46.4 cm	44.4 cm	53.4 cm	50.1 cm	46.5 cm
Cucumber	Number of emerged seedlings/ replicate	day 7	9.25	9.75	9.75	10.0	9.75	7.50
		day 14	9.25	9.75	9.75	10.0	10.0	7.50
		day 21	9.25	9.75	10.0	10.0	10.0	7.50
	Number of surviving seedlings/replicate		9.25	9.75	10.0	10.0	10.0	7.50
	Mean seedling dry wt.		0.4423 g	0.3954 g	0.4448 g	0.3756 g	0.4561 g	0.4144 g
	Seedling height		14.4 cm	13.4 cm	15.3 cm	13.5 cm	15.9 cm	15.0 cm
Onion	Number of emerged seedlings/ replicate	day 7	6.75	6.50	5.50	8.25	8.50	8.75
		day 14	7.75	9.00	8.50	9.00	9.00	8.75
		day 21	7.75	9.00	8.25	9.00	9.00	8.75
	Number of surviving seedlings/replicate		7.75	9.00	7.75	8.50	8.75	8.50
	Mean seedling dry wt.		8.02 mg	6.40 mg	6.41 mg	7.08 mg	9.58 mg	8.28 mg
	Seedling height		6.9 cm	6.0 cm	6.0 cm	7.1 cm	7.7 cm	8.1 cm
Ryegrass	Number of emerged seedlings/ replicate	day 7	9.00	9.25	9.25	8.50	9.50	9.75
		day 14	9.00	9.25	9.25	8.75	9.75	9.75
		day 21	9.00	9.25	9.25	8.75	9.75	10.0
	Number of surviving seedlings/replicate		8.75	9.25	9.25	8.25	9.50	10.0
	Mean seedling dry wt.		22.2 mg	18.1 mg	23.3 mg	23.0 mg	29.4 mg	23.8 mg
	Seedling height		13.1 cm	12.0 cm	13.1 cm	12.1 cm	15.4 cm	13.9 cm

Table 3.27 continued overleaf

Table 3.27 continued

Plant	Endpoint		Nominal treatment level (mg/kg dry wt.)					
			Control	391	781	1,563	3,125	6,250
Soybean	Number of emerged seedlings/ replicate	day 7	10.0	10.0	9.75	7.25*	9.75	9.75
		day 14	10.0	10.0	9.75	8.00*	9.75	9.75
		day 21	10.0	10.0	9.75	8.00*	9.75	9.75
	Number of surviving seedlings/replicate		10.0	9.75	9.75	8.00*	9.75	9.75
	Mean seedling dry wt.		0.7058 g	0.6555 g	0.6734 g	0.6337 g	0.6854 g	0.6845 g
	Seedling height		31.2 cm	32.1 cm	32.7 cm	20.7* cm	32.3 cm	30.7 cm
Tomato	Number of emerged seedlings/ replicate	day 7	5.00	3.50	6.00	6.00	5.75	5.75
		day 14	9.00	6.75*	8.75	8.25	9.00	8.75
		day 21	9.25	7.00*	9.25	8.25	9.50	8.75
	Number of surviving seedlings/replicate		9.25	7.00*	9.25	8.25	9.25	8.75
	Mean seedling dry wt.		0.0466 g	0.0359 g	0.0406 g	0.0346 g	0.0759 g	0.0735 g
	Seedling height		6.2 cm	5.6 cm	5.9 cm	5.7 cm	7.4 cm	6.8 cm

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

The visual observations carried out during the test revealed no signs of treatment-related phytoxicity in any species and any treatment level. For corn, cucumber, onion and ryegrass, 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).

For soy bean, statistically significant differences between the control group and the 1,563 mg/kg treatment group were seen at day 21 in mean emergence, survival and plant height. However, as the responses at all other treatment levels were similar to those in the control group, these differences were not considered dose-responsive in the test report and therefore not treatment-related.

For tomato, statistically significant differences between the control group and the 391 mg/kg treatment group were seen in mean emergence and survival. Again, as the responses at all other treatment levels were similar to those in the control group, these differences were not considered dose-responsive in the test report and therefore not treatment-related.

Overall, the NOEC from these studies was given as ≥6,250 mg/kg dry soil based on nominal values or ≥5,349 mg/kg dry soil based on the mean measured concentration in soil at the start of the test.

3.2.2.2 Toxicity to earthworms

A 56-day earthworm reproduction study has been carried out with decabromodiphenyl ether. The available data from the study indicated a provisional NOEC for survival and reproduction of around 2,500 mg/kg dry soil and a LOEC of around 5,000 mg/kg dry soil. 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 28.6 compared with 30 required in the

test guideline), and so the test is not considered valid. 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% kaolin 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 98, 103 and 107% of the nominal values in the low dose soil and 97.7. 97.9 and 103% 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 taken from a synchronous population and were approximately nine months old. The weight of the worms was in the range 347.4 to 587.3 mg/worm at start of the test, with the mean initial weight being 447.0 mg/worm in the control population and 402.1-456.8 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 decabromodiphenyl ether used in the test were 312.6, 650.0, 1,250, 2,500 and 5,000 mg/kg dry weight. The test soils were prepared by adding pulverised decabromodiphenyl ether directly to the 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 decabromodiphenyl ether present in the soil was measured at day 0, day 28 and day 56 of the test. The mean concentrations found were 320, 668, 1,240, 2,480 and 4,910 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±2^{o}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 decabromodiphenyl 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 6%. The adult mortality in the treatment groups was in the range 5 to 10% 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 decrease in weight by an average of 0.051 g/replicate (or 1.1% of the total replicate mass) during the first 28 days of the study, whereas the worms in the treatment groups all increased in weight by 0.419-0.814 g/replicate (or 9.4-20% of the replicate animal mass) over the same period.

The average number of young worms in the control was 60 juveniles/replicate at the end of the study. The coefficient of variation in the control data was 36% which is above the figure of 30% specified in the protocol. The reproductive output in all treatment groups was 85-120 juveniles/replicate and was higher than found in the control population. The test report indicated that, given this finding, the variation found in the control population was unlikely to have adversely affected the test result.

Overall, no significant adverse effects on survival or reproduction were seen in this study and so the NOEC is ≥ 4,910 mg/kg dry weight.

In this study, the concentration of decabromodiphenyl ether was also determined in the surviving adults from the first 28-day exposure period. These worms were allowed to purge their guts for 48 hours prior to analysis using HPLC with UV detection. Decabromodiphenyl ether was found to be present in some of the earthworms but the concentration was below the limit of quantification of the method used (<0.75 mg/kg) at all exposure levels.

3.2.2.3 Derivation of $PNEC_{soil}$

Toxicity data are available for plants and earthworms. No effects were seen on plants at concentrations up to 5,349 mg/kg dry weight. The NOEC from the earthworm study is ≥ 4,910 mg/kg dry weight.

Based on the NOEC of ≥ 4,910 mg/kg dry weight and an assessment factor of 50 (NOECs are available for two species) then the $PNEC_{soil}$ can be estimated as ≥ 98 mg/kg dry weight. This is equivalent to a $PNEC_{soil}$ of ≥ 87 mg/kg wet weight using the default water contents given in the Technical Guidance Document.

The $PNEC_{soil}$ can also usually be calculated using the equilibrium partitioning method with the PNEC for aquatic organisms and the soil/water partitioning coefficient. For decabromodiphenyl ether such an approach is not possible since no toxic effects were seen in the aquatic toxicity tests. In Section 3.2.1.5, two possible approaches for deriving a tentative PNEC for water were given. These are open to some uncertainty but could be used to derive a tentative PNEC for sediment using the equilibrium partitioning method.

$$PNEC_{soil} = \frac{K_{soil-water}}{RHO_{soil}} \times PNEC_{water} \times 1000$$

where $K_{soil\text{-}water}$ = soil - water partition coefficient = 47,660 m^3/m^3
RHO_{soil} = bulk density of wet soil = 1,700 kg/m^3

Thus the $PNEC_{soil}$ = >28.0 mg/kg wet weight or >5.6 mg/kg wet weight. As is the case for sediment, there is a large uncertainty in this approach for decabromodiphenyl ether. These values are consistent with the value of ≥87 mg/kg wet weight estimated based on the available soil toxicity data and this value will be used in the risk characterisation.

3.2.3 Atmosphere

Direct emissions of decabromodiphenyl ether to the atmosphere are likely to be very low. No biotic or abiotic effects are likely because of the limited release and the low volatility of decabromodiphenyl ether. Very low concentrations of decabromodiphenyl ether are predicted for the atmospheric compartment. Removal is likely to be mainly via wet and dry deposition,

although photodegradation may occur to some extent. Thus decabromodiphenyl 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 Non-compartment specific effects relevant for the food chain (secondary poisoning)

The toxicity of decabromodiphenyl ether to mammalian systems has been extensively reviewed in Section 4 as part of the human health assessment. The lowest long-term NOAEL was 1,120 mg/kg bw/day or 25,000 mg/kg food for systemic effects in a two year chronic study in rats. As this result is from a chronic study, an assessment factor of 10 is appropriate, giving a $PNEC_{oral}$ of 2,500 mg/kg food.

Recently, it has been reported that decabromodiphenyl ether causes behavioural disturbances (as determined by disruption of habituation) in neonatal mice exposed to decabromodiphenyl ether in a single dose of 2.22 to 20.1 mg/kg body weight on postnatal day 3 (Viberg et al., 2001; see Human Health assessment). This effect was not seen in mice exposed on postnatal day 10 or postnatal day 19. The toxicological significance of these findings is unclear.

Using the conversion factors given in the Technical Guidance Document a single dose of 2.2-20.1 mg/kg body weight is equivalent to a single dose of 18.3-167 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.

Also of concern with regard to secondary poisoning is the possible formation of lower brominated diphenyl ethers as a result of photolysis/degradation of decabromodiphenyl ether in the environment. It is known that some lower brominated diphenyl ethers (e.g. tetra- and pentabromodiphenyl ether) are potentially much more bioaccumulative and toxic than decabromodiphenyl ether.The available evidence indicates that the lower brominated diphenyl ethers, if formed, are likely to be only minor products of these reactions, but there is some uncertainty over the actual significance of the process in the environment. 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 involving articles containing decabromodiphenyl ether (e.g. incineration, landfill (where fires could occur), metal recycling (if the metal is contaminated with plastic containing decabromodiphenyl ether - for example, decabromodiphenyl ether may be used in cabling), or accidental fires). The available information is discussed in Appendix A and Section 2.4. The consequences are discussed qualitatively in the risk characterisation section.

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 products. At the regional level, releases to the environment are predicted to be dominated by losses to wastewater due to washing of textiles over their service life, and to a lesser extent by volatilisation losses to air from plastic articles over their service life and particulate waste generated over their service life and disposal. It is possible that further decabromodiphenyl ether could be imported into (or exported from) the EU in finished articles or masterbatch, but it is not possible to quantify these amounts; it is thought that the net import of decabromodiphenyl ether in these types of product into the EU will be small when compared to the amounts currently considered to be used within the EU in the assessment.

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) or accidental fires) (discussed in Section 2.4 and Appendix A). Overall it can be concluded that decabromodiphenyl ether, as a source of bromine, can contribute to the formation of halogenated dibenzo-*p*-dioxins and debenzofurans generated during such processes. It is not possible from the available data (and it is beyond the scope of this risk assessment) to quantify the actual contribution that decabromodiphenyl 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 decabromodiphenyl 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

Table 3.28 shows the PECs derived for decabromodiphenyl ether. Based on the currently available toxicity data, it is not possible to derive a PNEC for the aquatic compartment as no effects are expected at concentrations up to the water solubility of the substance. The risk to the aquatic compartment (surface water) from decabromodiphenyl ether itself can be considered to be low. 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.

Table 3.28 PECs for the aquatic compartment (surface water)

Scenario	PEC (µg/l)
PEC_{local} (production)[a]	0.9
PEC_{local} (polymer processing)	0.33
PEC_{local}(textiles – compounding)	2.6
PEC_{local}(textiles – application)	1.3
PEC_{local}(textiles – combined compounding/application site)	3.8
$PEC_{regional}$	0.093-0.094

Note: a) Production now ceased in the EU.

3.3.1.2 Sediment

A $PNEC_{sed}$ of ≥148 mg/kg wet weight has been estimated for decabromodiphenyl ether. The estimated PEC/PNEC ratios for the sediment compartment are shown in **Table 3.29**.

Table 3.29 PECs for the sediment compartment

Scenario	PEC (mg/kg wet weight)	PEC/PNEC
PEC_{local} (production)[a]	31	≤0.21
PEC_{local} (polymer processing)	10.8	≤0.073
PEC_{local}(textiles - compounding)	89.0	≤0.60
PEC_{local}(textiles - application)	46.1	≤0.30
PEC_{local}(textiles - combined compounding/application site)	131	≤0.89
$PEC_{regional}$	5.66-5.72	≤0.039
Measured data	1.2-2	≤0.014

Note: a) Production now ceased in the EU.

Recent measurements from the United Kingdom indicate that the levels in sediment associated with use of decabromodiphenyl ether are lower than those predicted, although it is not known how representative the measured levels are for the whole of the EU. There is also some evidence that the levels found in sediments may be increasing over recent years (see Section 3.1.2.2.2), although these levels are still well below the PNEC (the maximum concentration of decabromodiphenyl ether measured in Europe from the more recent studies is around 2 mg/kg wet weight, which gives a PEC/PNEC ratio of ≤0.014). Further information on releases of decabromodiphenyl ether to the aquatic environment from polymer processing and use in textiles would be useful to refine the PECs for these endpoints. Even so, the estimated PEC/PNEC ratios for sediment indicate that the risk to the sediment compartment is low.

In addition, the possibility of decabromodiphenyl 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 decabromodiphenyl ether is ≥1.5 mg/l. The resulting PEC/PNEC ratios for wastewater treatment plants, based on the estimated effluent concentrations for the scenarios considered are shown in **Table 3.30**. The risk to wastewater treatment processes is low.

Table 3.30 PEC/PNEC ratios for wastewater treatment processes

Scenario	PEC (effluent concentration) (mg/l)	PEC/PNEC
PEC_{local} (production)[a]	0.21-1.25	≤0.14-≤0.83
PEC_{local} (polymer processing)	0.008	≤0.005
PEC_{local} (textiles - compounding)	0.042	≤0.028
PEC_{local} (textiles - application)	0.084	≤0.056
PEC_{local} (textiles - combined compounding/application site)	0.126	≤0.084

Note: a) Production now ceased in the EU.

3.3.1.4 Summary

The following conclusions apply to the aquatic compartment.

Result

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 applies to the assessment for surface water, sediment and wastewater treatment plants from local and regional sources of decabromodiphenyl ether.

3.3.2 Terrestrial compartment

A $PNEC_{soil}$ of ≥87 mg/kg wet weight has been estimated from the available data. The resulting PEC/PNEC ratios are shown in **Table 3.31**.

Table 3.31 PECs for soil

Scenario	PEC (mg/kg wet weight)	PEC/PNEC
PEC_{local} (production)[a]	negligible	<1
PEC_{local} (processing)	3.30	≤0.038
PEC_{local} (textiles - compounding)	34.0	≤0.39
PEC_{local} (textiles - application)	17.1	≤0.20
PEC_{local} (textiles - combined compounding/application site)	51.0	≤0.59
$PEC_{regional}$ (agricultural soil)	27.0	≤0.31
$PEC_{regional}$ (industrial/urban soil)	17.8-19.0	≤0.20-≤0.22

Note: a) Production now ceased in the EU.

Based on this, no risk to soil organisms is identified.

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 or for risk reduction measures beyond those which are being applied already.

The assessment indicates no risk for the terrestrial compartment.

3.3.3 Atmosphere

Neither biotic or abiotic effects are considered likely because of the limited release and low volatility of decabromodiphenyl ether. The predicted atmospheric concentrations of decabromodiphenyl ether are all very low (<45 ng/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 or for risk reduction measures beyond those which are being applied already.

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

The information available indicates that decabromodiphenyl ether is present in the food chain only at low concentrations. A $PNEC_{oral}$ for secondary poisoning of 2,500 mg/kg food has been determined. The resulting PEC/PNEC ratios for the fish food chain are shown in **Table 3.32**.

Table 3.32 PEC/PNEC ratios for secondary poisoning via the fish food chain

Scenario	PEC (µg/kg wet weight)	PEC/PNEC
Production[a]	0.27	$1.1 \cdot 10^{-7}$
Polymer processing	0.72	$2.9 \cdot 10^{-7}$
Textiles - compounding	4.4	$1.8 \cdot 10^{-6}$
Textiles - application	2.4	$9.6 \cdot 10^{-7}$
Textiles - combined compounding/application	6.4-6.5	$2.6 \cdot 10^{-6}$

The concentrations predicted in the earthworm food chain are not considered to be reliable, but even so, the highest concentration predicted (~100 mg/kg wet weight) is still below the PNEC value. Therefore the PEC/PNEC ratios for secondary poisoning indicate that the current levels of decabromodiphenyl ether in the food chain are not of concern.

Additional uncertainties

The current approach to risk assessment implies that there is no risk of secondary poisoning, and the PEC/PNEC ratios are much less than 1 (in fact below 10^{-5}) for the commercial decabromodiphenyl ether product. 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 it is present at (relatively) low concentrations in fish, marine mammals and predatory birds' eggs (those of bird-eating Peregrine Falcons and fish-eating Common Terns). These findings appear to contradict the conventional wisdom that molecules such as decabromodiphenyl ether are too large to pass through biological membranes and should not accumulate in organisms. As discussed in Section 3.1.5.2 there are uncertainties with some of the analytical data that indicate the presence of decabromodiphenyl ether at or near the detection limit of the method. Some of the positive determinations may also have been influenced by the presence of decabromodiphenyl ether in the gut contents rather than in body tissues, or analytical artefacts. Nevertheless, the findings of decabromodiphenyl ether in lipid tissues of some higher mammals and birds' eggs indicates that decabromodiphenyl ether may be bioavailable in the environment. The route of uptake, i.e. whether by food, air and/or water, is currently uncertain.

There is also some evidence that the concentrations of decabromodiphenyl ether may be increasing in sediments (see Section 3.1.2.2.2). If this is a true trend, then the increasing number of apparently positive findings of decabromodiphenyl ether in organisms in the environment in the more recent studies might reflect a more general increase in the amount of decabromodiphenyl ether in the environment. Other possible explanations for the findings from the more recent studies are that:

- the uptake rate by these organisms is very slow (i.e. the levels may be increasing with time),
- more sensitive analytical methods are being used (so are able to detect lower concentrations of decabromodiphenyl ether), or
- simply a wider variety of species is being sampled.

It is not currently possible to distinguish between these different possibilities.

The levels 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. Coupled with questions over analytical problems, levels need to be confirmed.

It is not possible to assess the effects of the concentrations of decabromodiphenyl ether 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 may cause irreversible behavioural disturbances (as determined by disruption of habituation) in adult mice (such effects have also been seen for hexabromodiphenyl ether).

The toxicological significance of these findings (in terms of population survival) is unclear. However, the dose range is below those at which no effects were observed in standard mammalian toxicity tests (behavioural effects have been noted at levels 500 times lower than the standard NOAEL obtained from a 2-year chronic study in rats - a NOAEL has not been established for the behavioural effect).

Even if the study represents 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, it does imply that the standard toxicity tests might not have picked out subtle effects 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 decabromodiphenyl 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 under laboratory conditions. Lower brominated diphenyl ether congeners have been identified among the degradation products from these studies (some products remain unidentified). It is known that some lower brominated diphenyl ethers (e.g. tetra- and pentabromodiphenyl ether) are potentially much more bioaccumulative and toxic than decabromodiphenyl ether. The available experimental evidence indicates that the lower brominated diphenyl ethers, if formed, are likely to be only minor products, but 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. If debromination of decabromodiphenyl ether to lower brominated congeners, in particular 2,2',4,4'-tetrabromodiphenyl ether (the most common congener present in biota in the environment) is a significant process, then it may be possible to derive some information on the process from trends in the available monitoring data for that substance. However, such an analysis is complicated by the fact that this congener is present in substantial amounts in the commercial pentabromodiphenyl ether product and the use of this product in the EU has declined in the EU in recent years (ECB, 2000). Thus, any possible trends in the amount of 2,2',4,4-tetrabromodiphenyl ether (or other lower brominated diphenyl ether congeners) linked to the use of decabromodiphenyl ether is likely to be masked as a result of the changing use pattern. There is evidence that the concentrations of lower brominated diphenyl ether congeners in human breast milk in Europe has fallen recently following an increase up to the late 1990s (Meironyte Guvenius and Norén, 2001) but the recent trend in the levels of these congeners in other biota in Europe is less clear (e.g. Lundstedt-Enkel et al., 2001).

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 in inconclusive on this point, and further work might be needed.

Result

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 decabromodiphenyl 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 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 can not 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 decabromodiphenyl ether is highly persistent, and of particular note, 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.]

4 HUMAN HEALTH

4.1 HUMAN HEALTH (TOXICITY)

4.1.1 Exposure assessment

4.1.1.1 General discussion

DBDPO is a solid with a very low vapour pressure ($4.6 \cdot 10^{-6}$ Pa at 21°C) and a calculated saturated vapour pressure (SVC) of 25 µg/m^3 at 21°C. Therefore exposure to the vapour will not exceed 25 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 DBDPO 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 DBDPO on heating may also be a potential source of inhalation exposure.

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

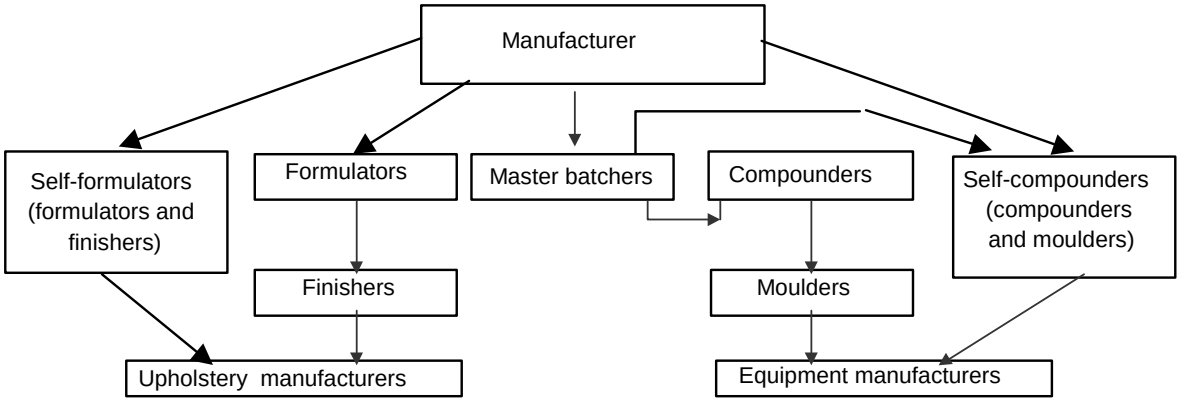
Oral exposure is not considered to be a significant route of exposure under normal working practices.

According to the data provided by the producers, the substance will generate respirable dust (particle size <5 µm).

4.1.1.2 Occupational exposure

A workplace exposure level of 5 mg/m^3 (8-hour TWA for 40-hour week) has been recommended for DBDPO in USA (American Industrial Hygiene Association - AIHA, 1981). It was set on the basis of the nuisance effect of the dust.

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



Formulation and use of hotmelt adhesive containing DBDPO may also be a source of occupational exposure.

4.1.1.2.1 Manufacture

DBDPO was manufactured only in one plant within the EU in quantities lower than 1,000 tonnes/year until 1999.

DBDPO is produced in a closed system. Highest inhalation and dermal exposure 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.

During an industrial hygiene survey in 1977 and 1978 in a DBDPO manufacturing plant in Sayreville, NJ, USA, analysis of personal samples collected on workers in the mill area indicated that the airborne levels of DBDPO ranged from 0.08 to 0.21 mg/m^3 as a 8-hour TWA. Following a spill in the mill area, personal airborne levels ranged from 1.3 to 1.9 mg/m^3 (Bialik, 1982).

Surveys have determined employee 8-hour TWA exposures of 1-4 mg/m^3 with excursions up to 42 mg/m^3 during short-term tasks (Norris et al., 1973).

The available information was not sufficient to evaluate carefully the quality of these measured data and their representativeness for the risk assessment.

To further determine the exposure, the EASE model was used, assuming 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).

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 in the plastic industry is the production of flame retarded pellets by specialized compounders. DBDPO is incorporated to a polymer (mainly polypropylene and polystyrene) 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 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) may 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 DBDPO in plastic industry can be split in two areas which are described below:

- compounding and master batching;
- moulding.

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

Compounding and master batching

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 DBDPO bags are emptied in the mixer. The use of antimony trioxide in association with DBDPO 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 difficult 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 (Breysse and Kacergis, 2000).

No other measured data are available either for DBDPO 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 does 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 DBDPO 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 extraction ventilation will be likely 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. As the polymer is in a non-dusty pellet form, the potential for exposure is likely to be negligible.

Moulding

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 pellets is likely to be negligible.

Temperatures used by injection moulders are generally similar to those used for extrusion. Release of DBDPO 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 emission.

4.1.1.2.3 Textile industry

Following manufacture, the first step in the use of flame retardant for the textile industry is the production of flame retarded coatings for textiles by specialized formulators. The coatings are then supplied to finishers who apply it on textiles.

It is thought that there are 3 or 4 large formulators in the EU (7 or 8 in total). The total number of formulators and self formulators (companies who formulate the coating and apply it) in the EU is 25 and the number of textile finishers is about 20-30. The UK is the largest producer of flame retarded upholstery, due to national legislation covering domestic upholstery, followed by Germany and Belgium.

The use of DBDPO in textile industry can be split in two sectors: formulators and finishers.

Formulation

The process includes a fully enclosed vessel where DBDPO and antimony trioxide are mixed with 30% water. This mixture is then piped to another vessel where it is mixed with a polymer. All the process is carried out at ambient temperature.

Dust exposure is likely to be intermittent and may occur during the loading of the first mixer. The use of antimony trioxide in association with DBDPO should impose strict processing procedures with high standard dust control. However occupational hygiene practice may change significantly from one company to another. Handling the liquid coating is unlikely to result in dust exposure.

One air sampling during the loading of the substance to the hopper was carried out by a large formulator (HSE, 1995); it gave an exposure of 1.4 mg/m^3 (respirable dust) or 6.9 mg/m^3 (total

particulate) during the 30 minute period of the task. The representativeness of these data is questionable because it represents only one air sample.

No other measured exposure data are available in the workplace during formulation. As the highest exposure will be during bag emptying, the situation is similar to bagging during compounding and master batching. Consequently the same level of exposure (5 mg/m^3 for dust exposure and 1 mg/cm^2/day for skin exposure) will be used in the risk characterisation.

Finishing

The process involves the spreading of the coating on the back of the fabric, then passing the wet coated fabric through an oven (extracted to atmosphere) at 130°C-160°C, sometimes up to 160°C, in order to remove the water.

No measured exposure data are available. Exposure is expected to be low because of the inclusion of the substance in the matrix of the coating. The low vapour pressure of the substance will minimise emission during heating.

4.1.1.2.4 Formulation of adhesives

A minor application of DBDPO is the use as a component of flame retarded hotmelt adhesives. The content of DBDPO in these adhesives is between 10 and 20%. During formulation, dust exposure will occur during bag emptying, the situation is similar to the plastic or textile industry. Consequently the same level of exposure (5 mg/m^3 for dust exposure and 1 mg/cm^2/day for skin exposure) will be used in the risk characterisation.

4.1.1.2.5 Equipment and upholstery manufacture

Workers will handle either plastic parts or coated fabric. Exposure is expected to be low because of inclusion of the substance in the polymer or coating 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).

A minor application is the use of hotmelt adhesives containing 10 to 20% DBDPO for the production of plaster or mineral fibre board. Because these adhesives are used in the molten state at high temperature, skin exposure is likely to be minimal. Releases of DBDPO fumes may be a source of exposure but the low vapour pressure of the substance and the presence of extraction ventilation will minimise emission.

4.1.1.2.6 Use of the final products

The fire retardant is physically bound within the polymer matrix, however it is not chemically bound and could theoretically migrate. Therefore release of DBDPO 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 (PBDPOs) lead to negligible migration:

- An investigation was conducted to determine the emission of PBDPOs 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 m^3/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 were 97 pg/m^3. Indoor dust sampling contained PBDPO at high ppb levels (Ball et al., 1992).

- Quantitative measurements of PBDPOs in the air at ordinary offices show concentrations of DBDPO of at most 0.08 ng/m^3 (Carlsson, 1999 quoted in Sjödin et al., 1999). In ambient air at a plant for dismantling electronics, concentrations of DBDPO and 2,2',3,4,4',5',6-HpBDPO were detected in the range of 12-200 ng/m^3 and 6.3-87 ng/m^3 respectively. High levels of particle-bound DBDPO and 2,2',3,4,4',5',6-HpBDPO have been determined in the ambient air. 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 (see study from Sjödin et al. (1999) in Section 4.1.2.1.2 Studies in humans).

- Samples of dust were collected during the year 2000 from Parliament buildings in 8 European countries and also from the offices of a Dutch computer/internet provider and analysed for brominated flame retardants. PBDPO were detected in all samples, especially DBDPO. Levels of DBDPO varied from 0.26 to 6.9 mg/kg (ppm) dust. A variety of source, including furnishings and electronic equipment may have contributed to different degrees in different buildings. But these data cannot be used to identify specific sources (Greenpeace Research Laboratories, 2001).

The occupational exposure data are summarised in **Table 4.1**. In conclusion, exposure to DBDPO during subsequent use of flame retarded equipment is likely to be negligible.

Table 4.1 Conclusion of occupational exposure

Scenario	External inhalation exposure(mg/m^3)	External dermal exposure (mg/cm^2/day)
1 Manufacture (bagging and cleaning activities)	5	1
2 Compounding and master batching - bag emptying - extrusion	 5 extremely low	 1 negligible
3 Moulding	extremely low	negligible
4 Textile industry (bag emptying)	5	1
5 Formulation of hotmelt adhesive (bag emptying)	5	1
6 Equipment and upholstery manufacture	extremely low	negligible
7 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 and in upholstery textiles 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 DBDPO from consumer product.

4.1.1.3.2 Use of DBDPO 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 DBDPO used in plastics are 10-15% (EBFRIP, 1995).

There are no measured data into the indoor environment. On the other hand, quantitative measurements of DBDPO in the air at offices were carried out which show concentrations of DBDPO of at most 97 pg/m^3 (Ball et al., 1992). This confirms that exposure to DBDPO from polymer matrices will be very small; this will be because DBDPO is immobile within the matrices (EBFRIP, 1995).

4.1.1.3.3 Use of DBDPO in upholstery

DBDPO is used for this application (although other classes of flame retarding chemicals can be used) and direct dermal contact with flame retarded textiles at home may give dermal exposure. However, dermal exposure cannot be assessed since no data on leaching are available but given the low frequency and duration of any dermal contact, dermal exposure with textiles is expected to be very low.

4.1.1.3.4 Summary of consumer exposure

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) (WHO, 1994), it is felt that consumer exposure to DBDPO is likely to be negligible.

4.1.1.4 Humans exposed via the environment

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

Table 4.2 Estimated daily doses for exposure of humans via the environment

Scenario	Route	Predicted concentration	Estimated daily dose (mg/kg bw/day)
Local - Production (generic)[a]	Wet fish	$7.1 \cdot 10^{-3}$ mg/kg	$1.2 \cdot 10^{-5}$
	Root tissue of plants	39.1 mg/kg	0.21
	Leaves of plants	$4.3 \cdot 10^{-3}$ mg/kg	$7.3 \cdot 10^{-5}$
	Drinking water	$3.0 \cdot 10^{-3}$ mg/l	$8.6 \cdot 10^{-5}$
	Meat	0.76 mg/kg	$3.3 \cdot 10^{-3}$
	Milk	0.24 mg/kg	$1.9 \cdot 10^{-3}$
	Air	$6.6 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$
	Total local daily dose		0.22
Local - Production (site specific)[a, b]	Wet fish	$1.6 \cdot 10^{-4}$ mg/kg	$2.7 \cdot 10^{-7}$
	Root tissue of plants, leaves of plants, meat and milk	negligible	negligible
	Air	$6.6 \cdot 10^{-6}$ mg/m^3	$1.4 \cdot 10^{-6}$
	Total local daily dose		$1.7 \cdot 10^{-6}$
Local - Polymer processing	Wet fish	$1 \cdot 10^{-3}$ mg/kg	$1.7 \cdot 10^{-6}$
	Root tissue of plants	1.5 mg/kg	$8.4 \cdot 10^{-3}$
	Leaves of plants	0.028 mg/kg	$4.8 \cdot 10^{-4}$
	Drinking water	$1.2 \cdot 10^{-4}$ mg/l	$3.4 \cdot 10^{-6}$
	Meat	0.12 mg/kg	$5.1 \cdot 10^{-4}$
	Milk	0.038 mg/kg	$3.0 \cdot 10^{-4}$
	Air	$4.4 \cdot 10^{-5}$ mg/m^3	$9.5 \cdot 10^{-6}$
	Total local daily dose		$9.7 \cdot 10^{-3}$
Local - Textiles (compounding)	Wet fish	$8.5 \cdot 10^{-3}$ mg/kg	$1.4 \cdot 10^{-5}$
	Root tissue of plants	15.7 mg/kg	0.086
	Leaves of plants	$4.3 \cdot 10^{-3}$ mg/kg	$7.4 \cdot 10^{-5}$
	Drinking water	$1.2 \cdot 10^{-3}$ mg/l	$3.5 \cdot 10^{-5}$
	Meat	0.31 mg/kg	$1.4 \cdot 10^{-3}$
	Milk	0.099 mg/kg	$7.9 \cdot 10^{-4}$
	Air	$6.8 \cdot 10^{-6}$ mg/m^3	$1.5 \cdot 10^{-6}$
	Total local daily dose		0.088

Table 4.2 continued overleaf

Table 4.2 continued

Scenario	Route	Predicted concentration	Estimated daily dose (mg/kg bw/day)
Local - Textiles (application)	Wet fish	$4.4 \cdot 10^{-3}$ mg/kg	$7.3 \cdot 10^{-6}$
	Root tissue of plants	7.86 mg/kg	0.043
	Leaves of plants	$3.9 \cdot 10^{-3}$ mg/kg	$6.6 \cdot 10^{-5}$
	Drinking water	$6.1 \cdot 10^{-4}$ mg/l	$1.7 \cdot 10^{-5}$
	Meat	0.16 mg/kg	$7.0 \cdot 10^{-4}$
	Milk	0.052 mg/kg	$4.1 \cdot 10^{-4}$
	Air	$6.1 \cdot 10^{-6}$ mg/m^3	$1.3 \cdot 10^{-6}$
	Total local daily dose		0.044
Local - Textiles (combined compounding and application site)	Total local daily dose		0.132
Regional	Wet fish	$3.7 \cdot 10^{-4}$ mg/kg	$6.1 \cdot 10^{-7}$
	Root tissue of plants	12.4 mg/kg	0.068
	Leaves of plants	$3.5 \cdot 10^{-3}$ mg/kg	$5.9 \cdot 10^{-5}$
	Drinking water	$9.6 \cdot 10^{-4}$ mg/l	$2.8 \cdot 10^{-5}$
	Meat	0.60 mg/kg	$2.6 \cdot 10^{-3}$
	Milk	0.19 mg/kg	$1.5 \cdot 10^{-3}$
	Air	$5.4 \cdot 10^{-6}$ mg/m^3	$1.2 \cdot 10^{-6}$
	Total local daily dose		0.072

Note: a) Production no longer occurs in the EU.
b) At the production site, no application of sewage sludge to agricultural soil occurred.

There is considerable uncertainty inherent in the approach taken by EUSES (and the Technical Guidance Document) for estimating the concentrations of substances with high log Kow values in various parts of the food chain. For instance, the concentrations in drinking water are high, frequently close to or above the water solubility of the substance, and are sometimes higher than the concentrations predicted/found in surface waters. The reason for this is that within EUSES the drinking water concentrations are related to the soil pore water concentrations. For poorly soluble substances like decabromobiphenyl ether, very high concentrations in soil are predicted due to application of sewage sludge containing the substance. This then leads to high values for the estimated soil pore water concentrations (and hence drinking water concentrations), which in turn leads to very high concentrations in plant roots, and hence other parts of the food chain e.g. leaves, meat and milk. The partition coefficients for the various parts of the food chain depend crucially on the log Kow value of the substance (for decabromobiphenyl ether only a measured fish bioconcentration value was available, all other partition coefficients were estimated from log Kow), but it is not known if the assumptions/methods used in EUSES are valid for substances with very high log Kow values. This may be a particular problem for decabromobiphenyl ether since the available bioconcentration and uptake data indicate that the actual uptake by organisms is very much less than would be predicted from the log Kow value. Thus the figures in **Table 4.2** are likely to grossly overestimate the actual daily human intake.

The predicted daily human intake figures for decabromobiphenyl ether are 220 µg/kg bw/day for production, 9.7 µg/kg bw/day for polymer processing, 88 µg/kg bw/day for textiles (compounding), 44 µg/kg for textiles (application), 132 µg/kg for textiles (combined compounding/application) and 72 µg/kg at the regional level. In all cases, uptake from root crops is predicted to account for the vast majority (≥90%) of the daily dose. As mentioned above, there are considerable uncertainties in these figures, particularly regarding the soil pore water concentrations and whether decabromobiphenyl ether in soil pore water is actually taken up by plant roots.

If it is assumed that the maximum soil pore water concentration is 0.1 µg/l (i.e. the upper limit for the water solubility of decabromobiphenyl ether), then the resulting maximum concentration in plant roots can be estimated using the following equation:

$$Croot_{plant} = \frac{K_{plant-water} \times C_{porewater}}{RHO_{plant}}$$

where $Croot_{plant}$ = concentration in root tissue
$K_{plant\text{-}water}$ = partition coefficient between plant tissue and water = 9,050 m^3/m^3 for a log Kow value of 6.27.
RHO_{plant} = bulk density of plant tissue = 700 kg/m^3
$C_{porewater}$ = concentration in soil pore water

Using a soil pore water concentration of 0.1 mg/m^3 (i.e. 0.1 µg/l), the resulting concentration in plant roots is 1.29 mg/kg. This results in a daily human intake of 7 µg/kg bw/day, assuming an adult body weight of 70 kg and a daily consumption of 0.384 kg of root crops. This figure is the maximum possible intake from this source as it is based on the soil pore water being saturated with decabromobiphenyl ether, and assuming that the uptake from water can be estimated based on the log Kow value.

Some of the other estimated concentrations in food are also sensitive (indirectly) to the soil pore water concentration (i.e. the concentration in plant roots affects the estimated concentration in plant leaves and hence the concentration in meat and so the concentration in milk) but the interrelation between the various media is complex. Calculations using EUSES with the same release estimates as used for **Table 4.2**, but where the soil pore water and drinking water concentrations are set to a maximum value of 0.1 µg/l, indicate that the maximum total daily human dose from all sources is around 12 µg/kg bw/day for production, 8 µg/kg bw/day for polymer processing, 9 µg/kg bw/day for textile (compounding), 8 µg/kg bw/day for textile (application), and 11 µg/kg bw/day at a regional level. Again, the majority of the dose is predicted to come from root crops.

4.1.1.5 Combined exposure

The estimated maximum human intake from environmental sources is estimated to be in the range 8-12 µg/kg bw/day from local and regional sources.

The maximum occupational exposure is predicted to be 5 mg/m^3 by inhalation, resulting in a body burden of 0.4 mg/kg/day (see also comments on dermal exposure in Section 4.1.3.2).

Consumer exposure to DBDPO is thought to be negligible.

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

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

Oral absorption, distribution, excretion and metabolism

In NTP (1986) and El Dareer et al. (1987), the disposition of [^{14}C] DBDPO (97.9-99.2% pure) was determined in F344/N male rats dosed by feeding (from 238 ppm to 51,100 ppm). The radiochemical purity of [^{14}C] DBDPO was 97.9-99.2% in study from NTP, 1986. Rats were fed on days 1-7 and 9-11 unlabelled DBDPO and on day 8 [^{14}C] DBDPO. The average daily consumption of DBDPO was estimated for 50,000 ppm to be 3,718 mg/kg/day for male and 3,826 mg/kg/day for female.

Results of this study indicate that, in the 72 hours after exposure at all doses in the diet, 91.3% ± 4% to 101% ± 4% of the radioactivity recovered was excreted in the feces. Recovery was not related to the administered dose of DBDPO. Although the amount of radioactivity in liver and fat was low, there was a tendency for rats fed the smaller amounts of unlabelled DBDPO to have more radioactivity in those tissues. The amounts ranged in the liver from 0.064% of the dose for group VI (238 ppm) to 0.008% of the dose for group I (51,100 ppm) and, in the fat from 0.157% of the dose for group VI and 0.09% of the dose for group I. A notable result of exposure to DBDPO was a dose-related liver weight increase (approximately 14 g in group I vs. 10 g in group VI).

In a second feeding study from El Dareer et al. (1987) and NTP (1986), rats were dosed by feeding 48,000 ppm (about 4.5 g/kg bw–5 g/kg bw) or 277 ppm (about 22 mg/kg bw–25 mg/kg bw) of labelled or unlabelled DBDPO. Rats were fed on days 1-7 and 9 or 9-10 or 9-11 (depending on the groups) unlabelled DBDPO and on day 8 [^{14}C] DBDPO. Rats were killed at days 10, 11 and 12.

Recovery of radioactivity in the feces ranged from 82.5% ± 4.7% to 86.4% ± 8.5% and was not related to the administered dose or to the time of sacrifice (24, 48 or 72 hours) after consumption of [^{14}C] DBDPO. The total recovery of radioactivity in this study ranged from 83.2 to 89.3%. For rats fed the low amount of DBDPO, the liver contents of radioactivity were related to the time of sacrifice and were as follows: 0.449% ± 0.01% at 24 hours after feeding, 0.213% ± 0.016% at 48 hours and 0.109% ± 0.029% at 72 hours. In extracts of liver at day 10, only DBDPO was identified (retention time of 23 minutes). Consistent with the previous study, liver weights increased in a dose-related manner. Excretion in the urine accounted for approximately 0.01% or less of the dose. Analysis of all the major organs and tissues following oral dosing indicated trace levels of radioactivity in most tissues. After gastrointestinal tissues, the highest concentrations were found in liver, kidney, lung, skin and adipose tissue. For these tissues, the maximum values were in rats fed the lower dose. In extracts of feces, DBDPO and three main metabolites (retention times: 3-6 min., 6-12 min. and 12-17 min.) were detected. The percent of metabolites tended to increase as the concentration of DBDPO in the diet increased (1.5% of

total recovery at 250 ppm vs. 27.9% at 25,000 ppm) but DBDPO remained the major eliminated compound.

In an intravenous study (NTP, 1986 and El Dareer et al., 1987), F344/N male rats were injected with 1.07 mg/kg [^{14}C] DBDPO and were killed 72 hours after dosing. At 72 hours following the intra-venous dose of [^{14}C] DBDPO, 74% of the dose was found in the feces and gut contents suggesting significant biliary excretion. The remainder was shared into different tissues, the most significant being muscles, skin, liver and fat. Only traces of radioactivity were in the urine, spleen and brain. Extraction of the feces showed that the excreted material was mainly unchanged DBDPO (36.5% of the total for the 0-48 hour collection period and 40% for the 48-72 hour period) and three main metabolites (31.4% of the total for the 0-48 hour collection period and 49.8% for the 48-72 hour period) with metabolite retention times of 3-6 min., 6-12 min. and 12-17 min.

In a last study, biliary excretion after intravenous administration of 0.9 mg/kg of [^{14}C] DBDPO to Fischer 344/N rats was studied (NTP, 1986 and El Dareer et al., 1987). Bile was collected over a 4-hour period. Of the dose administered, 7.17% appeared in the bile in 4 hours. The rate of excretion from 1.5 to 4 hours was 2.2% of the dose per hour. No metabolite identification was apparently carried out in the NTP (1986) study. However in the El Dareer et al. (1987) study, it was specified that a single metabolite (retention time of 4 minutes) was detected which may be the same as the principal metabolite present in feces after intravenous dosing.

Based on the available data, no statement can be drawn on the possibility or non possibility that DBDPO can be metabolised to PeBDPO since the metabolites detected in the NTP study were not identified. The only information available on these metabolites are their retention times and no internal standards were used to allow their identifications.

Those observations are consistent with the following:

- Norris et al. (1973 - 1975) showed that within the first 24 hours following oral administration of 1 mg/kg of commercial DBDPO to rats, 90.6% of the [^{14}C] activity of the dose was found in the feces. The distribution of radioactivity was measured in various tissues on day 16, no [^{14}C] activity was present except for adrenal and splenic tissues (present in the limit of detection).

- The half-life for disappearance of [^{14}C] activity from the body of DBDPO treated rats was less than 24 hours (Norris et al., 1975).

Estimates of DBDPO absorption from the gastrointestinal tract can be calculated by comparing tissue levels after oral exposure versus intravenous administration at similar time points.

$$\text{Percent absorption} = \frac{oral\ sample}{intravenous\ sample}$$

In the NTP report (1986), the oral absorption estimate was 0.33% ± 0.19% and was likely based on a comparison of the liver tissue concentrations following intravenous and oral administration at the highest dose (50,000 ppm). However, when the calculation is made on urine radioactivity concentration, the value obtained is higher: approximately 9.3% at 277 ppm and 6.2% at 48,000 ppm and with blood or plasma at 277 ppm, the value obtained is 3.5%. It should also be noticed that if comparison of the liver tissue concentrations following intravenous and oral administration is made at the lowest oral dose (277 ppm), the percentage is higher (approximately 2.5%) than the value obtained at the highest dose. Therefore, in contrast with

NTP assessment, more conservative values of 6 or 9% may be retained. It may be admitted that these values might be overestimated since these values might take into account unchanged DBDPO as well as DBDPO's metabolites formed either in the gut following pre-systemic metabolism or in liver during absorption in contrast with the value retained by NTP which refers only to unchanged DBDPO measured in the liver. But since the toxicological properties of the DBDPO's metabolites formed are unknown and therefore their harmlessness, a more conservative value in some extent is retained which is 6%.

Results of these studies indicate that, after exposure at all doses in the diet, greater than 99% of the radioactivity recovered was detected in the feces within 72 hours. Excretion in urine accounted for approximately 0.01% or less of the dose. After intravenous administration, 61% of the recovered radioactivity was excreted in feces in 72 hours suggesting significant biliary excretion and approximately 0.1% was excreted in urine. The rate of biliary excretion following an intravenous administration was 2.2% of the dose per hour from 1.5 to 4 hours. Analysis of all the major organs and tissues following oral dosing indicated trace levels of radioactivity in most tissues. The highest concentrations were found in gastrointestinal tissues, liver, kidney, lung, skin and adipose tissue. By comparing tissue levels after oral exposure versus intravenous administration, estimation of DBDPO absorption from the gastrointestinal tract was approximately 6%. In extracts of liver after diet administration, presence of DBDPO was demonstrated which indicates that some DBDPO is absorbed intact from the intestine. The increase in liver size with increased consumption of DBDPO confirms an absorption of DBDPO by the oral route. In extracts of feces after diet or intravenous administration, DBDPO was detected as well as three main metabolites of DBDPO with the same retention time whatever the route of administration. These results show that DBDPO may be eliminated intact and that the similar metabolites are produced whatever the route of administration. Moreover, since the major metabolite identified in bile had the same retention time as the major metabolite in feces after intravenous dosing, this implies that DBDPO is subject to hepatic metabolism. However a definite conclusion on the sites of metabolisation cannot be drawn since the biliary excretion study was not extensively studied. Nevertheless, El Dareer et al. (1987) made the assumption that since oral absorption was low, most of the metabolism of [^{14}C] DBDPO apparently took place in the gastrointestinal tract.

Klasson Wehler et al. (2001) and Mörck and Klasson Wehler (2001) have investigated the metabolism of ^{14}C-labelled decabromodiphenyl ether (purity not given) using conventional and bile duct-cannulated rats. An abstract of this study is only available. Sprague-Dawley rats were given a single oral dose of 3 μmol/kg (~2.9 mg/kg) of the test material suspended in a vehicle (Lutrol F127, soya phospholipid, water). Excreta were collected over the following 72 hours and analysed for ^{14}C content and phenolic metabolites. The results of the study showed that the major route of excretion (~90% of the dose within 3 days) was via the feces, with only minor amounts (<0.05% of the dose) being excreted via urine. Excretion via the bile accounted for ~9.5% of the dose within 3 days. Approximated 3% of the total administered radioactivity was present in tissues 3 days after dosing and was distributed mainly in liver (~0.9%), muscle (~0.7%), skin (~0.4%), adipose tissue (~0.3%), colon wall (~0.25%), jejunum wall (~0.05%), jejunum content (~0.05%), with minor amounts (<0.05%) in plasma, kidney, heart, lung, adrenals, testis, red blood cells, thymus and spleen. More detailed analysis of the feces showed that 22%, 42% and 45% of the radioactivity present at day 1, 2 and 3 respectively was present as 8 phenolic metabolites. DBDPO is metabolised via oxidative debromination, as deduced from the presence of debrominated dihydroxylated diphenyl oxides, the dehydroxylation was always on one phenyl ring. Oxidation to an epoxide and further to a diol could explain the formed metabolites. Debrominated diphenyl oxides was not observed except for trace amount of three nonaBDOs.

The remaining radioactivity present in the feces was identified as unchanged decabromodiphenyl ether.

Viberg et al. (2001) recently reported the findings of a study to investigate the uptake and retention of decabromodiphenyl oxide in the brain of neonatal mice. A single oral dose of ^{14}C-labelled decabromodiphenyl oxide (purity >98%) was given on postnatal day 3, 10 or 19 to neonatal NMRI mice. Two litters in each age categories were given 1.5 [^{14}C]PBDO MBq/kg body weight. The radioactivity in the brain was determined after 24 hours or 7 days after dosing in each of the two litters from the three different age categories. The results of the study showed that ^{14}C was taken up into the brain, but there were differences in the amount of radioactivity found in the different age mice. The mice exposed on postnatal day 3 or 10 had around $4^0/_{00}$ of the total administered dose of ^{14}C in the brain at 24-hours after dosing, whereas only $0.6^0/_{00}$ of the total administered dose was found at 24-hours in the brains of mice dosed on postnatal day 19. At day-7 after administration the amount of radioactivity in the brain had increased by around a factor of 2 in the mice exposed on postnatal days 3 or 10, whereas no noticeable change in the amount of radioactivity present had occurred in brains of the mice dosed on postnatal day 19. According to the authors this investigation shows that DBDPO can be taken up in the neonatal mouse and that the uptake is more efficient in younger animals since radioactivity is found in the brain and increases during the first week of administration. However, it should be noticed that those results are only reported in an abstract, the raw data are not available, only a single dosage was carried out, and no statistical evaluation of variations of measurements in relation to time and organs was done. Therefore the toxicological significance of these findings remains unclear.

Xenobiotic metabolism

DBDPO did not alter xenobiotic metabolism. In a study from Carlson (1980), designed largely to investigate hepatic enzyme induction, groups of four rats were administered DBDPO (of high purity but no indication on the chemical composition was provided) at 0.1 mmol/kg/day (corresponding to 95.9 mg/kg/day) for 14 days (with seven administrations). Control animals received vehicle only. No positive controls were included in this experiment. Moreover, it was not specified if the samples were tested randomly. Following this treatment liver enlargement (relative liver weight: 4.75 vs. 3.80 in the control group) was observed with no concurrent induction of any of the 4 systems involved in xenobiotic metabolism (O-ethyl-O-p-nitrophenyl phenylphosphonothioate detoxification, p-nitroanisole demethylation - UDP Glucuronyl transferase - Benzo[a]pyrene hydroxylase), neither on NADPH cytochrome c reductase and cytochrome P450. In the same study, with OBDPO and PeBDPO (commercial mixtures), relative liver weight was increased as well (5.54 and 6.25 respectively vs. 3.80 in the control group) but a potential inducer effect was observed. It was concluded by the author that commercial brominated diphenyl ethers are fairly potent inducers of xenobiotic metabolism. Moreover it was assumed that the degree of bromination is important, since PeBDPO in most cases gave greater induction than the OBDPO whereas DBDPO was without effect except with regard to liver enlargement. Consequently the author suggested that very highly brominated compounds might not be effective inducers. This would be in accordance with the poor inducing properties of fully brominated benzene (Carlson, 1977). Indeed in this latter study, hexabromobenzene, a fully brominated benzene was a weak inducer compare to effective inducer such as di and tribromobenzene. Hexabromobenzene was effective only when high doses from 200 to 800 mg/kg/day were tested and no dose-dependency was observed. Therefore, the absence of inducer effect observed at a relatively low concentration of DBDPO (around 96 mg/kg/day compared to NOAEL established in subchronic study in rats 3,350 mg/kg/day) does not preclude

a lack of an inducer effect at higher concentrations. Given these limitations, no firm conclusion can be drawn pertaining to the absence of hepatic enzyme induction with DBDPO.

Percutaneous absorption

Pertaining to percutaneous absorption, no data are available on DBDPO, or on OBDPO, PeBDPO or other polybrominated biphenyl compounds. Nevertheless based on DBDPO 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: (i) diffusion into and through the lipid-rich intercellular matrix of the stratum corneum, or (ii) 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 lipohilicity 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 DBDPO, high log Kow (6.27), poor water solubility (<0.1 µg/l), low solubility in organic solvents (Albermale, 1998) and high molecular weight (959.2) 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 hour 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 atoms would be less than 1% (Garner and Matthews, 1998). If this pattern is also applied to PBDPOs. This would lead to predict a maximum absorption of 1% DBDPO.

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 and Paustenbach, 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 DBDPO, a possible reservoir effect can not be dismissed.

In conclusion, dermal absorption of DBDPO is assumed to be low and may be estimated at the maximum to 1%, associated with a possible trend towards accumulation in the stratum corneum which behaves as a storage site, leading to a slow systemic release over time.

Retention and turnover

A tissue accumulation study over a period of 2 years was carried out on rats maintained on diet providing 0, 0.01, 0.1 or 1 mg of DBDPO/kg/day (purity DBDPO 77.4%; NBDPO 21.8%; OBDPO 0.8%). During the first 180 days of the study, no increase in the bromine concentration was observed in any of the tissues examined (kidney, skeletal muscle, serum, testes and liver) except in adipose tissue, where the bromine content was statistically increased. In liver, low-level steady-state conditions were attained by 12 months.

Adipose tissue showed a time- and dose-related increase in bromine content subsequent to ingestion of 1 or 0.1 mg DBDPO/kg/day (respectively 16.2 and 3.1 ppm after 12 months versus 2 ppm for controls) (Norris et al., 1973 - 1975; Kociba et al., 1975).

A study on elimination of bromine from various tissues of rats maintained for 90 days on diet providing 1 mg of DBDPO/kg/day revealed low level of bromine in the liver and adipose tissue (approximately 5 μg/g). The bromine concentrations in the adipose tissue remained unchanged during the recovery (90 days) period whereas after 10 days on recovery the bromine concentration in the liver did not differ from that of in control (Norris et al., 1975).

In these studies, some accumulation of brominated compounds in adipose tissue has been observed. However, as the test substance used contains some less brominated compounds, the bromine content observed may be not only related to the DBDPO itself.

4.1.2.1.2 Studies in humans

In a briefly summarised paper, DBDPO was detected at concentrations up to 5 μg/kg in samples of human hair taken from 40 individuals in communities near the bromine industry in El Dorado and Magnolia, Arkansas. This study was initiated to examine the environmental contamination due to the bromine industry. The human contamination was assessed in collecting human hair samples in nearby communities. The author estimated that at least 5% of the surveyed population had detectable levels of DBDPO in their hair (DeCarlo, 1979).

DBDPO has been estimated in human adipose tissues (National Human Adipose Tissue Survey Repository) to range from non-detected to 700 pg/g (Stanley et al., 1991). The samples analysed 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 and neither on the pattern of exposure. The authors conclude that the presence of polybrominated diphenyl ethers (PBDPEs) in human adipose tissues suggests exposure to those compounds from commercial products as well as environmental pathways. On the other hand, DBDPO was not found in human adipose tissue obtained from a hospital in Osaka, Japan (Watanabe et al., 1987b).

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. The results are shown in **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. The age distribution, employment time and fish consumption of all study subjects were reported. Blood samples from the electronics-dismantling workers were drawn immediately before their summer vacation and immediately before they resumed work for 11 of them. The median occupational exposure free-period between the blood samples was 28 days.

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'-tetraBDE	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'-hexaBDE	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'-hexaBDE	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-heptaBDE	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' - decaBDE	<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

Notes: [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.

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 more 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. However, DBDPO was present in higher levels than HpBDPO in the air at the dismantling plant (see results from Carlsson (1999) in Section 4.1.1.2.). The observed higher levels of HpBDPO in serum might thus be due to a more rapid turnover of DBDPO than of HpBDPO or better bioavailability of the heptabrominated than the decabrominated diphenyl oxide. It is currently not possible to verify mechanisms of uptake and elimination of DBDPO or HpBDPO in the electronics dismantling workers. 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.

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 the 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.

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
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

Patterson et al. (2000) quantified the levels of PBDPOs congeners including DBDPO in serum from US blood donors (n=12) in 1988. DBDPO was found at levels above the limit of quantification (1 pmol/g l.w.) in five out of twelve serum samples analyzed.

Since breast-milk excretion is one of the concerns for some PBDPOs and at least for PeBDPOs, it was deemed useful to include in this report the available data on PBDPOs breast-milk excretion. In the Meironyté et al. (1998 and 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 rate was taken into account in the final results.

Ryan and Patry (2001) reported the findings from a recent survey of the levels of decabromodiphenyl ether in human milk and commercial foods from Canada. The analysis of decabromodiphenyl ether in these samples was reported to be difficult, and the presence of decabromodiphenyl ether in laboratory blanks made quantification in the samples uncertain. However, little or no decabromodiphenyl ether could be detected in 72 human milk samples from 1992.

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 polluants 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 the mothers' age, the alcohol or the fish consumption, the place of residence or the birth weight of the child, the computer usage frequency although an increase in concentration with increasing cigarette smoking was suggested. However it is not established if smoking habits is a causal effect for the increase of PBDPOs in human breast milk. No data on HpBDPO, OBDPO or DBDPO are reported. 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. These results can be compared with that from Krüger (1988) who reported a range of values between 600 to 11,000 pg/g milk fat (these partial results were provided by Kemi (1998)).

4.1.2.1.3 Summary of toxicokinetics, metabolism and distribution

Only limited data on human toxicokinetic are available. Those data indicate that DBDPO can be absorbed into the body and are distributed to the blood and the adipose tissue. Few data on human hair samples reveal the presence of DBDPO but the route of exposure is unknown. Some results show that DBDPO and others PBDPOs congeners are bioavailable and that in some occupational conditions, slightly increased plasma levels of DBDPO are observed. There are no data available on the rate of elimination or of bioaccumulation of DBDPO in human adipose tissue neither for PeBDPO or OBDPO but given the low rate of oral absorption in rats, a low

bioaccumulation potential might be anticipated. Following pregnancy HxBDPO and others PBDPOs such as TeBDPO and PeBDPOs are excreted in the breast milk. Based, on the low rate of oral absorption in rats and the low bioaccumulation potential of DBDPO, the rapporteur might anticipate a rather low excretion of this compound in the breast milk. A recent survey of the levels of DBDPO in human milk was conducted by Ryan and Patry (2001) in Canada. The analysis of decabromodiphenyl ether in these samples was reported to be difficult. However, little or no decabromodiphenyl ether could be detected in human milk samples. Therefore a rather low excretion of this compound in the breast milk might be anticipated. Animal data indicate that in rats there is a low absorption of DBDPO through the gastro-intestinal tract (approximately 6-9.5%) and that the principal route of elimination is via the faeces. Some DBDPO is absorbed intact from the intestine and excreted intact or in the form of metabolites (e.g. debrominated hydroxylated diphenyl oxides). DBDPO following intravenous administration is subject to hepatic metabolism with production of three main metabolites. However, a gastrointestinal metabolisation may also be assumed. Only trace amount of bromine compounds was found in tissues and in brain of neonatal mice exposed on postnatal day 3, 10 or 19. However the toxicological significance of this last finding is unclear. Accumulation is only observed in liver at a low level and in adipose tissue. DBDPO is not an inducer of xenobiotic metabolism including UDPG-transferase. However, the absence of inducer effect observed at a relatively low concentration of DBDPO does not preclude a lack of an inducer effect at higher concentrations. There are no data on dermal absorption neither on DBDPO nor on PeBDPO or OBDPO. However based on DBDPO physicochemical properties and analogy with PCBs, a maximal dermal absorption of 1% may be assumed.

Experimental data do not allow to assess pulmonary absorption. Pulmonary exposure may occur due to the small particle size (<5 μm), however, systemic absorption via the pulmonary route is unknown.

4.1.2.2 Acute toxicity

4.1.2.2.1 Oral route (rat)

Intragastric intubation of a single dose of a 10% corn oil suspension of DBDPO (Dow FR-300-BA: 77.4% DBDPO, 21.8% NonaBDPO and 0.8% OBDPO) to female Sprague Dawley rats resulted in the survival of all rats at doses of 126 – 252 – 500 - 1,000 or 2,000 mg/kg. No indications of toxicity after intubation or during the 14-day period were observed. No gross pathological changes were observed at necropsy carried out on one rat/dose level (Norris et al., 1973).

In a briefly reported study, groups of 5 male albino Spartan rats were administered single doses of 50, 500 and 5,000 mg/kg of DBDPO (DE-83) in corn oil. All rats were observed for mortality for a period of 14 days. No death and normal weight gain during a 14-day period were observed. Necropsies were not performed. (Great Lakes, 1974a).

4.1.2.2.2 Dermal route (rabbit)

Groups of 2 male and 2 female New Zealand White rabbits were administered single doses of 200 or 2,000 mg/kg of DBDPO (DE-83) applied neat under occlusive wraps for 24 hours: all the animals survived. Animals were observed for 14 days. At the 2,000 mg/kg dosage level all

rabbits exhibited normal body weight gains. Local and general signs of toxicity were not reported and necropsies not performed (Great Lakes, 1974b).

4.1.2.2.3 Inhalation route (rat)

Groups of 5 male and 5 female Spartan rats were exposed for one hour to 2 or 48.2 mg/l DBDPO (DE-83) in air and subsequently observed for 14 days. All rats survived. Dyspnea and ocular discharge were noted from 2 mg/l concentration (one animal); moreover, in the 48.2 mg/l group, eye squint and increasing motor activity were observed. All rats were normal at the end of 14-day-observation period. Necropsies were not performed (Great Lakes, 1974c).

The usefulness of this assay is dubious since no data on particle size distribution are given.

4.1.2.2.4 Summary of acute toxicity

DBDPO exhibits a low acute oral, dermal and inhalation toxicity.

4.1.2.3 Irritation

4.1.2.3.1 Animal data

Skin irritation

Studies, conducted on shaved skin under occlusion, in 2 groups of 3 New Zealand White rabbits with commercial DBDPO as dry solid (500 mg), cause no irritation on intact or abraded skin. No erythematous and oedematous response was observed after a single exposure for 24h and followed by an observation period of 72h (Great Lakes, 1974d). This study was also reported in an other paper (Norris et al., 1974) where the DBDPO composition is given as: 74.4% DBDPO, 21.8% nonabromodiphenyl oxide, 0.8% octabromodiphenyl oxide. An other dermal irritation study was shortly reported in Norris et al. (1973 and 1974) where DBDPO applied as dry solid on shaved skin of New Zealand albino rabbits caused essentially no response on intact skin and a slight erythematous and edematous response on abraded skin after a single confined exposure of 24 hours.

In a briefly summarised paper from Norris et al. (1973) repeated exposures to intact skin for five days/week for two weeks and to abraded skin for three days did not alter the responses observed following a single administration. No more information is available.

Although the studies (dermal acute toxicity and skin irritation) were not conducted according to EU or OECD methods, particularly no vehicle was used, the substance can be considered as a non irritant. Moreover a cross reading with less brominated congeners such as OBDPO indicates no concern about skin irritation.

Eye irritation

Studies with 3 male and 3 female New Zealand White rabbits showed that 100 mg DBDPO (93 - 98.5% purity) as dry solid caused transient (reversible in 48h) mild irritation of the conjunctival membranes (grade 1). The cornea, iris and lens were unaffected (Ethyl Corporation, 1986). This

study was carried out in accordance with the GLP procedures. In an old study (Great Lakes, 1974e) conducted with 3 male and 3 female New Zealand White rabbits single application of 100 mg DBDPO caused mild irritation of the conjunctival membrane as well. Conjunctival redness was transient (reversible in 72 hours) with at 24 hours a very slight erythema in 3/6 animals and slight erythema in 1/6 and at 48 hour a very slight erythema in only one animal. Chemosis (very slight) was also noticed in 2/6 animals at 24 and 48 hours which remains in only one animal at 72 hours and at day 7. Signs of discharge were observed in one animal at 24 hours and 72 hours (slight discharge) and in one animal at 48 hours (moderate).

Given the mild irritation observed in these two studies and although this effect was not completely reversible in a no GLP study, it is considered that DBDPO does not deserve a Xi R36. Moreover a cross reading with less brominated congeners such as OBDPO indicates no concern about eye irritation.

Respiratory irritation

In the inhalation toxicity study, marked dyspnea was observed in one animal at 2 mg/l and in 3 rats at 48.2 mg/l. No more information is available on this end-point.

4.1.2.3.2 Human data

In the study reported in the paragraph 4.1.2.5, it is concluded that none of test material would be considered as a primary skin irritant.

4.1.2.3.3 Summary of irritation

DBDPO is not an irritant for skin or eyes.

4.1.2.4 "Chloroacnegenic" activity

"Chloroacnegenic" activity was studied on the ear of 4 New Zealand white male and female rabbits. The test material was administered once daily at 0.1 ml/day, 5 times per week, for 4 weeks, at concentrations of 0.1, 1, 10, 100% suspended in chloroform. No positive controls were included in the assay. Observations were recorded prior to the initial dose and at 7, 14, 21, and 28 days of dosing. DBDPO as a 10% chloroform solution caused a slight erythematous response and slight exfoliation in one rabbit but no chloroacne-type" response was observed during the study. This assay was conducted in accordance with GLP procedures. (Ethyl Corporation, 1981).

In the period 1971-74, approximately 40 samples of DBDPO (pilot plant samples), mother liquor, mother liquor still pot residue, and still bottom samples were studied for their chloracnegenic activity. In these studies, the samples (0.1 ml) were applied as such, or as a 5 or 10% solution in chloroform, on the rabbit ear, 5 days per week for 4 weeks. The samples of DBDPO did not induce any response, but responses to the mother liquor and still bottom samples were positive, except in a few cases where the result was equivocal (Rampy, 1971-1974).

In summary, DBDPO topical application does not result in "chloroacnegenic" activity.

4.1.2.5 Sensitisation

4.1.2.5.1 Animal data

No animal data are provided on DBDPO; however a Magnusson and Kligman test was carried out on 20 Guinea pigs exposed to a mixture of polybrominated diphenyl oxides (commercial OBDPO) with varying degrees of bromination and a small percentage of DBDPO (less than 3%). Guinea pigs were exposed to commercial OBDPO intradermally (at a concentration of 2.5% in corn oil) and topically (with neat article moistened in corn oil) at induction and challenge. No animal was sensitised. This study was conducted in accordance with GLP procedures and OECD 406 guidelines. (Chemical Manufacturers Association, 1996). Moreover, data on another less brominated diphenyloxide PeBDPO do not demonstrate any skin sensitisation potential. Therefore a cross reading with smaller, more reactive, related compounds such as OBDPO and PeBDPO which give unequivocal negative results indicate no concern about skin sensitisation.

4.1.2.5.2 Human data

In 50 human subjects, repeated application of a suspension of 5% DBDPO in petrolatum 3 times a week for 3 weeks and challenged two weeks subsequent to the last induction application did not result in skin sensitisation. Skin irritation was observed in 9 out of the 50 persons (Norris et al., 1974; WHO, 1994).

Human volunteers (80 males and 120 females) were treated with 9 induction patches of 2 batches of DBDPO (no information on purity is provided). The first sample was evaluated as received, and the second as a 2% (w/v) aqueous solution. The patches were applied once every 2 days and allowed to contact the skin for 24h, then the skin was graded for irritation. 15 subjects among the 200 volunteers showed some slight irritation reactions: very slight erythema - barely perceptible in 14/1,800 patches and mild – well defined erythema in 2/1,800 patches and very slight edema – barely perceptible in 1/1,800 patches. After a non-patching period of 12 days, the challenge patch was applied to detect sensitisation. This study did not reveal any evidence of skin sensitisation with either of the test materials in any of the subjects tested (Industrial Bio-Test Laboratories, 1975).

It should be noted that the concentrations used (2 and 5%) are very low.

4.1.2.5.3 Summary of sensitisation

Taking into account the negative results from studies in animals on OBDPO and in regard with the two quite large human studies reported on DBDPO, this substance can be considered as a non skin sensitiser.

No direct information is available from studies in humans or animals on respiratory sensitisation.

4.1.2.6 Repeated dose toxicity

4.1.2.6.1 Animal data

Subacute and sub-chronic toxicity

Oral administration

Mouse

In NTP (1986) 14-day study, groups of five male and 5 female B6C3F1 mice were fed diets containing 0 - 5,000 - 10,000 - 20,000 - 50,000 - 100,000 ppm DBDPO (99% pure). The average daily consumption of DBDPO was estimated for 50,000 ppm to be 12,475 mg/kg/day for female and 7,633 mg/kg/day for male. No effects on health, survival or body weights were observed and no compound-related clinical signs or gross pathological effects on major tissues or organs were reported. This study was carried out in accordance with GLP procedures.

The NOAEL (NOEL) derived from this test is the highest dose tested: 100,000 ppm (approximately 25,000 mg/kg/day for female and 15,000 mg/kg/day for male).

In the NTP (1986) 13-week study, groups of 10 male and 10 female B6C3F1 mice were administered 0 - 3,100 - 6,200 - 12,500 - 25,000 - 50,000 ppm DBDPO (two batches were used : one 99%, the other 97% pure) in diet. The average daily consumption of DBDPO was estimated for the two highest doses to be 3,309 and 6,942 mg/kg/day for male and 5,196 and 10,732 mg/kg/day for female. Survival, food consumption or final mean body weights were not adversely affected by DBDPO. No compound related clinical signs or gross or microscopic pathology were observed. Major tissues and organs (including the thyroid gland, marrow, mandibular or mesenteric lymph nodes, spleen, thymus, liver, kidneys, testes, prostate, ovaries or uterus) were examined histologically for control and high dose groups. This study was carried out in accordance with GLP procedures.

The NOAEL (NOEL) derived from this test is the highest dose tested: 50,000 ppm (approximately 11,000 mg/kg/day for female and 7,000 mg/kg/day for male).

Rat

In the NTP (1986) 14-day study, concentrations of 0 - 5,000 - 10,000 - 20,000 - 50,000 - 100,000 ppm DBDPO (99%) administered in the diet to groups of 5 male and 5 female F344/N rats, did not affect health, survival, body weight and no compound-related clinical signs or gross pathological effects on major tissues and organs were seen. The average daily consumption of DBDPO was estimated for 50,000 ppm to be 3,718 mg/kg/day for male and 3,826 mg/kg/day for female. This study was carried out in accordance with GLP procedures.

The NOAEL (NOEL) derived from this test is the highest dose tested: 100,000 ppm (approximately 7,500 mg/kg/day).

In a 28-day study, groups of 10 males and 10 females were exposed to concentration of 0 - 100 - 1,000 ppm (male: 7 and 70 mg/kg/day and female: 8 and 80 mg/kg/day respectively) DBDPO (purity unknown) in the diet. No changes considered to be related to compound were seen in behaviour, appearance, body weights or food consumption. At necropsy no compound related gross pathologic lesions or variations in organ weights were observed. No microscopical lesions were observed in any of the tissues examined (liver - kidneys - thyroid). Increases in bromine

content were seen in liver (respectively 13, 42, 47 ppm) and fat samples (respectively 1.4, 3, 4.6 ppm) (Great Lakes, 1977).

The NOAEL (NOEL) derived from this test is the highest dose tested: 1,000 ppm (70 mg/kg/day for male and 80 mg/kg/day for female).
In a 30-day study in male Sprague Dawley rats (number of treated animals unspecified), at 0 - 100 - 1,000 - 10,000 ppm of DBDPO, (77.4% DBDPO - 21.8% NBDPO (nonabromodiphenyl oxide) - 0.8% OBDPO (octabromodiphenyl oxide)) in the diet, providing approximate doses of 0, 8, 80, 800 mg/kg/day no clinical signs of toxicity, no alterations in food consumption or body weight and no effect on hematological values or urinary parameters were observed. No treatment related effect on weight of organs examined (heart, testes and kidneys) was found.

Enlarged livers were found on the 1,000 and 10,000 ppm levels of DBDPO. Hepatic centrilobular cytoplasmic enlargement and vacuolisation and renal hyaline degenerative cytoplasmic changes were found in the 10,000 ppm dose group. Thyroid hyperplasia was reported in the 1,000 and 10,000 ppm dose group (Norris et al., 1973).

In this test the NOAEL is assumed to be 100 ppm (8 mg/kg/day), with a LOAEL of 1,000 ppm. However the result of this test is of low significance for risk assessment because of the low purity of the test substance (77%) compared to purity of the products currently supplied in the EU (> 97%).

In the NTP (1986) 13-week study doses of 0 - 3,100 - 6,200, 12,500 - 25,000 - 50,000 ppm DBDPO (97 - 99%) were administered in the diet to groups of 10 male and 10 female F344/N rats. The average daily consumption of DBDPO was estimated for 25,000 ppm to be 1,459 mg/kg/day for male and 1,516 mg/kg/day for female and for 50,000 ppm, 2,865 mg/kg/day for male and 3,826 mg/kg/day for female. No effects on survival, health body weight or feed consumption were observed. No gross or microscopical effects were reported. Major tissues and organs (including the thyroid gland, marrow, mandibular or mesenteric lymph nodes, spleen, thymus, liver, testes, prostate, ovaries or uterus) were examined histologically for control and high dose groups. This study was carried out in accordance with GLP procedures.

The NOAEL (NOEL) derived from this test is the highest dose tested: 50,000 ppm (approximately 3,800 mg/kg/day for female and 2,800 mg/kg/day for male).

Intratracheal administration

Rat

50 male Sprague Dawley rats were given an intratracheal injection of 20 mg DBDPO (77.4%) dust (length mean diameter 3.17 μm). The half-life of DBDPO in lungs was determined to be 150 days. No untoward effects were observed, except on days 10 and 556 (but not on days 30 and 416); the lungs of treated rats contained scattered focal aggregates of alveolar macrophages showing clear, angulated, cytoplasmic vacuoles or spaces, which probably represented the location of the dust particles. A very slight focal thickening of the interalveolar septae was noted in 2 rats. Particles were not present in the regional lymph nodes. No evidence of fibrosis or other proliferative response was detected in the lungs or regional lymph nodes (Jersey et al., 1976).

Chronic toxicity

Mouse

In the two-year carcinogenicity study (also reported in Section 4.1.2.8.1), groups of 50 male and 50 female B6C3F1 mice (9 weeks old), were fed 0 - 25,000 - 50,000 ppm DBDPO (purity 97% ; main impurities were identified as unspecified isomers of nonabromodiphenyl oxide) in the diet for 103 weeks and all survivors were killed in weeks 112 to 113. The average daily consumption of DBDPO was estimated to be 3,200 and 6,650 mg/kg for low dose and high dose male mice and 3,760 and 7,780 mg/kg for low dose and high dose female mice respectively. Body weights and food consumption of treated animals were comparable to those of the controls. No compound-related clinical signs of toxicity were reported. Loss of control male mice (presumably due to fighting) was significant during the first part of the study at least until a 15-month period. No significant differences in survival were observed between any groups of either sexes at terminal kill period. This study was carried out in compliance with GLP procedures.

In this carcinogenicity study, an increased incidence of non neoplastic lesions was observed in several tissues. In the liver, there were increased incidence of granulomas in males low dose group and of centrilobular hypertrophy with enlarged hepatocytes with frothy vacuolated cytoplasm in both low and high dose male mice. Follicular cell hyperplasia of the thyroid gland was increased in treated male mice (control, 2/50, low dose, 10/50, high dose, 19/50). An increased incidence of ulcers of the stomach was observed in high dose female mice (NTP, 1986).

The NOAEL was not established in this study. It can be assumed that the LOAEL is 25,000 ppm (approximately 3,700 mg/kg/day for female and 3,200 mg/kg/day for male).

Rat

In the two year carcinogenicity study, groups of 50 male and 50 female Fisher 344/N rats (7-8 weeks old), were fed 0 - 25,000 or 50,000 ppm DBDPO (purity 94 - 97%; main impurities were identified as unspecified isomers of nonabromodiphenyl oxide), in the diet for 103 weeks, and all survivors were killed in weeks 111 to 112. The average daily consumption of DBDPO was estimated to be 1,120 and 2,240 mg/kg for low dose and high dose male rats and 1,200 and 2,550 mg/kg/day for low dose and high dose female rats. No clinical signs of toxicity were reported for either sex of rats. No significant differences in survival were observed between any groups of either sex except low dose male rats (not considered compound related). This study was carried out in compliance with GLP procedures.

Several non neoplastic lesions were observed in this two year carcinogenicity study (also reported in Section 4.1.2.8.2) : high dose males exhibited increased incidence of thrombosis and degeneration in the liver without foci of necrosis associated, fibrosis of the spleen and lymphoid hyperplasia of the mandibular lymph nodes. The incidence of hematopoiesis in spleens of dosed female rats (control, 12/49, low dose, 24/48, high dose, 17/50) and acanthosis of the forestomach in dosed male rats (control, 0/49, low dose, 2/50, high dose, 5/49) was slightly increased. In males, there was also a dose dependent decreased incidence of C-cell hyperplasia of the thyroid gland (NTP, 1986).

A NOAEL of 25,000 ppm (1,120 mg/kg/day for male) is assumed for systemic toxicity. At the highest dose tested in rat males, non neoplastic lesions such as an increased incidence of thrombosis and degeneration in the liver as well as spleen fibrosis and lymphoid hyperplasia of

the mandibular lymph nodes were observed. For local effects, a LOAEL of 25,000 ppm is assumed based on the slight increase of the forestomach acanthosis observed from 25,000 ppm.

Groups of 25 male and 25 female Sprague-Dawley rats, were fed 0, 0.01, 0.1 or 1 mg/kg body weight/day DBDPO (purity DBDPO 77.4% ; NBDPO 21.8% ; OBDPO 0.8%) in the diet for 100 to 105 weeks. Ingestion of up to 1 mg/kg/day DBDPO did not influence survival rates; appearance, mean body weights, feed consumption, hematology, urinalysis, clinical chemistry (blood urea nitrogen, alkaline phosphatase and glutamic pyruvic transaminase activities) and organ weights of treated groups were similar to those of controls. Gross and microscopic examinations performed on all rats killed or dying during the course of the study, did not reveal any significant finding, all the observed changes or variations from normal occurred with similar frequency and severity in the treated and control groups of rats. All these changes were considered spontaneous in nature and unrelated to ingestion of DBDPO. No significant difference in the number of rats developing tumours, the total number of tumours or the specific type of tumours was observed between treated and control groups (Kociba et al., 1975).

The maximum dose tested was very low and did not produce any toxicity. For this reason, the significance of this test is limited.

Summary

The summary of the experiments considered for the NOAEL identification are summarized in **Table 4.5**.

Table 4.5 Synthesis of subacute, subchronic and chronic toxicity results of studies conducted on DBDPO

	Duration treatment	Doses Tested	Body weight	Clinical signs	Organ weight	Macroscopy	Microscopy	Br content	Biochem Parameters	Hematol Parameters	Urine Parameters	NOAEL	LOAEL	Bibliographic references
Mice	14 days	99% pure ->100,000 ppm	No change	No change		No change *						100,000 ppm ≈ 20,000 mg/kg/d		NTP, 1986
	90 days	97-99% pure -> 50,000 pm	No change	No change		No change *	No change* including on the thyroid gland					50,000 ppm ≈ 9,000 mg/kg/d		NTP, 1986
	2 years	(94-97% Pure) 25,000-50,000 ppm (≈ 3,000-6,000 mg/kg/d)	No change	No change			Non neoplastic lesions in the liver and the thyroid from 25,000 ppm and in the stomach at 50,000 ppm						25,000 ppm ≈ 3,500 mg/kg/d	NTP, 1986
Rats	11 days	(purity unknown) 250 - 500 - 2,500 - 5,000 - 25,000 - 50,000 ppm	No change	No change	Increased liver weight from 2,500 ppm			Increased in liver						NTP, 1986
	14 days	99% pure ->100,000 ppm	No change	No change		No change *						100,000 ppm ≈ 7,500 mg/kg/d		NTP, 1986
	28 days	(purity unknown) ->1,000 ppm (80 mg/kg/d)	No change	No change	No change	No change	No change in liver, kidneys and thyroid	Increased in liver and fat from 100 ppm				1,000 ppm ≈ 80 mg/kg/d		Great Lakes, 1977

Table 4.5 continued overleaf

Table 4.5 continued

	Duration treatment	Doses Tested	Body weight	Clinical signs	Organ weight	Macros copy	Micros copy	Br content	Biochem Parame-ters	Hematol Parame-ters	Urine Parame-ters	NOAEL	LOAEL	Bibliographic references
Rats	30 days	(77% pure) 100 - 1,000 - 10,000 ppm	No change	No change	Liver enlargement from 1,000 ppm. No change on testes and kidneys weights		Thyroid hyperplasia from 1000 ppm; liver + renal changes at 10,000 ppm			No change	No change	= 100 ppm ≈ 8 mg/kg/d	1,000 ppm	Norris et al., 1973
	90 days	(97-99% pure) -› 50,000 pm	No change	No change		No change	No change* including on the thyroid gland					50,000 ppm ≈ 3,350 mg/kg/d		NTP, 1986
	2 years	(94-97% pure) 25,000 - 50,000 ppm (≈ 1,000 and 2,000 mg/kg/day)	No change	No change			Non neoplastic lesions in the spleen and fore-stomach from 25,000 ppm and in the liver and lymph nodes at 50,000 ppm.					For systemic toxicity: 25,000 ppm ≈ 1,100 mg/kg/d	For local effects: 25,000 ppm ≈ 1,100 mg/kg/d	NTP, 1986
	2 years	(77% pure) -›1 mg/kg/d	No change	No change	No change	No change	No change		No change	No change	No change			Kociba et al.,1975

Note: *No change on major tissues or organs.

The subchronic and chronic oral toxicity of DBDPO is low. NOAELs of 7,000 mg/kg/day (in male mice) and 2,800 mg/kg/day (in male rats) were obtained in subchronic studies (90 days). In chronic studies (2 years), in mice, LOAEL of 3,200 mg/kg/day (in male) was established and in rats, NOAEL (systemic toxicity) of 1,120 mg/kg/day (in male) and LOAEL (local effects) of 1,120 mg/kg/day were established with only moderate effects observed either at this dose when LOAEL was established or at the just above tested dose when NOAEL was determined. For risk characterisation, the lowest NOAEL for systemic toxicity determined in the chronic toxicity study will be used. Pertaining to the LOAEL determined for local effects (forestomach acanthosis), this LOAEL will not be used in the risk characterisation since local effects observed with this route of administration (oral route) are not considered relevant for the risk characterisation.

4.1.2.6.2 Human data

Case reports and epidemiological studies.

A health assessment of workers exposed for at least 6 weeks to polybromodiphenyls and polybromodiphenyl oxides, including DBDPO, during manufacture revealed a higher than normal prevalence of primary hypothyroidism with elevated serum concentrations of thyrotropin and low or borderline-low, serum T4 and free thyroxine indexes in 4 of the 35 occupationally exposed vs. 0 of the 89 control subjects (Bahn et al., 1980b). A significant reduction in sensory and fibula motor velocities was also observed. This primary hypothyroidism was partially reversible in 1 of the 3 workers re-evaluated one year after the initial study. The 2 other workers reassessed still exhibited low free thyroxine indexes and high thyrotrophin values. Unfortunately the authors could not conclude whether these effects were caused by polybromodiphenyl oxides or by polybrominated diphenyls, which were also produced at earlier period in the plant. DBDPO was not detected in the serum of the workers (Bahn et al., 1980a).

4.1.2.7 Mutagenicity

4.1.2.7.1 *In vitro* assays

Studies conducted by SRI International Laboratory in accordance with GLP procedures were reported in NTP report (1986). Assuming that samples were the same as those used in carcinogenicity tests, purity of DBDPO is supposed to be 97%. DBDPO was tested in *Salmonella typhimurium* TA 100, 98, 1537, 1535 strains in the presence or absence of an exogenous metabolic system from male rat-liver S9 and male Syrian hamster-liver S9 previously induced by Aroclor 1254 in concentrations of 100 - 333 - 1,000 - 3,333 - 10,000 µg/plate in DMSO. An equivocal response was occasionally seen in a scattered incidence (TA 98 - TA 100) with metabolic activation. A dose-related increase in the number of revertant colonies was observed on *Salmonella typhimurium* TA98 in the presence of metabolic activation (hamster-S9) with a doubling at 10,000 µg/plate. On *Salmonella typhimurium* TA100, a slight increase was observed at 3,333 µg/plate without a dose-related relationship. No sign of cytotoxicity was observed. NTP concluded to an absence of mutagenicity.

Two independent studies were conducted with Muster 83 and 88 (no data available on purity). The samples tested (Muster 83 and Muster 88) were referenced in EPA's file as DBDPO (CAS No 1163-19-5) and submitted by BASF as DBDPO (CAS No 1163-19-5). But in the

corresponding reports only the name of the samples namely Muster 83 and 88 were indicated and neither the CAS number nor the chemical name of the substance tested. These studies gave a clear reproducible evidence of mutagenic activity on TA 1535 - TA 98 and TA 100 *Salmonella typhimurium* with and without Aroclor 1254 induced male rat-liver S9. No positive response was observed on TA 1537 and 1538 with and without S9. Samples were tested at 50 - 150 - 500 - 1500 - 5,000 µg/plate in DMSO (EPA/OTS, Doc # 86-900000367 and Doc # 86-900000368). Cytotoxicity was observed from 50 µg/plate on TA 1537 and at 5,000 µg/plate on TA98 with Muster 83. With Muster 88, cytotoxicity was also observed on TA 1537 and 1538. Positive results were only observed approximately from 500 µg/plate and might come from the presence of an impurity which might not exist in the current commercial products. As the purity of the test substance is unknown, this hypothesis cannot be proved.

An assay was performed on DBDPO (98% pure) using the plate incorporation method. A preliminary toxicity assay was carried out with *Salmonella typhimurium* TA98-100-1535-1537 and *Escherichia coli* WP2 *uvrA* (two plates 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 ≥500 µg/plate but no appreciable toxicity was observed. In the mutagenicity assay, *Salmonella typhimurium* TA98-100-1535-1537 and *Escherichia coli* WP2 *uvrA* were exposed to DBDPO concentrations of 15, 150, 500, 1,000, 1,500 and 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 generally observed at ≥500 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's BFRIP, 1998).

In studies reported by NTP (1986), DBDPO tested in the mouse lymphoma L 5178 Y/TK$^{+/-}$ assay for gene mutation in the presence or absence of Aroclor 1254-induced male F344 rat liver S9 at 7, 8, 9, 10 µg/plate in DMSO was not mutagenic. This study was carried out in accordance with GLP procedures. The value of this test is limited since the range of concentrations is narrow. The maximum concentration tested should have been increased up to a concentration providing an evident toxicity.

In studies reported by NTP (1986), DBDPO (50 - 100 - 200 - 500 µg/ml in DMSO) did not induce sister chromatid exchanges or chromosomal aberrations in Chinese hamster ovary cells in vitro in the presence or absence of S9 prepared from livers of Aroclor 1254-induced male Sprague-Dawley rats. Only an early fixation time (8h without S9 and 10h with S9) was carried out, which limits the full significance of the negative results. This study was carried out in accordance with GLP procedures.

4.1.2.7.2 *In vivo* assays

Cytogenetic examination of bone marrow cells taken at necropsy from the femur of the parental rats from a reproduction study (100 - 30 - 3 mg/kg/day in diet) as well as from the neonates at weaning showed no increase in cytogenetic aberrations when compared with controls (Norris et al., 1975). The significance of those results is limited: low doses, no positive control, details not given.

4.1.2.7.3 Summary of mutagenicity

On the whole, results from different *Salmonella* tests can be considered as negative. DBDPO does not exhibit any cytogenetic effects *in vitro* nor *in vivo*. It is noticeable that some of these tests present some limitations. However given the absence of alert-structure for genotoxicity according to Tenant and Ashby (1991), the negative results obtained in the mutagenicity tests with DBDPO and also with OBDPO and PeBDPO, no concern about mutagenicity may be assumed.

4.1.2.8 Carcinogenicity

4.1.2.8.1 Mouse

Groups of 50 male and 50 female B6C3F1 mice (9 weeks old), were fed 0 - 25,000 - 50,000 ppm DBDPO (purity 97% ; main impurities were identified as unspecified isomers of nonabromodiphenyl oxide) in the diet for 103 weeks and all survivors were killed in weeks 112 to 113. The average daily consumption of DBDPO was estimated to be 3,200 and 6,650 mg/kg for low dose and high dose male mice and 3,760 and 7,780 mg/kg for low dose and high dose female mice respectively. Body weights and food consumption of treated animals were comparable to those of the controls. No compound-related clinical signs of toxicity were reported. Loss of control male mice (presumably due to fighting) was significant during the first part of the study at least until a 15-month period. No significant differences in survival were observed between any groups of either sexes at terminal kill period. This study was carried out in compliance with GLP procedures. The results are summarised in **Table 4.6**.

Liver

Non neoplastic lesions (granulomas and centrilobular hypertrophy) were observed at increased incidences in the liver (cf. **Table 4.6** values and also Section 4.1.2.6.1). Neoplasia that occurred at significantly increased incidence was limited to the livers of male mice. Hepatocellular adenomas or carcinomas (combined) were observed in low dose male mice at a significantly greater incidence than in the controls (control, 8/50; low dose, 22/50; high dose, 18/50; historical incidence in male, 30 ± 8%). The incidence of hepatocellular carcinoma is the following: control, 5/50; low dose, 14/50; high dose, 8/50.

Thyroid

Thyroid gland follicular cell adenomas or carcinomas (combined) in male were observed at marginally increased incidence (control, 0/50; low dose, 4/50; high dose, 3/50; historical incidence in male, 1,7 ± 2%). The significance of this lesion in males was supported by an increased incidence of follicular cell hyperplasia in male (control, 2/50; low dose, 10/50; high dose, 19/50). But it should be noticed that only one carcinoma is observed in one male at the lowest dose and in one female at the highest dose.

The evidence of carcinogenicity in male is weakened by the early loss of control animals and the lack of a statistically significant effect at the high dose. Therefore, the increased incidence of hepatocellular neoplasms in low dose animals and the less than significant increase in thyroid gland tumours is considered equivocal evidence of carcinogenicity of DBDPO in male mice (NTP, 1986).

Table 4.6 Incidence of non neoplastic or neoplastic lesions in the liver and thyroid gland of mice fed DBDPO for 103 weeks

Incidence of non neoplastics or neoplastics lesions in the liver and thyroid gland of mice fed DBDPO for 103 weeks.						
Sex	Males			Females		
Dose groups	0	25,000 ppm	50,000 ppm	0	25,000 ppm	50,000 ppm
Number of animals examined	50	50	50	50	50	50
Liver:						
Granulomas	8/50 (16%)	22/50 (44%)	12/50 (24%)	23/50 (46%)	27/50 (54%)	24/50 (48%)
Centrilobular hypertrophy	0/50	34/50 (68%)	32/50 (64%)	-	-	-
Hepatocellular adenoma						
Overall rates[a]	4/50 (8%)	12/50 (24%)	12/50 (24%)	5/50 (10%)	10/50 (20%)	7/50 (14%)
Adjusted rates[b]	19%	46.2%	39%	16.8%	31.2%	21.9%
Terminal rates[c]	3/19 (16%)	11/25 (44%)	7/24 (29%)	4/27 (15%)	9/31 (29%)	7/32 (22%)
Week of first observation	81	100	60	83	102	103
Hepatocellular carcinoma						
Overall rates[a]	5/50 (10%)	14/50 (28%)	8/50 (16%)	3/50 (6%)	4/50 (8%)	7/50 (14%)
Adjusted rates[b]	20.7%	42.9%	26.8%	10.7%	12.1%	20.8%
Terminal rates[c]	1/19 (5%)	8/25 (32%)	4/24 (17%)	2/27 (7%)	3/31 (10%)	6/32 (19%)
Week of first observation	81	72	76	101	93	96
Hepatocellular adenoma or carcinoma						
Overall rates[a]	8/50 (16%)	22/50 (44%)	18/50 (36%)	8/50 (16%)	13/50 (26%)	13/50 (26%)
Adjusted rates[b]	33.9%	67.7%	56.5%	26.7%	39.1%	39.1%
Terminal rates[c]	4/19 (21%)	15/25 (60%)	11/24 (46%)	6/27 (22%)	11/31 (35%)	12/32 (38%)
Week of first observation	81	72	60	83	93	96

Table 4.6 continued overleaf

Table 4.6 continued

Incidence of non neoplastics or neoplastics lesions in the liver and thyroid gland of mice fed DBDPO for 103 weeks.						
Sex	Males			Females		
Dose groups	0	25,000 ppm	50,000 ppm	0	25,000 ppm	50,000 ppm
Number of animals examined	50	50	50	50	50	50
Thyroid:						
Hyperplasia, follicular cell	2/50 (4%)	10/50 (20%)	19/50 (38%)	4/50 (8%)	9/50 (18%)	7/50 (14%)
Follicular cell adenoma						
Overall rates[a]	0/50	3/50 (6%)	3/50 (6%)	1/50 (2%)	3/50 (6%)	2/49 (4%)
Adjusted rates[b]	0%	10.8%	12.5%	2.9%	7.8%	6.3%
Terminal rates[c]	0/19 (0%)	2/25 (8%)	3/24 (13%)	0/27 (0%)	1/31 (3%)	2/32 (6%)
Week of first observation		90	103	95	80	103
Follicular cell adenoma or carcinoma (combined)						
Overall rates[a]	0/50 (0%)	4/50 (8%)	3/50 (6%)	1/50 (2%)	3/50 (6%)	3/49 (6%)
Adjusted rates[b]	0%	14.7%	12.5%	2.9%	7.8%	9.4%
Terminal rates[c]	0/19 (0%)	3/25 (12%)	3/24 (13%)	0/27 (0%)	1/31 (3%)	3/32 (9%)
Week of first observation		90	103	95	80	103

Notes: a) Number of tumor-bearing animals/number of animals examined at the site.
b) Kaplan-Meier estimated tumor incidences at the end of the study after adjusting for intercurrent mortality.
c) Observed tumor incidence at terminal kill.

4.1.2.8.2 Rat

A two-year dietary feeding study was reported by Kociba et al. (1975) (reported in Section 4.1.2.6.1) and no increasing number of tumours was observed but the dose levels used were very low (1 mg/kg/day).

In NTP report (1986), groups of 50 male and 50 female Fisher 344/N rats (7-8 weeks old), were fed 0 - 25,000 or 50,000 ppm DBDPO (purity 94 - 97%; main impurities were identified as unspecified isomers of nonabromodiphenyl oxide), in the diet for 103 weeks, and all survivors were killed in weeks 111 to 112. The average daily consumption of DBDPO was estimated to be 1,120 and 2,240 mg/kg for low dose and high dose male rats and 1,200 and 2,550 mg/kg/day for low dose and high dose female rats. No clinical signs of toxicity were reported for either sex of rats. No significant differences in survival were observed between any groups of either sex except low dose male rats (not considered compound related). This study was carried out in compliance with GLP procedures. The results are summarised in **Table 4.7**.

Liver

At the end of the study, neoplastic nodules in livers of male and female rats were observed with significant positive trends, and the incidence of neoplastic nodules in dosed male and high dosed

female rats were significantly greater than those in the controls and considered compound related (male: 1/50, 7/50, 15/49 ; historical incidence: 3.5 %; female: 1/50, 3/49, 9/50; historical incidence: 2.6%). The incidences of neoplastic nodules in rats increased with dose in both males and females and appeared to be compound related. Microscopically, the neoplastic nodules were generally spherical and occupied an area greater than other liver lobule. Demarcation from surrounding hepatic parenchyma was due either to compression of peripheral normal liver or by a discontinuity between the plates of the nodule and those of adjacent unaffected liver. Hepatocytes within the neoplastic nodules had variations in size, tinctorial characteristics, cytoplasmic vacuolization and nuclear atypia. The incidence of hepatocellular carcinomas was low in all groups and was apparently not compound related. Therefore, the increased incidences of neoplastic nodules were considered by NTP as some evidence of DBDPO carcinogenicity in rats.

Other tumours

Other tumours observed in dosed rats but at a less than significant incidence were Zymbal gland carcinomas in low dose female rats and osteosarcomas in low dose males. No significant increase of the incidence of thyroid gland tumours (C-cell adenoma or carcinoma) was observed. Moreover, one nonneoplastic lesion, C-cell hyperplasia of the thyroid gland, decreased in a dose-dependent fashion in both sexes. Acinar cell adenomas of the pancreas occured in high dose male rats and the incidence was marginally greater than that of the controls. This effect was not considered a compound-related effect by the Working Group NTP. A high incidence of mononuclear-cell leukemia (MNLC) was observed in treated and control rats of each sex. In males, the overall rates were 30/50 controls and 33/50 low-dose and 35/50 high-dose animals; the adjusted rates were 67.9%, 81.9% and 82.8%, respectively. The incidence of MNCL in male rats increased slightly with dose, but because of the exceptionally high incidence in control rats, the marginal nature of the increase, and the lack of significant increase in female rats, the increase in treated male rats was not considered biologically significant.

A TD50[4] of 2,220 mg/kg/bw per day has been calculated for male rat and indicates a very low carcinogenic potency (McGregor, 1992).

[4] TD50: chronic dose rate (in milligrams per kilogram body weight per day) that would give one-half of the animals tumours within some standard experimental time - the “standard lifespan” - for the species.

Table 4.7 Incidence of liver neoplastic nodules and carcinoma in rats fed DBDPO for 103 weeks

Incidence of liver neoplastic nodules and carcinoma in rats fed DBDPO for 103 weeks						
Sex	Males			Females		
Dose groups	0	25,000 ppm	50,000 ppm	0	25,000 ppm	50,000 ppm
Number of animals examined	50	50	49	50	49	50
Liver:						
Neoplastic nodules						
Overall rates[a]	1/50 (2%)	7/50 (14%)	15/49 (31%)	1/50 (2%)	3/49 (6%)	9/50 (18%)
Adjusted rates[b]	2.9%	27.1%	52.7%	2.5%	9.1%	24.4%
Terminal rates[c]	1/35 (3%)	6/24 (25%)	13/26 (50%)	1/40 (3%)	3/33 (9%)	7/34 (21%)
Week of first observation	104	89	87	104	104	87
Historical incidence	3.5%			2.6%		
Neoplastic nodule or Hepatocellular carcinoma						
Overall rates[a]	2/50 (4%)	8/50 (16%)	15/49 (31%)	1/50 (2%)	5/49 (10%)	9/50 (18%)
Adjusted rates[b]	5.2%	31.1%	52.7%	2.5%	15.2%	24.4%
Terminal rates[c]	1/35 (3%)	7/24 (29%)	13/26 (50%)	1/40 (3%)	5/33 (15%)	7/34 (21%)
Week of first observation	97	89	87	104	104	87

Notes: a) Number of tumor-bearing animals/number of animals examined at the site.
b) Kaplan-Meier estimated tumor incidences at the end of the study after adjusting for intercurrent mortality.
c) Observe tumor incidence at terminal kill.

4.1.2.8.3 Summary of carcinogenicity

The carcinogenicity data are summarised in **Table 4.8**.

Under the conditions of these two-year feed studies of DBDPO conducted by NTP, there was:

- In male B6C3F1 mice: equivocal evidence of carcinogenicity as shown by increased incidence of hepatocellular adenomas or carcinomas (combined) in the low dose group and marginally increased incidence of thyroid gland follicular cell adenomas or carcinomas (combined) in both dosed groups. Several non neoplastic lesions were observed at increased incidence, the most notable being thyroid gland follicular cell hyperplasia.

- In female B6C3F1 mice: no evidence of carcinogenicity.

- In male and female F344/N rats: some evidence of carcinogenicity as shown by a dose-dependent increased incidence of neoplastic nodules of the liver in low dose (25,000 ppm) males and high dose (50,000 ppm) groups of each sex.

Table 4.8 Summary of carcinogenicity data

Summary of carcinogenicity data				
Liver	Hepatocellular carcinoma	rat	male	-
			female	-
		mice	male	↑ at 25,000 ppm
			female	-
	Neoplastic nodules	rat	male	↑ from 25,000 ppm (dose dependent)
			female	↑ at 50,000 ppm
	Hepatocellular adenoma	mice	male	↑ from 25,000 ppm
			female	↑ at 25,000 ppm
Thyroid	Follicular cell hyperplasia	rat	male	↓
			female	↓
		mice	male	↑ from 25,000 ppm
			female	↑ from 25,000 ppm
	Follicular cell adenoma or carcinoma (combined)	rat	male	-
			female	-
		mice	male	marginal↑ from 25,000 ppm
			female	marginal↑ from 25,000 ppm

4.1.2.8.4 Discussion

On liver, in B6C3F1 mice, hepatocellular adenomas or carcinomas (combined) occurred from 25,000 ppm without a dose-effect relationship and were considered as equivocal evidence of carcinogenicity. This effect was not confirmed in Fischer 344/N rats since no malignant tumors have been observed. But in rats, a dose-related increase in liver tumours (neoplastic nodules) were observed in both sexes that allows to some evidence of carcinogenicity.

The well-documented existence of strong interspecies and interstrains differences in liver tumours susceptibility should be kept in mind, B6C3F1 mouse being characterized by a high liver tumour background incidence. Although there appears to be a general agreement that nodules and hepatic neoplasms occuring in the rat as a result of treatment represent a higher risk to man than nodules induced in the mouse, perception of risk is greatly dependent on whether nodules are considered simply reactive hyperplasias or exaggeration of a spontaneous change, whether nodules represent end-stage benign neoplasms or a stage in the evolution of hepatocellular carcinoma (Greaves and Path, 1990). However no increase in hepatocellular carcinomas was detected in rats even at an extremely high doses.

On thyroid, marginal increase in incidence of thyroid tumours in mice but not in rats, supported by an increased incidence of follicular cell hyperplasia is observed. It is recognized that there are marked species differences in thyroid gland biochemistry and physiology and that the rodent thyroid gland is markedly more active and operates at a considerably higher level with respect to thyroid hormone turnover as compared to primate (McClain, 1995). In rodents, thyroid hyperplasia may be caused by a hepatic inducer effect which involves an increase in UDPG

transferase activity. It was shown for OBDPO and PeBDPO that these compounds are enzyme inducers whereas an absence of inducer effect was observed with DBDPO at a relatively low concentrations. But it was assumed that this absence of response does not preclude a lack of inducer effect at higher concentrations. Therefore this mechanism of action at the best of our knowledge can not be dismissed.

DBDPO presents a non-genotoxic profile as well as other polybrominated congeners such as OBDPO and PeBDPO and is devoid of alert-structure for genotoxicity according to Tenant and Ashby (1991).

In International Agency for Research and Cancer (IARC, 1990) evaluation, it has been concluded to a limited evidence for the carcinogenicity of DBDPO in experimental animal and has been classified in Group 3: "Not classifiable as to its carcinogenicity to humans".

Therefore, based on these results and the argumentation mentioned above, a classification for carcinogenicity is not proposed. But following a cautious approach, a LOAEL for carcinogenicity of 1,120 mg/kg/day is stated based on the increased incidence of liver neoplastic nodules from the lowest tested dose (1,120 mg/kg/day) and considered for the risk characterisation.

4.1.2.9 Toxicity for reproduction

The two following studies (Norris et al., 1973 and 1975) were performed with a former commercial DBDPO (77.4% DBDPO, 21.8% NBDPO and 0.8% OBDPO).

One generation reproduction study

10 male and 20 female Sprague-Dawley rats at the two lowest dose levels and 15 male and 30 female rats at the highest dose level were given 3 - 30 or 100 mg DBDPO/kg body weight/day in the diet (weekly adjustment) for 60 days prior to mating, 15 days during mating and subsequently throughout gestation and lactation up to weaning. 20 male and 40 female rats served as controls.

There were no signs of toxicity observed in the adult rats or the neonates during the study or at the necropsy. Unaffected parameters included body weight gain and food consumption by adults, reproductive parameters (per cent and number of pregnancies, pup survival indices, neonatal body weights, sex ratio on day 21, and length of gestation), preterminal urinalysis and clinical chemistry (urea, alkaline phosphatase and Serum Glutamic Pyruvic Transaminase activities) in adult rats, relative and absolute organ weights in adult rats (including liver and testes), gross examination of all adult rats and microscopic examination of tissues (including liver, testes, ovaries and uterus) from both age groups (Norris et al., 1975; WHO, 1994). At the necropsy examination of neonates at weaning, a variety of internal and external developmental variations were observed in soft tissues and skeletal structures, but neither at an incidence different from those found in the control litters nor with a dose-response relation-ship. The microscopic examination in weanling rats were performed in one male and one female from each litter. Only a summary of the study was provided (individual data are not available). This study was conducted up to 100 mg/kg and this top dose did not elicit any parental toxicity which limits the significance of the results.

In this study, the NOAEL, which is the highest dose tested, is 100 mg/kg/day for parents and conceptus. However, a higher dose should have been tested to produce a parental toxic effect. No adverse effect on fertility was observed.

Effects on reproductive organs

In study reported by NTP (1986), no macroscopic or histological changes were seen in testes, prostate, ovaries or uterus when rats and mice were treated for 13 weeks (with up to 50,000 ppm) and for two years (with up to 50,000 ppm) with DBDPO (>94% purity). Tissues were preserved in 10% neutral buffered formalin, embedded in paraffin, stained with hematoxylin and eosin; use of Bouin's fixative for these tissues would have been more appropriate. In Norris et al. (1975), no macroscopic or histological changes were observed in testes, ovaries or uterus when rats were treated with DBDPO (purity of 77.4%) for 118 days but no indications on the preservation and fixation methods are available.

Developmental toxicity

20 pregnant female Sprague-Dawley rats were given 10 - 100 or 1,000 mg DBDPO/kg body weight/day, suspended in corn oil by intragastric gavage on days 6-15 of gestation (the number of animal is not indicated) and 30 pregnant rats received the vehicle.

There were no indications of toxicity among the dams during gestation. Liver bromine content was statistically increased in maternal liver at 1,000 mg/kg/day but no increase was observed in foetal liver. The terminal liver weight of the treated rats was not different from those of the controls. Similarly no differences were seen between the treated and control rats with respect to the position and number of foetuses *in utero*, the number of corpora lutea, individual pup weight, crown rump ratio and sex ratio. A statistically significant increase in resorptions was found from 10 mg/kg/day: 12/141 resorptions/implantation sites (9%) at 10 mg/kg/d, 13/135 (10%) at 100 mg/kg/d and 9/203 (4%) at 1,000 mg/kg/d vs. 3/288 (1%) in the control group. The resorption rate observed at 10 and 100 mg/kg/d was outside the historical control values however no dose-response relationship was observed. No gross external abnormalities were seen in the foetuses from dams treated at any dose level. Soft tissue and skeletal examinations revealed a statistically significant increase of the numbers of litters with subcutaneous edema (in 13/97 foetuses examined vs. 2/143 in the control group) and delayed ossification of normally developed bones of the skull (in 14/97 foetuses at 1,000 mg/kg/d vs. 2/142 in the control group for interparietal skull delayed ossification) of the foetuses of dams treated with 1,000 mg/kg/day, but not at 100 mg/kg body weight/day. These values were at least for the subcutaneous edema outside the historical control values. Analysis of maternal and foetal livers for total bromine revealed a significant increased concentration in maternal livers of rats treated with 1,000 mg/kg. At the two lower dose levels, no difference was found. In livers of foetuses from dams receiving any dose level of DBDPO, no increase in total bromine content was observed (Norris et al., 1973, 1974, 1975 and Dow's letter, 1985). Only a summary is provided.

Administration of commercial DBDPO (77.4 %purity) to the dams resulted in effects on the conceptuses including increased embryo/foetal death (resorption) from 10 mg/kg/day without a dose-response relationship and a delayed ossification of the skull and subcutaneous edema at 1,000 mg/kg/day. Based on the limited data available, it can be assumed that the maternal NOAEL is 1,000 mg/kg/day and the foetal LOAEL is 10 mg/kg/day since it can not be shown that the observed effects are without toxicological significance.

NOAEL (dams) = 1,000 mg/kg/day
LOAEL (conceptus) = 10 mg/kg/d

In a recent prenatal developmental toxicity study (BFRIP, 2000), well-conducted (according to GLP procedures) and well reported, female rats (Crl:CD(SD)IGS BR were given 0 - 100 - 300 - 1,000 mg/kg/day of DBDPO (purity of 97.34%) in corn oil by gavage on days 0-19 of gestation.

The test article, DBDPO, used was a composite of 3 lots of commercial DBDPO produced by Albermarle Corporation, Great Lakes Chemical corporation and Ameribrom (Dead Sea Bromine). Observations of the dams included clinical signs, gestational body weights and food consumption. Females were euthanized on day 20 of gestation and given a post-mortem macroscopic examination. Gravid uterine weights and liver weights were recorded. Litters were delivered by caesarean section. Total number of corpora lutea, uterine implantation, early and late resorption, viable and non-viable foetuses and the sex and individual weights of foetuses were recorded. All foetuses were given a gross external examination. Approximately one-half of the foetuses in each litter were examined for visceral abnormalities and the remaining were evaluated for skeletal/cartilaginous malformations and ossification variations.

No adverse treatment related effect was seen in maternal clinical findings, body weight, body weight gain, adjusted body weight change, liver weights and necropsy. A slight increase of food consumption was observed at 1,000 mg/kg/d but this effect was not considered as an adverse effect.

No adverse treatment related effect with DBDPO was evident from external malformations or variations, skeletal variation or ossification.

Regarding foetal visceral malformations, a low incidence of vascular malformations was seen in the 100 and 1,000 mg/kg/day groups. Enlarged heart ventricles were seen in one foetus from the litter of 100 mg/kg/day. In the 1,000 mg/kg/day group, a malformation of the aortic arch (constricted aortic arch, dilated pulmonary artery, absence of the semilunar valves and missing subclavian artery) and enlarged heart ventricles were observed in one foetus at 1,000 mg/kg/day. Based on the low incidence of these malformations in the treated groups, this effect was not considered indicative of a treatment-related effect.

No adverse treatment related effect with DBDPO was evident from foetal weight, sex ratio, total resorption and late resorption. Pertaining to early resorption, the mean number per animal in the 1,000 mg/kg/day was statistically higher than controls (1.4 vs. 0.6), however this value was at the upper limit of the historical control data of the laboratory and therefore was not taken into consideration. A dose-dependent decrease of the percentage of the viable foetuses per implant was observed from 300 mg/kg/day (93.14 at 300 mg/kg/day, 90.67 at 1,000 mg/kg/d vs. 95.61 control group) but without statistical significance; an increase of the post-implantation loss was also noted from 300 mg/kg/day (6.86 at 300, 9.33 at 1,000 vs. 4.39 control group) without statistical significance as well. These effects were not statistically significant and were not considered biologically significant. Therefore they were not taken into consideration for the determination of a NOAEL.

In this recent prenatal developmental toxicity study (BFRIP, 2000), no maternal or developmental toxicity was observed up to the highest dose tested of 1,000 mg/kg/day.

Concerning fertility neither the results of one generation study nor examination of reproductive organs in rats and mice treated for 13 weeks or two years with up to 50,000 ppm of DBDPO are indicative of an adverse effect on fertility.

In terms of developmental effects, in an old teratology study (Norris et al., 1975), commercial DBDPO of low purity (purity 77.4%) leads to some effects on foetus: embryo/foetal death from 10 mg/kg/day without a dose-response relationship and subcutaneous oedema and delayed ossification of bones of the skull at a high dose (1,000 mg/kg/day) which does not seem to cause any maternal toxicity. Only a summary of the study is available and consequently the reliability of the estimated NOAEL for dams and LOAEL for foetuses is dubious. Furthermore, the purity of the test substance is lower than the purity of the products currently supplied in the EU. The

recent well conducted, prenatal developmental toxicity study (BFRIP, 2000), carried out with a composite of commercial DBDPO of greater purity (97.4%) was judged preferable to assess the developmental toxicity. In this recent prenatal developmental toxicity study, no adverse treatment related effect was observed on external or internal malformations or variations neither on foetal weight, sex ratio, total resorption and late resorption. A slight increase of the mean number of early resorptions per animal and of the post-implantation loss and, a slight decrease of the percentage of the viable foetuses per implant were observed, however these effects were either not statistically significant or dose-related and therefore were not taken into consideration for the determination of a NOAEL. Thus based on this recent prenatal developmental toxicity, no concern for adverse effects on development may be assumed.

4.1.2.10 Additional data

4.1.2.10.1 Porphyrinogenic action of fire retardants

Koster et al. (1980) did not found any porphyrinogenic effect in cultures of chick embryo liver cells at concentrations of 10 µg commercial DBDPO/ml medium, with and without pretreatment by ß-naphtoflavone, an enzyme inducer.

4.1.2.10.2 Immunotoxicity evaluation

In contrast with polybrominated biphenyls, no immunotoxic properties have been identified throughout histological examination of lymphoid organs in rats and mice in the 90-day and 2-year studies (NTP, 1986).

4.1.2.10.3 Liver weight evaluation

In a study conducted by NTP (1986) in rats (3 rats per dose) exposed to DBDPO obtained from Fluka Chemical Corporation (no purity was specified) at 238 - 496 - 2,510 - 4,730 - 25,400 and 51,100 ppm in the diet for 11 days, a dose-dependent increase in liver weight was observed at the two highest concentrations (approximately 40% greater than the controls). Liver weights of animals exposed at 2,510 and 4,730 ppm were increased by 30%-40%. Liver weights of animals exposed at the two lowest doses were unaffected. In a one generation study from Norris et al. (1975), no significant liver weights changes were observed in male or female rats treated for 118 days.

4.1.2.10.4 Endocrine disruptor potential

Alterations in thyroid homeostasis were reported with organochlorine compounds and a thyroid hormonelike affinity for the serum transport protein transthyretin was explored.

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 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 affinities 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-foetal 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., 1997). However, to our knowledge, no studies on transthyretin-T_4 competition have been carried out on DBDPO neither on OBDPO.

4.1.2.10.5 Neurotoxicity

In a behavioural study 3 days-old and 19 days-old mice were given 2.22 or 20.1 mg/kg b.wt. of DBDPO (purity not given) and 10 days-old mice were given 1.34, 13.4 or 20.1 mg/kg b.wt (Viberg et al., 2001). Mice serving as controls received 10 ml/kg b.wt. of the 20% fat emulsion vehicle in the same manner. Each group contained 3-5 litters. The spontaneous 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. The spontaneous motor behaviour data states a disruption of habituation in adult mice exposed to DBDPO on postnatal day 3, but this disruption in habituation can not be seen in mice exposed to DBDPO on postnatal day 10 or 19. 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 groups of the three age categories as well as in the animals exposed to DBDPO on postnatal day 10 or 19. The animals exposed to the highest dose of DBDPO, on postnatal day 3, showed this non-habituating behavioural profile at 2, 4 and 6 months of age. At 6 months of age mice exposed to the lower dose of DBDPO, on post-natal day 3, showed this non-habituating behavioural profile.

The toxicological significance of these findings is unclear. The authors indicate that PCBs have been shown to induce this type of behavioural profile when administered on post-natal day 3, but this response is always accompanied by a response in animals exposed to the toxic compound on post-natal day 10. However, a clear interpretation of the significance for human health of the behavioural differences seen in mice has not been established and thus uncertainty as to their significance remains. Moreover only an abstract of this study is available. Some information are lacking such as the housing condition, randomisation, description of the severity of the effects

pending on the dose, statistical treatment of the results. Moreover, as no standard deviation data are presented, it is difficult to judge the degree of variability that might be expected within this study and no details regarding the historical negative control are reported.

4.1.3 Risk characterisation

4.1.3.1 General aspects

Few toxicological information is available in human except for sensitisation. An epidemiological study was reported but the identified effect (primary hypothyroidism) could not be related to the DBDPO exposure.

Only limited data on human toxicokinetic are available. Those data indicate that DBDPO can be absorbed into the body and are distributed to the blood and the adipose tissue. Few data on human hair samples reveal the presence of DBDPO but the route of exposure is unknown. Some results show that DBDPO and others PBDPOs congeners are bioavailable and that in some occupational conditions, slightly increased plasma levels of DBDPO are observed. There are no data available on the rate of elimination or of bioaccumulation of DBDPO in human adipose tissue neither for PeBDPO or OBDPO but given the low rate of oral absorption in rats, a low bioaccumulation potential might be anticipated. Following pregnancy HxBDPO and others PBDPOs such as TeBDPO and PeBDPOs are excreted in the breast milk. Based, on the low rate of oral absorption in rats and the low bioaccumulation potential of DBDPO, the rapporteur might anticipate a rather low excretion of this compound in the breast milk. A recent survey of the levels of DBDPO in human milk was conducted by Ryan and Patry (2001) in Canada. The analysis of decabromodiphenyl ether in these samples was reported to be difficult. However, little or no decabromodiphenyl ether could be detected in human milk samples. Therefore a rather low excretion of this compound in the breast milk might be anticipated. Animal data indicate that in rats there is a low absorption of DBDPO through the gastro-intestinal tract (approximately 6-9.5%) and that the principal route of elimination is via the faeces. Some DBDPO is absorbed intact from the intestine and excreted intact or in the form of metabolites (e.g. debrominated hydroxylated diphenyl oxides). DBDPO following intravenous administration is subject to hepatic metabolism with production of three main metabolites. However, a gastrointestinal metabolisation may also be assumed. Only trace amount of bromine compounds was found in tissues and in brain of neonatal mice exposed on postnatal day 3, 10 or 19. However the toxicological significance of this last finding is unclear. Accumulation is only observed in liver at a low level and in adipose tissue. DBDPO is not an inducer of xenobiotic metabolism including UDPG-transferase. However, the absence of inducer effect observed at a relatively low concentration of DBDPO does not preclude a lack of an inducer effect at higher concentrations. There are no data on dermal absorption neither on DBDPO nor on PeBDPO or OBDPO. However based on DBDPO physicochemical properties and analogy with PCBs, a maximal dermal absorption of 1% may be assumed.

Experimental data do not allow to assess pulmonary absorption. Pulmonary exposure may occur due to the small particle size (<5 μm), however, systemic absorption via the pulmonary route is unknown.

Assessment of the available data clearly indicates that DBDPO is of low acute toxicity in animals. DBDPO does not cause skin, nor eye irritation and does not exhibit a chloroacnegenic activity. There is no indication of skin sensitisation: no skin sensitisation was reported either in

animals with OBDPO and PeBDPO or in a quite large human population study with DBDPO. There is no information on respiratory sensitisation in animals; no such effects have been reported in human. Therefore **conclusion (ii)** is drawn for all these end-points for all populations.

Repeated exposure by oral route indicates a low systemic toxicity even at high dose level in mice or rat especially when the degree of purity is high. NOAELs of 7,000 mg/kg/day (in male mice) and 2,800 mg/kg/day (in male rats) were obtained in subchronic studies (90 days). In chronic studies (2 years), in mice, LOAEL of 3,200 mg/kg/day (in male), was established and in rats, NOAEL (systemic toxicity) of 1,120 mg/kg/day (in male) and LOAEL (local effects) of 1,120 mg/kg/day were established with only moderate effects observed at these doses. For risk characterisation, the lowest NOAEL for systemic toxicity (including non neoplastic lesions exclusively) determined in the chronic study is used namely 1,120 mg/kg/day. In this chronic study, at the highest dose tested (2,240 mg/kg/day) in rat males, non neoplastic lesions such as an increased incidence of thrombosis and degeneration in the liver as well as spleen fibrosis and lymphoid hyperplasia of the mandibular lymph nodes were observed. For local effects, a LOAEL of 1,120 mg/kg/day is determined based on the slight increase of the forestomach acanthosis observed from 1,120 mg/kg/day. But since local effects observed with this route of administration (oral route) are not considered relevant for the risk characterisation, this LOAEL will not be used in the risk characterisation.With regard to mutagenesis:

On the whole, results from different *Salmonella* can be considered as negative. DBDPO does not exhibit any cytogenetic effects *in vitro* nor *in vivo*. It is noticeable that some of these tests present some limitations. However given the absence of alert-structure for genotoxicity according to Tenant and Ashby (1991), the negative results obtained in the mutagenicity tests with DBDPO and with OBDPO and PeBDPO as well, no concern about mutagenicity may be assumed. Therefore DBDPO is of no concern with regard to mutagenicity and **conclusion (ii)** is drawn for this endpoint.

With regard to carcinogenicity:

On liver, in B6C3F1 mice, hepatocellular adenomas or carcinomas (combined) occurred from 25,000 ppm without a dose-effect relationship and were considered as equivocal evidence of carcinogenicity. This effect was not confirmed in Fischer 344/N rats since no malignant tumors have been observed. But neoplastic nodules were observed in rats with a dose effect relationship in both sexes that allows to some evidence of carcinogenicity.

The well-documented existence of strong interspecies and interstrains differences in liver tumours susceptibility should be kept in mind, B6C3F1 mouse being characterized by a high liver tumour background incidence. Although there appears to be a general agreement that nodules and hepatic neoplasms occuring in the rat as a result of treatment represent a higher risk to man than nodules induced in the mouse, perception of risk is greatly dependent on whether nodules are considered simply reactive hyperplasias or exaggeration of a spontaneous change, whether nodules represent end-stage benign neoplasms or a stage in the evolution of hepatocellular carcinoma (Greaves and Path, 1990). However no increase in hepatocellular carcinomas was detected in rats even at an extremely high doses. Following a cautious approach, a LOAEL for carcinogenicity of 1,120 mg/kg/day is stated based on the increased incidence of liver neoplastic nodules from the lowest tested dose (1,120 mg/kg/day) and considered for the risk characterisation.

On thyroid, marginal increase in incidence of thyroid tumours in mice but not in rats, supported by an increased incidence of follicular cell hyperplasia is observed. It is recognized that there are marked species differences in thyroid gland biochemistry and physiology and that the rodent

thyroid gland is markedly more active and operates at a considerably higher level with respect to thyroid hormone turnover as compared to primate (McClain, 1995).

In rodents, thyroid hyperplasia may be caused by a hepatic inducer effect which involves an increase in UDPG transferase activity; however, this mechanism of action could not be considered relevant since, contrasting with less brominated compounds, DBDPO does not induce UDPG transferase in the test provided. It was shown for OBDPO and PeBDPO that these compounds are enzyme inducers whereas an absence of inducer effect was observed with DBDPO at a relatively low concentrations. But it was assumed that this absence of response does not preclude a lack of inducer effect at higher concentrations. Therefore to the best of our knowledge, this mechanism of action can not be dismissed.

Finally, it should be reminded that DBDPO presents a non-genotoxic profile as well as other polybrominated congeners such as OBDPO and PeBDPO and is devoid of alert-structure for genotoxicity according to Tenant and Ashby (1991).

With regard to reproduction:

There is no effect on fertility and development in a one generation study although parental toxic doses were not tested. The NOAEL is >= 100 mg/kg/day for parents and conceptus. Concerning fertility no changes were seen in the reproductive organs in rats and mice treated for 2 years with up to 50,000 ppm of DBDPO.

In terms of developmental effects, in an old teratology study (Norris et al., 1975), commercial DBDPO of low purity (purity 77.4%) leads to some effects on foetus: embryo/foetal death from 10 mg/kg/day without a dose-response relationship and subcutaneous oedema and delayed ossification of bones of the skull at a high dose (1,000 mg/kg/day) which does not seem to cause any maternal toxicity. Only a summary of the study is available and consequently the reliability of the estimated NOAEL for dams and LOAEL for foetuses is dubious. Furthermore, the purity of the test substance is lower than the purity of the products currently supplied in the EU. In a recent well conducted, prenatal developmental toxicity study (BFRIP, 2000), carried out with a composite of commercial DBDPO of greater purity (97.4%), no adverse treatment related effect was observed on external or internal malformations or variations neither on foetal weight, sex ratio, total resorption and late resorption. A slight increase of the mean number of early resorptions per animal and of the post-implantation loss and, a slight decrease of the percentage of the viable foetuses per implant were observed, however these effects were either not statistically significant or dose-related and therefore were not taken into consideration for the determination of a NOAEL. Thus based on this recent prenatal developmental toxicity, no concern for adverse effects on development may be assumed and **conclusion (ii)** is drawn for this end-point.

With regard to breast feeding:

Following pregnancy HxBDPO and others PBDPOs such as TeBDPO and PeBDPOs have been identified in breast milk but such measurements were not carried out on DBDPO neither on OBDPO. Based on the low rate of oral absorption in rats and the low bioaccumulation potential of DBDPO the rapporteur might anticipate a rather low excretion of this compound in the breast milk. Moreover since DBDPO presents a low systemic toxicity even at high dose level in mice or rats the rapporteur might assume a low concern for this end point. However it is obvious that quantitative measurements in breast milk would allow to reinforce this assumption.

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 (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. To our knowledge, no studies on transthyretin-T_4 competition have been carried out on DBDPO neither on OBDPO. However given that extremely large dose of DBDPO (>94% purity) were tested for either 13 weeks and over a lifetime, that no effects were found in either sex of two species after 13 weeks treatment and that only mild effects (follicular cell hyperplasia and marginally increased incidence of thyroid follicular cell adenomas or carcinomas) were found in one species after a life time exposure. Additional testing for this end-point was not judged necessary. **Conclusion (ii)** is drawn for this end-point.

With regard to neurotoxicity:

Recently, it has been reported that DBDPO causes behavioural disturbances in neonatal mice exposed to DBDPO in a single dose of 2.22 to 20.1mg/kg/bw on post-natal day 3. This effect was not seen in mice exposed on post-natal day 10 or 19. The toxicological significance of these findings is unclear. The authors indicate that PCBs have been shown to induce this type of behavioural profile when administered on post-natal day 3, but this response is always accompanied by a response in animals exposed to the toxic compound on post-natal day 10. However, a clear interpretation of the significance for human health of the behavioural differences seen in mice has not been established and thus uncertainty as to their significance remains. Moreover only an abstract of this study is available. Some information are lacking such as the housing condition, randomisation, description of the severity of the effects pending on the dose, statistical treatment of the results. Moreover, as no standard deviation data are presented, it is difficult to judge the degree of variability that might be expected within this study and no details regarding the historical negative control are reported. Therefore, no conclusion can be drawn from this end-point.

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 practices.

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

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

Limited measured exposure data are available. Consequently, a full-shift exposure of 5 mg/m^3 predicted with the EASE model will be used to describe a reasonable worst-case scenario during manufacture, compounding or master batching, textile coating and adhesive formulation.

No information is available on the extent of absorption of DBDPO following inhalation. Assuming a 100% absorption and that a 70 kg worker breathes 10 m^3/working day, the estimated body burden 0.7 mg/kg/day is achieved.

Maximum skin exposure of 1 mg/cm^2/day is predicted by the EASE modelling. Assuming that the skin exposed on the hands represents 840 cm^2, a worker's weight of 70 kg and a maximum skin absorption of 1% (based on physicochemical properties and analogy with PCBs), the calculated body burden amounts 0.12 mg/kg/day.

4.1.3.2.1 Repeated dose toxicity

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

Inhalation route

No inhalation toxicological data or absorption data are available neither in human nor in animals. Therefore the oral NOAEL determined for systemic toxicity will be used. A NOAEL of 1,120 mg/kg/day was identified in an oral chronic toxicity study in rats which leads to "internal" NOAEL of 67.2 mg/kg/day since the oral absorption of DBDPO was estimated to approximately 6%-9.5%. This is based on an oral absorption rate of 6% which leads to the lowest internal NOAEL. Compared to a daily intake of 0.7 mg/kg/day, the safety factor 96 is considered sufficient.

Dermal route

No dermal toxicological data are available neither in human nor in animals. Therefore the oral NOAEL determined will be used. A NOAEL of 1,120 mg/kg/day was identified in an oral chronic toxicity study in rats which leads to "internal" oral NOAEL of 67.2 mg/kg/day since the oral absorption was estimated to approximately 6%-9.5%. This is based on an oral absorption rate of 6% which leads to the lowest internal NOAEL. Assuming no correction factors to extrapolate from animal to man, the "internal" NOAEL by oral route can be estimated to be 67.2 mg/kg/day. The ratio internal NOAEL/body burden is of 560. This value is not of concern. Furthermore the estimated exposure does not take into account the normal safety practice which should strongly reduce the exposure.

The internal exposure of the worker as a result from uptake via both dermal and inhalation routes will not give rise to concern as well (MOS ≥82).

Consequently, the likelihood that an adverse effect occurs by skin or inhalation exposure is very low, there is at present no need for further actions: **conclusion (ii)** for all scenarios.

4.1.3.2.2 Carcinogenicity

There is some evidence of carcinogenicity in rats and equivocal evidence of carcinogenicity in mice. But the observed effects do not deserve a classification for carcinogenicity. Following a cautious approach, a risk characterisation for this end point is carried out. The LOAEL obtained for carcinogenicity is 1,120 mg/kg/day. Each route of exposure will be considered separately for the initial assessment.

Inhalation route

No inhalation toxicological data or absorption data are available neither in human nor in animals. Therefore the oral LOAEL determined will be used. A LOAEL of 1.120 mg/kg/day was identified in an oral chronic toxicity study in rats which leads to "internal" LOAEL of 67.2 mg/kg/day since the oral absorption of DBDPO was estimated to approximately 6%-9.5%. This is based on an oral absorption rate of 6% which leads to the lowest internal NOAEL. Compared to a body burden of 0.7 mg/kg/day, the safety factor is of 96. This MOS is considered sufficient since the inhalation absorption estimation of 100% is probably overestimated compared to the oral measured absorption data retained (namely 6%). Moreover the observed effects do not deserve a classification for carcinogenicity and the estimated exposure does not take into account the normal safety practice which should strongly reduce the exposure. Hence **conclusion (ii)** is drawn.

Dermal route

No dermal toxicological data are available neither in human nor in animals. Therefore the oral LOAEL determined will be used. A LOAEL of 1,120 mg/kg/day was identified in an oral chronic toxicity study in rats which leads to "internal" oral LOAEL of 67.2 mg/kg/day since the oral absorption was estimated to approximately 6%-9.5%. This is based on an oral absorption rate of 6% which leads to the lowest internal NOAEL. Assuming no correction factors to extrapolate from animal to man, the “internal” LOAEL by oral route can be estimated to be 67.2 mg/kg/day. The ratio internal LOAEL/body burden is of 560. This value is not of concern. Furthermore the estimated exposure does not take into account the normal safety practice which should strongly reduce the exposure.

The internal exposure of the worker as a result from uptake via both dermal and inhalation routes will not give rise to concern as well (MOS ≥82).

Consequently, the likelihood that an adverse effect occurs by skin or inhalation exposure is very low, there is at present no need for further actions: conclusion (ii) for all scenarios.

4.1.3.3 Consumers

Due to the lack of detailed information about consumer exposure to DBDPO, 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 (WHO, 1994), it is felt that consumer exposure to DBDPO is likely to be negligible, with no resulting risk for consumers.

Conclusion (ii).

4.1.3.4 Humans exposed via the environment

The estimated maximum human intake from environmental sources is estimated to be in the range 8. -12 µg/kg bw/day from local and regional sources.

4.1.3.4.1 Repeated dose toxicity/carcinogenicity

A NOAEL of 1,120 mg/kg bw/day was identified in an oral chronic toxicity study in rats. As the exposure via the environment is mainly through root crops, this value will be used directly.

With a maximum intake of 12 µg/kg bw/day, a MOS of 93,333 can be derived. This value does not lead to concern.

Conclusion (ii).

4.1.3.5 Combined exposure

Combined environmental exposure and occupational exposure will not influence the characterisation of the risks which are outlined 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 and coating formulation).

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

DBDPO 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

DBDPO gives no reason for concern in relation with its physico-chemical properties. There is no need for further information and/or testing.

5 RESULTS

5.1 INTRODUCTION

Decabromodiphenyl ether was produced at one site within the EU but production at this site ceased in 1999. The decabromodiphenyl ether currently used in the EU is imported. Information on the current amounts used within the EU would be useful for the risk assessment.

Decabromodiphenyl ether is used in the plastics and textile industries as a flame retardant. In the plastics industry, it is used as an additive flame retardant in a wide range of plastic types. In the textile industry, decabromodiphenyl ether is generally backcoated onto the textile in a latex binder. The commercially supplied decabromodiphenyl ether is a mixture of brominated diphenyl ethers, consisting mainly of decabromodiphenyl ether, with small amounts (0-3%) of other brominated diphenyl ethers such as nonabromodiphenyl ether. The product is a solid of very low water solubility and vapour pressure.

5.2 ENVIRONMENT

Local releases to the environment may occur from polymer processing and use in textile finishing. In addition, volatilisation and leaching of the flame retardant from articles, and also release of particulates containing decabromodiphenyl ether, may occur during the lifetime of the article (and at disposal for particulates). These releases have been quantified in the risk assessment and used to calculate PECs for various environmental compartments.

For the aquatic compartment, the risk from exposure via surface water is thought to be low. Exposure of organisms via sediment is thought to be much more relevant for this substance and, although the available measured levels in sediment are lower than the predicted levels, the risk to sediment dwelling organisms was also found to be low. No risk was identified for sewage treatment processes or the terrestrial compartment. No adverse effects are expected on the atmosphere from the production and use of decabromodiphenyl ether.

The available information indicates that the risk of secondary poisoning, as determined by the conventional PEC/PNEC ratio, resulting from use of decabromodiphenyl ether is low. There are, however, considerable uncertainties in the secondary poisoning assessment, and a strict PEC/PNEC approach may not be appropriate for this substance. In addition, the possibility of degradation 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 can not 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. 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

5.3.1 Human health (toxicity)

5.3.1.1 Workers

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 being applied already.

5.3.1.2 Consumers

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 being applied already.

5.3.1.3 Humans exposed via the environment

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 being applied already.

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.

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ABBREVIATIONS

The following abbreviations are used in the Human Health assessment.

ADI	Acceptable Daily Intake
AF	Assessment Factor
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
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 50 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	Hexabromodiphenyloxide
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
MNLC	Mononuclear-cell leukemia
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
PEC	Predicted Environmental Concentration
pH	logarithm (to the base 10) (of the hydrogen ion concentration $\{H^+\}$
pKa	logarithm (to the base 10) of the acid dissociation constant
pKb	logarithm (to the base 10) of the base dissociation constant
PNEC	Predicted No Effect Concentration
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
TWA	Time Weighted Average
UC	Use Category
UDS	Unscheduled DNA Synthesis
UN	United Nations
UNEP	United Nations Environment Programme
US EPA	Environmental Protection Agency, USA
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products of Biological material
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^{o}C for 60 seconds, of which 3-5 seconds were within 20^{o}C of the desired final temperature. The flame retardant was added as a solution in toluene (200 µl of a 1 mg flame retardant/ml toluene solution) and the vials were sealed after evaporation of the toluene. After pyrolysis, the residues were analyzed by GC/MS and the amounts of the various compounds present were determined semiquantitatively by a GC-MS (TIC) technique using reference to 2,3,7,8-tetrabromodibenzofuran standard. For the pentabromodiphenyl ether, at 510^{o}C around 10% of the compound was found to decompose and the amount of PBDFs/PBDDs formed were around 0.5-1% total yield. At 630^{o}C, the pentabromodiphenyl ether was found to be 97-98% decomposed and the total yield of PBDFs/PBDDs formed was around 10%. Mono- through to pentabrominated PBDFs/PBDDs were detected at both temperatures, with the major components being tetra- and penta-BDF and two isomeric tri-BDDs. The octabromodiphenyl ether was found to be around 96% decomposed on pyrolysis at 630^{o}C and the yield of PBDFs/PBDDs being around 5%. Tri- to hepta- PBDFs/PBDDs were detected, the major components being two penta-BDDs and a hexa-BDFs. The decabromodiphenyl ether was about 90% decomposed on pyrolysis with tetra- to octa- PBDFs/PBDDs being formed in 1-2% yield, with the main component being a hepta-BDF. In all cases where tetra-BDFs were formed, the 2,3,7,8- isomer was found to be only a minor component of the total tetrabrominated isomers. The technical products were also analysed for the presence of brominated dibenzofurans and dibenzo-*p*-dioxins but none could be detected.

Thoma et al. (1987a) studied the pyrolysis of several commercial brominated diphenyl ether flame retardant formulations. In the experiments 1 g of the flame retardant was heated in a quartz tube for 10 minutes at either 700^{o}C, 800^{o}C or 900^{o}C. The residue was then analyzed for polybrominated dibenzo-*p*-dioxins and dibenzofurans by a GC/MS technique (SIM mode), using 1,2,3,4-tetrabromodibenzo-*p*-dioxin as a standard for quantifying both the PBDD and PBDF concentrations. The results of the experiment are shown in **Table A1**. The results at 800^{o}C are also reported in Zacharewski et al. (1988 and 1989), although the values obtained for Bromkal 70-DE and Bromkal 70-5-DE have been swapped over.

As can be seen from **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^{o}C. The amounts of brominated dioxins and furans formed from the pyrolysis of decabromodiphenyl ether is much lower than that observed with the pentabromo compounds.

Table A1 Formation of brominated dibenzo-*p*-dioxins and dibenzofurans from the pyrolysis of polybrominated diphenyl ethers (Thoma et al., 1987a)

PBDD/ PBDF	Bromkal 70 DE residues (mg/kg)			Bromkal 70-5-DE residues (mg/kg)			Bromkal G1 residues (mg/kg)			Fr 300 BA residues (mg/kg)		
	700°C	800°C	900°C	700°C	800°C	900°C	700°C	800°C	900°C	700°C	800°C	900°C
MBDF	2834	2122	3175	402	767	1631	2200	2100	1800	nd	nd	nd
MBDD	10136	6248	3108	1302	1638	1620	8400	4400	3400	nd	nd	nd
DBDF	50824	89090	45394	9189	14092	26984	44900	39500	31800	nd	nd	nd
DBDD	145219	75279	26005	30491	26208	16379	138600	64800	36300	nd	nd	nd
T_3BDF	243621	177124	131149	54744	71009	87808	199400	150000	120500	nd	nd	nd
T_3BDD	95825	54880	19967	28202	23557	14258	92300	42300	25700	nd	nd	nd
T_4BDF	211709	181624	98575	95131	109402	105013	330400	213600	176900	26	93	nd
T_4BDD	12949	10436	5670	7601	7455	4826	15400	9200	7400	nd	nd	nd
PeBDF	8167	13590	5760	11958	14319	12584	37900	21800	22000	24	nd	259
PeBDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
HxBDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	46	166	178
HxBDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
H_7BDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	482	1304	4357
H_7BDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	33	142	153
OBDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	1885	5600	10792
OBDD	nd	nd	nd	nd	nd	nd	nd	nd	nd	805	3630	2621

Notes: 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 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°C and an air flow rate of 100 cm^3/min, a large proportion of the decabromodiphenyl ether sample had decomposed into a variety of products including the hepta- and octabrominated dibenzofurans and dibenzo-*p*-dioxins but at the same temperature using an air flow-rate of 400 cm^3/min, only a small amount of decomposition of the decabromodiphenyl ether was seen. At higher temperatures (800-1,000°C), using low air flow-rates, only trace amounts of decomposition products could be detected, indicating a possible complete degradation of the decabromodiphenyl ether to hydrogen bromide, carbon dioxide and carbon monoxide.

Striebich et al. (1990) studied the pyrolysis of a 1:1 mixture of two commercial polybrominated diphenyl ether products (contained tri- to decabromodiphenyl ethers). The mixture, dissolved in toluene, was injected onto quartz wool in a flow reactor system. The solvent was evaporated and the mixture was vaporised by temperature programming (75-300°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°C in either air or nitrogen. The products were analysed by GC-MS in either SIM or TIC mode. At 800°C in either air or nitrogen atmospheres, the polybrominated diphenyl ethers were essentially completely decomposed to HBr or other non-detectable products (no brominated dibenzofurans or dibenzo-*p*-dioxins were detected). At lower temperatures, detectable amounts of brominated dibenzofurans and dibenzo-*p*-dioxins were found (see **Table A4**) along with other products such as brominated benzenes, brominated alkanes and brominated alkenes.

Table A4 Results of Striebich et al. (1990) for the pyrolysis of a mixture of polybrominated diphenyl ethers

PBDD/PBDF	Maximum yield	
	Nitrogen atmosphere 650°C	Air atmosphere 625°C
DBBF	0.03%	ND
DBDD	ND	0.04%
T_3BDF	0.03%	0.03%
T_3BDD	ND	0.04%
T_4BDF	0.03%	0.03%
T_4BDD	ND	0.01%

Note: nd = Not detected

Luijk et al. (1991) investigated the pyrolysis of commercial penta-, octa- and decabromodiphenyl ethers using a similar micropyrolysis method to that used by Buser. Sealed vials of the flame retardant were placed in a heating furnace set a 100°C above the desired temperature. When the desired temperature was reached (after 60-70 seconds) the vials were heated for a further 10 seconds. The samples were then extracted and analysed for the presence of brominated dibenzofurans and brominated dibenzo-*p*-dioxins by GC-MS in SIM mode. The results are shown in **Table A5**.

Table A5 Results from micropyrolysis experiments of Luijk et al. (1991)

PBDD/PBDF	Amount of PBDD/DF produced with various brominated diphenyl ether/temperatures			
	Penta at 500°C	Penta at 600°C	Octa at 600°C	Deca at 600°C
T_4BDD	5,300 mg/kg	41,000 mg/kg	4,100 mg/kg	110 mg/kg
T_4BDF	6,200 mg/kg	65,000 mg/kg	700 mg/kg	80 mg/kg
PBDD	220 mg/kg	13,000 mg/kg	2,000 mg/kg	360 mg/kg
PBDF	80 mg/kg	150,000 mg/kg	4,600 mg/kg	160 mg/kg
H_6BDD	-	1,000 mg/kg	23,000 mg/kg	380 mg/kg
H_6BDF	-	3.800 mg/kg	22,000 mg/kg	570 mg/kg

Pyrolysis of flame retarded polymers

Pyrolysis experiments were carried out using mixtures of the flame retardants with polyethylene or polystyrene (Thoma et al., 1987a). In these tests, 0.95 g of plastic and 0.05 g of flame retardant were mixed and then melted for 3 minutes at 200°C to produce an homogeneous phase. The resulting plastic was then pyrolysed for 10 minutes at either 700, 800 or 900°C. The residue was then analyzed for polybrominated dibenzo-*p*-dioxins and dibenzofurans by a GC/MS technique (SIM mode), using 1,2,3,4-tetrabromodibenzo-*p*-dioxin as a standard for quantifying both the PBDD and PBDF concentration. In the plastic/pentabromodiphenyl ether mixtures, only brominated dibenzofurans were formed (possibly due to a low oxygen concentration in the system). The concentrations found were of the same order as those found in the pyrolysis experiments with flame retardant alone (although it is not clear whether the concentrations are measured on a mass/mass of flame retardant added, mass/mass of total plastic added or mass/mass of residue formed). In the case of the decabromodiphenyl ether/plastic mixtures, both polystyrene and polyethylene appeared to enhance the brominated dibenzofuran formation, resulting in the formation of considerable amounts of mono- to tribrominated compounds as well as the higher brominated compounds previously seen in the pyrolysis of pure decabromodiphenyl ether.

Thoma et al. (1987b) carried out identical experiments to those above using Bromkal 70-5-DE flame retardant (pentaBDPE) and PVC as the plastic at a pyrolysis temperature of 800°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
T_3BDF	58	145	14	0.41	0.85	20.2	397	102	nd
T_3BDD				0.034	0.11	5.0	5	48	nd
T_4BDF	151	52	51	0.88	0.71	4.9	305	1547	nd
T_4BDD				0.023	0.013	0.81	10	43	nd
PeBDF	114	396	nd	0.013	nd	nd	87	98	nd
PeBDD							2	6	nd
HxBDF	175	652	nd				nd	5	nd
HxBDD									
H_7BDF	3	8	nd						
H_7BDD									
OBDF									
OBDD									

Note: nd = not detected

Dumler et al. (1989b and 1989c) studied the decomposition of three commercial polybutylene terephthalate polymer samples containing varying amounts of decabromodiphenyl ether (9-11% by weight) and antimony (III) oxide (2.7-7% by weight) at temperatures between 300 and 800°C in a VCI oven for 10 minutes. A sample of commercial decabromodiphenyl ether alone was also pyrolysed under the same conditions (see Section 2.1). Brominated dibenzofurans and dibenzo-*p*-dioxins were analysed by GC-MS in SIM mode using one pure isomer for each congener group for the brominated dioxins/furans as reference. Polybrominated dibenzofurans were found to be formed during the pyrolysis of the polymer samples under certain conditions at yields of up to 16%, based on the concentration of flame retardant initially present. The maximum conversion to PBDFs occurred at temperatures between 400 and 500°C and it was thought that the antimony (III) oxide might play a catalytic role in the formation of PBDFs. The results of the experiments are shown in **Tables A7-9**.

Table A7 Results of 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_3BDF	-	15,033	15,952	1,738	36	15
T_4BDF	-	17,836	17,463	901	9	12
PBDF	-	9,127	3,349	391	-	-
H_6BDF	464	2,457	901	82	-	-
H_7BDF	2,375	1,329	246	36	-	-
OBDF	trace	trace	-	-	-	-

Lenoir et al. (1994) studied the effects of water and various metals on the pyrolysis of polybutylene terephthalate containing 10% decabromodiphenyl ether and 6% antimony trioxide in a BIS apparatus under a nitrogen atmosphere. The presence of water in the atmosphere was shown to increase the concentrations of polybrominated dibenzofurans and dibenzo-*p*-dioxins formed at 600°C. Experiments using D_2O and $H_2{}^{18}O$ indicated that neither the hydrogen or oxygen from the water molecule is incorporated into the dibenzofuran or dibenzo-*p*-dioxin products formed. It was thought that the presence of water would shift the equilibrium (Sb_2O_3 + 6HBr $\Leftrightarrow$ $2SbBr_3$ + $3H_2O$) to favour Sb_2O_3, which has been shown in other experiments to enhance the yields of brominated dibenzofurans and dibenzo-*p*-dioxins. The effect of various metals (e.g. Cu, Fe, Zn, Pb, Sn) on the pyrolysis products from the system was also investigated by adding the powdered metal to the polymer at a concentration of 2.5% by weight. The yields of polybrominated dibenzofurans were found to be reduced in the presence of metals when pyrolysis of the plastic containing decabromodiphenyl ether was carried out at 500°C, but the yields of polybrominated dibenzo-*p*-dioxins were found to be increased (e.g. Sn showed a factor of 8 increase and Cu showed a factor of 67 increase). This effect was explained by the redox potential of the metals, which are related to the ability of the metals to act as electron donors. Metal oxides were also shown to affect the yields of brominated dibenzofurans and dibenzo-*p*-dioxins, with oxides of Zn and Cu reducing the yields strongly (both show reactivity to debromination resulting in formation of lower brominated products such as mono- and dibrominated dibenzofurans and dibenzo-*p*-dioxins), were as Fe_2O_3 increased the overall yields.

Pinkerton et al. (1989) studied the formation of brominated furans and dioxins during the pyrolysis of high impact polystyrene (HIPS) containing decabromodiphenyl ether and antimony (III) oxide using a mass burning apparatus at temperatures of 500-800°C. The soot and char residues were analysed for brominated dibenzofurans and dibenzo-*p*-dioxins by a GC-MS technique (no details were given of the reference compounds used). No PBDF or PBDD were detected (detection limit 100 μg/kg) in soot and char from pyrolysis of HIPS containing no decabromodiphenyl ether and no brominated dibenzo-*p*-dioxins were detected in soot or char in the experiments using HIPS with decabromodiphenyl ether. However, brominated dibenzofurans were detected in soot and char from the experiments with HIPS containing decabromodiphenyl ether and the results are shown in **Table A10**. It was estimated that the maximum concentration of 2,3,7,8-tetrabromodibenzofuran formed was 1.8 mg/kg in the soot/char, but it was stated that this is very much a maximum level as the exact level could not be determined due to interference from co-eluting peaks during the GC-MS analysis.

Table A10 Levels of brominated furans formed during burning of HIPS containing decabromodiphenyl ether at 500-800°C (Pinkerton et al., 1989)

PBDF	Concentration in char (mg/kg)	Concentration in soot (mg/kg)
Mono-	0.64	556
Di-	0.54	641
Tri-	0.23	352
Tetra-	<0.1	73
Penta-	<0.1	3.5
Hexa- to octa-	<0.1	<0.1

Lahaniatis et al. (1991) studied the formation of 2,3,7,8-tetrabromodibenzo-*p*-dioxin and 2,3,7,8-tetrabromodibenzofuran during the pyrolysis of several polymer/polybrominated diphenyl ether formulations. The experiments were carried out at 400-800°C using a BIS apparatus. Around 100 mg of the sample was pyrolysed for 10 minutes with an air flow of 500 ml/minute and the products formed were analysed by GC-ECD using external standards and by GC-MS (SIM mode) using ^{13}C-labelled 2,3,7,8-tetrabromodibenzofuran or dibenzo-*p*-dioxin as internal standard. The samples tested were polybutylene terephthalate (PBTP) containing 10% decabromodiphenyl ether and 6% antimony trioxide, PBTP containing 10% decabromodiphenyl ether alone, 5 samples of epoxide resin containing 3-6% decabromodiphenyl ether alone, and 2 samples of phenolic resin containing 3-6% pentabromodiphenyl ether and copper. The results are shown in **Table A11**. In similar experiments reported by Lahaniatis et al. (1989), Bieniek et al. (1989) and Clausen et al. (1987), samples of polybutylene terephthalate containing 10% decabromodiphenyl ether and 6% antimony trioxide were pyrolysed at various temperatures and the total amounts of brominated dibenzo-*p*-dioxins and dibenzofurans were determined. These results are shown in **Table A12**. Considering the results as a whole, it is clear that the 2,3,7,8-isomers make up only a very small fraction of the total amount of brominated dibenzo-*p*-dioxins and dibenzofurans apparently formed in these experiments.

Table A11 Formation of 2,3,7,8-tetrabromodibenzofuran and dibenzo-*p*-dioxin from pyrolysis of various polymer/flame retardant formulations (Lahaniatis et al., 1991)

Polymer sample	2,3,7,8-TBDD (mg/kg polymer)			2,3,7,8-TBDF (mg/kg polymer)		
	400°C	600°C	800°C	400°C	600°C	800°C
PBTP/10% decabromodiphenyl ether/6%Sb_2O_3	0.02	0.01	nd	52	5.7	nd
PBTP/10% decabromodiphenyl ether	nd	nd	nd	2.5	4.2	0.08
Epoxide resin/3-6% decabromodiphenyl ether	min 0.05 max 0.3	min 0.3 max 0.8	min 0.01 max 0.03	min 0.4 max 1.0	min 0.6 max 2.5	min 0.01 max 0.04
Phenolic resin/3-6% pentabromodiphenyl ether/Cu	/	7	/	/	5.7	/

Notes: nd - Not detected detection limit 0.01 mg/kg.
/ - Not determined.

Table A12 Formation of brominated dibenzofurans during the pyrolysis of PBTP containing 10% decabromodiphenyl ether and 6% antimony trioxide (Lahaniatis et al., 1989; Clausen et al., 1987; Bieniek et al., 1989)

PBDF	Concentration determined (mg/kg polymer)				
	400°C	500°C	600°C	700°C	800°C
MBDF	100	300	100	50	nd
DBDF	500	400	200	10	nd
T_3BDF	3000	2000	400	nd	nd
T_4BDF	4000	3000	600	nd	nd
PBDF	4000	1000	200	nd	nd
H_6BDF	1000	200	nd	nd	nd
H_7BDF	500	nd	nd	nd	nd

Notes: nd - Not detected - detection limit 20 mg/kg.

Donnelly et al. (1989) studied the pyrolysis of a polybutylene terephthalate resin at 400°C for 10 minutes in a quartz tube with an air passing over the sample. The resin contained 7% decabromodiphenyl ether, along with antimony trioxide (concentration between 2 and 9%). The analytical method used was a GC-MS method with extensive sample clean up to remove possible interferences. Further, checks were carried out to ensure that any polybrominated diphenyl ethers present did not interfere with the brominated dibenzofuran peaks. Thus, these results can be considered as being more reliable than many of those mentioned above although, again, there is a lack of analytical standards for quantification of the amounts present (in this case a 2,3,7,8-tetra- and 1,2,3,7,8-pentabromodibenzofuran and octabromodibenzo-*p*-dioxin were used and response factors for other brominated dibenzofurans and dibenzo-*p*-dioxins were estimated from these). The results from the analysis is given in **Table A13**. As can be seen from the results the levels measured are much smaller than those reported in some other experiments. Polybrominated xanthenes were also thought to be formed (e.g. total tetra- = 4.1 mg/kg, total penta = 1.2 mg/kg, total hexa- = 0.21 mg/kg and total heptabrominated xanthene = 0.07 mg/kg; all estimated concentrations).

Table A13 Pyrolysis of polybutylene terephthalate at 400°C containing decabromodiphenyl ether (Donnelly et al., 1989)

PBDF/PBDD	Concentration in pyrolysate (mg/kg polymer)
Tetrabromodibenzofuran	1.4
Pentabromodibenzofuran	1.1
Hexabromodibenzofuran	0.25
Heptabromodibenzofuran	0.043
Octabromodibenzofuran	0.0028
Tetrabromodibenzo-*p*-dioxin	0.35
Pentabromodibenzo-*p*-dioxin	0.86
Hexabromodibenzo-*p*-dioxin	1.2
Heptabromodibenzo-*p*-dioxin	0.13

The pyrolysis of samples (1 g) of HIPS containing decabromodiphenyl ether (10.3-12.7%) and antimony trioxide (4.7-5.5%) has been studied at various temperatures using a quartz tube

reactor (Luijk et al., 1991). Two experimental systems were used. In the first, the whole reactor (quartz tube) was heated in a furnace and in the second, only the sample in the reactor was heated. Nitrogen was passed through the system and the volatile pyrolysis products were collected in cold traps and a water scrubber. Analysis of the degradation products was carried out by GC-MS with octabromodibenzofuran used as internal standard (the relative response factor for other congeners were estimated from data for available standards). The analytical method used a series of criteria proposed by Donnelly et al. (1987) for confirmation of the detection and quantification of polybrominated dibenzo-*p*-dioxins and dibenzofurans in the presence of polybrominated diphenyl ethers. In the tests, little or no brominated dibenzo-*p*-dioxins were formed but detectable amounts of brominated dibenzofurans were found. In the experiments where the whole reactor system was heated (test system I), no significant difference in the yield of brominated dibenzofurans was seen over the temperature range 500-700^{o}C. This was because once the temperature inside the reactor reached the depolymerisation temperature of HIPS (>310^{o}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^{o}C. In the experiments it was found that highly brominated dibenzofurans were also formed when the HIPS was heated at 275^{o}C for 20 minutes (see **Table A14**). Pyrolysis-mass spectrometry studies indicated that the following reactions were occurring during the thermal decomposition of the flame retarded HIPS: emission of decabromodiphenyl ether; debromination of the decabromodiphenyl ether by exchange of H and Br (to form lower brominated diphenyl ethers); formation of antimony oxybromides and antimony bromides; formation of brominated dibenzofurans; and the addition of polybromophenoxy groups to the polymer chain.

Table A14 Pyrolysis of HIPS/decabromodiphenyl ether/Sb_2O_3 (Luijk et al., 1991)

Atmosphere	Temp.	Concentration of PBDF (mg/kg polymer)						
	(°C)	DBDF	T_3BDF	T_4BDF	PBDF	H_6BDF	H_7BDF	OBDF
Test system I								
nitrogen	500	40	190	370	260	130	na	na
nitrogen	625	40	240	510	340	170	na	na
nitrogen	695	90	200	260	170	40	na	na
nitrogen	780	50	240	620	400	130	na	na
nitrogen	860	60	130	200	90	3	na	na
air	500	10	20	70	60	20	na	na
air	700	30	130	310	190	50	na	na
Test system II								
nitrogen	275	0	0	0.3	10	260	710	3,300
nitrogen	360	60	130	130	560	250	60	50
nitrogen	450	50	30	50	90	130	40	10
nitrogen	560	50	20	20	20	20	4	3
nitrogen	640	2	0.7	0.3	0.2	0.3	0.03	0
nitrogen	720	0.1	0.04	0.03	0.02	0.02	0	0
nitrogen	825	0.03	0.03	0.03	0.02	0.01	0	0

Notes: na = Not analysed.

Other experiments

Bruckmann et al. (1990) studied the presence of brominated dibenzofurans and dibenzo-*p*-dioxins several hours after a fire in a stock house. The stock house was known to contain around 2.5 tonnes of a mixture of decabromodiphenyl ether and antimony trioxide. After the fire, the bags of flame retardant were found to be mostly intact and only the surface of some bags had been melted by the heat of the fire. In total, 4 wipe samples and 6 samples of fire residues were taken from the site and analysed for the presence of brominated dibenzofurans and dibenzo-*p*-dioxins by GC-MS. Tetra- to octabromodibenzofurans were found in the samples.

Benbow and Cullis (1975) looked at the overall emissions from burning polymers containing decabromodiphenyl ether. The polymer samples tested had the following composition: a) 100 g polystyrene, 15 g decabromodiphenyl ether, 4.3 g antimony trioxide; b) 100 g polystyrene, 15 g decabromodiphenyl ether; c) 100 g polypropylene and 10 g decabromodiphenyl ether. The fate of decabromodiphenyl ether during the combustion was found to depend on whether the polymer undergoes flameless degradation or is ignited and burns with a flame. During flameless combustion (temperature around 400^{o}C) decabromodiphenyl ether appeared to volatilise virtually unchanged from the polymer. However, when the polymer burned with a flame, decabromodiphenyl ether was converted almost quantitatively (86.5-93.0% for sample a, 96.6-98.7% for sample b and 95.2% for sample c) to HBr.

Fluthwedel and Pohle (1993) compared the levels of polybrominated dibenzofurans and dibenzo-*p*-dioxins in combustion residues of electronic equipment from both laboratory studies and real fires. The analysis looked at both the total levels formed and the sum of the levels for the congeners prescribed under the German Gefahrstoffverordnung (GefStoffV; which gives a limit of 2 µg/kg for the sum of 8 2,3,7,8-substituted congeners). The results of the analysis are shown in **Table A15**. In the test fire results, 2,3,7,8-substituted congeners accounted for around 3.1-8.7% of the total congeners found in the fire residues and 2.6-5.2% of the total congeners found in the soot deposits. In real fires, the proportion of 2,3,7,8-substituted congeners was around 5.4% of the total for the fire residues and 8.7-19.9% of the total for the soot deposits. The results show that the levels found in real fires are around 2-3 orders of magnitude lower than those seen in laboratory studies, although a direct comparison is not possible as few experimental details are reported in the paper.

Table A15 Comparison of polybrominated dibenzofuran and dibenzo-*p*-dioxins formed during combustion in laboratory tests and real fires (Fluthwedel and Pohle, 1993)

		Fire residues		Soot deposits on walls	
		Total PBDD/F (µg/kg)	PBDD/F as in GefStoffV (µg/kg)	Total PBDD/F (µg/m^2)	PBDD/F as in GefStoffV (µg/m^2)
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_4BDF=0.00226 Total PeBDF=0.0226 Total HxBDF=0.107 Total HpBDF=0.078 Total OBDF=0.00052
	Extreme extrusion conditions: 266-271°C, 7 minute cycle	Total T_4BDF=0.000012 Total PeBDF=0.0086 Total HxBDF=0.2 Total HpBDF=2.1 Total OBDF=3.2
PBTP with 6.5% weight decabromodiphenyl ether and antimony trioxide	Normal moulding conditions: 254°C	Total T_4BDF=0.001-0.0053 Total PeBDF=0.018-0.035 Total HxBDF=0.067-0.170 Total HpBDF=0.18-0.41 Total OBDF=0.52-1.5
	Normal extrusion conditions: 254°C, 23 second cycle	Total T_4BDF=0.0052-0.0097 Total PeBDF=0.061-0.130 Total HxBDF=0.62-1.6 Total HpBDF=2.3-3.8 Total OBDF=2.4-4.1
	Abusive extrusion conditions: 254°C, 5 minute cycle	Total T_4BDF=0.076-0.24 Total PeBDF=13-43 Total HxBDF=69-180 Total HpBDF=48-94 Total OBDF=1.2-11
	Extreme extrusion conditions: 254°C, 10 minute cycle	Total T_4BDF=1.02-2.59 Total PeBDF=68.2-82.8 Total HxBDF=272-708 Total HpBDF=72.5-108
PTBT with 5.2% decabromodiphenyl ether and antimony trioxide	Normal moulding conditions: 250°C	Total T_4BDF=0.0038-0.018 Total PeBDF=0.054-0.1 Total HxBDF=0.24-0.27 Total HpBDF=0.28-0.44 Total OBDF=0.71-2.3
PTBT with 7.0% decabromodiphenyl ether and antimony trioxide	Normal conditions: 250°C	Total T_4BDF=0.014-0.026 Total PeBDF=0.065-0.109 Total HxBDF=0.23-0.25 Total HpBDF=0.5-0.98 Total OBDF=0.41-1.6
PTBT with 8% decabromodiphenyl ether and antimony trioxide	Normal conditions: 250°C	Total T_4BDF=0.00088-0.0041 Total PeBDF=0.027-0.060 Total HxBDF=0.081-0.31 Total HpBDF=0.23-0.56 Total OBDF=0.5-1.3

Table A17 continued overleaf

Table A17 continued

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_4BDF=0.0028-0.0036 Total PeBDF=0.87-1.8 Total HxBDF=2.1-2.38 Total HpBDF=0.5-0.78 Total OBDF=0.026-0.064
	Abusive extrusion conditions: 246°C, 10 minute cycle	Total T_4BDF=0.15-0.17 Total PeBDF=29-34 Total HxBDF=8.2-10 Total HpBDF=0.5-0.92 Total OBDF=19

Use in television sets

Bruckmann et al. (1990) studied the possible emissions of brominated dibenzofurans and dibenzo-*p*-dioxins from television sets under normal operating conditions. A new television set was placed in a closed room (volume 26.8 m^3) and was operated between 7 am and 12 pm for three days. The surface temperature of the television back was usually 38-40°C. Although not explicitly stated in the report, the television set back presumably contained decabromodiphenyl ether. Air samples were collected on polyurethane foam cartridges. After extraction, the residues were analysed by GC-MS, using ^{13}C-labelled 2,3,7,8-tetrabromodibenzofuran as internal standard. Identification of the brominated dibenzofurans and dibenzo-*p*-dioxins was by their masses and isotope ratios and quantification was by means of external standards. The levels of brominated dibenzofurans found in the air in the room are shown in **Table A18**. Due to lack of suitable standards, an isomer specific analysis could not be undertaken. Brominated dibenzo-*p*-dioxins and hepta- and octabromodibenzofurans were not detected in this experiment (detection limit 0.1-0.2 pg/m^3). This experiment has, however, been criticised due to the lack of background levels measured in the room before the experiment was undertaken (Ranken et al., 1990).

Table A18 Formation of brominated dibenzofurans from the operation of a flame retarded television (Bruckmann et al., 1990)

Brominated furans formed	0.15 m above TV	Centre of room (2.2 m from TV; height 1.5 m)	Ambient air
Tribromo	143 pg/m^3	25 pg/m^3	<0.05 pg/m^3
Tetrabromo	11 pg/m^3	2.7 pg/m^3	0.16 pg/m^3
Pentabromo	0.5 pg/m^3	0.5 pg/m^3	<0.05 pg/m^3
Hexabromo	<0.1 pg/m^3	<0.1 pg/m^3	<0.05 pg/m^3

Ranken et al. (1990) carried out a similar experiment to measure possible emissions of polybrominated dibenzofurans and dibenzo-*p*-dioxins from televisions. In this series of experiments, three television sets were used, two bought locally and one supplied by a manufacturer. Analysis of the rear panels of the two purchased sets showed that they were made of polystyrene and had a bromine content of 11.5% which suggested that they contained

decabromodiphenyl ether. The back of the third set was known to be high impact polystyrene/decabromodiphenyl ether/antimony trioxide. The tests were carried out in a 1.81 m^3 test chamber, through which air was drawn and any compounds emitted were trapped on a silica gel sampler. Any brominated dibenzofurans and dibenzo-*p*-dioxins extracted from the samplers were analysed for using GC-MS in SIM mode using ^{13}C-labelled brominated dibenzofuran standards (2,3,7,8-tetrabromo-, 2,3,4,7,8-pentabromo and 1,2,3,7,8,9-hexabromodibenzofuran). The first experiment involved drawing air through the empty test chamber for 8 hours/day for 3 days in order to obtain the background level (total volume of air 17.95 m^3). Then, the two purchased televisions were placed in the chamber and the air was again sampled for 3 days and this was then repeated with the televisions operating for 3 days. A final analogous series of experiments were run using the television set provided by the manufacturers (3 days when the set was not operating and 24 hours continuous operation). No brominated dibenzofurans or dibenzo-*p*-dioxins were detected in any of the experiments. The detection limits are shown in **Table A19**.

Table A19 Detection limits for the determination of polybrominated dibenzofurans and dibenzo-*p*-dioxins (Ranken et al., 1990)

Dioxin/furan	Detection limit (pg/m^3)
2,3,7,8-tetrabromodibenzo-*p*-dioxin	0.17-1.53
Total tetrabromodibenzo-*p*-dioxin	0.17-1.53
1,2,3,7,8-pentabromodibenzo-*p*-dioxin	0.35-0.39
Total pentabromodibenzo-*p*-dioxin	0.35-0.39
2,3,7,8-tetrabromodibenzofuran	0.09-0.33
Total tetrabromodibenzofuran	0.09-0.33
1,2,3,7,8-pentabromodibenzofuran	0.14-0.19
2,3,4,7,8-pentabromodibenzofuran	0.14-0.19
Total pentabromodibenzofuran	0.14-0.19

Fluthwedel and Pohle (1993) reported the results of a series of experiments looking at the emissions of polybrominated dibenzofurans from various electronic equipment including televisions, printers and monitors. After 3 days sampling, the sum of polybrominated dibenzofurans released was estimated at around 320-1,800 pg/device. Investigations of air levels in a room containing electronic equipment gave a total air concentration of 1.27 pg/m^3 of polybrominated dibenzofurans.

Disposal

It has been estimated that in England, Wales, Germany, France and Spain, approximately 63% of old personal computers are disposed of to landfills, 22% are incinerated and 15% are subject to recycling (WWF, 1998). In the United Kingdom, it is thought that currently the vast majority of electrical and electronic equipment is disposed of to landfill or is incinerated. Recycling 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^{o}C) in Sweden when high loads of bromine were present. Low levels of monobromochloro dibenzo-*p*-dioxins and furans were found in the cleaned flue gas.

Lahl et al. (1991) found an increase in both the chlorinated and bromochlorinated dibenzo-*p*-dioxins and furans formed in the electrostatic precipitator ash after 2 kg of printed circuit board containing a polybrominated diphenyl ether was added to a municipal incinerator (oven capacity 14 tonnes/hour). The maximum increase (around 2-3 times) was seen around half an hour after the addition of the plates. Of the mixed halogenated compounds formed only species containing 1 bromine atom per molecule were formed. No increase in the halogenated dibenzo-*p*-dioxin and furan emissions was seen in the stack gas.

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^{o}C (FRS, 1998).

As high temperatures are involved, there is the possibility for formation of halogenated dibenzo-*p*-dioxins and furans under these conditions. However, the residence time of the substance in a landfill fire is likely to be much longer than found in the laboratory pyrolysis studies that have been carried out and so it is not possible to say anything about the extent of formation under these conditions.

Recycling

Plastics

A recent study in Germany looked at the formation of polybrominated dibenzofurans and dibenzo-p-dioxins as a result of recycling of plastics containing polybrominated diphenyl ether flame retardants (Riess et al., 1998). In the study, polymer samples were obtained from a recycling company and were analysed for plastic type and flame retardants present. A total of 78 television housings and 34 personal computer housings were analysed and polybrominated diphenyl ethers were identified in 78% of the samples. A sample of impact modified polystyrene containing a polybrominated diphenyl ether (not identified but possibly octabromodiphenyl ether) was further analysed for the presence of polybrominated dibenzofurans and dibenzo-p-dioxins both before and after undergoing recycling. The analytical method used incorporated a suitable clean-up method to ensure that the polybrominated diphenyl ether present did not interfere with the analysis of the brominated dioxins and furans. The analysis was carried out for the isomers required under the German "Dioxinverordnung" and the results are shown in **Table A22**. The limits under the Dioxinverordnung are 1 µg/kg for the sum of isomers 1-4 and 5 µg/kg for the sum of isomers 1-7 (higher limits of 10 µg/kg for the sum of isomers 1-4 and 60

µg/kg for the sum of isomers 1-7 apply until 15 July 1999; van Riel, 1995). As can be seen from the results, although the limits of the Dioxinverordnung were exceeded, there was no increase in the levels of the brominated dibenzofurans and dibenzo-p-dioxins as a result of the recycling process. There was also some evidence that the distribution of congeners for the polybrominated diphenyl ethers themselves and the polybrominated dibenzofurans and dibenzo-p-dioxins changed slightly in the samples before and after recycling with a slight reduction in the concentration of the higher brominated congeners and a slight increase in the concentration of the lower brominated congeners (e.g. the concentration of the octabromodiphenyl ether component decreased and the concentration of the hexa- and heptabromodiphenyl ether components increased slightly during the recycling step). The paper concluded that recycling of the flame retarded material might be practicable if it is mixed with other material (not containing polybrominated diphenyl ethers) prior to recycling.

Table A22 Levels of brominated dibenzofurans and dibenzo-*p*-dioxins in impact modified polystyrene containing brominated diphenyl ether both before and after recycling (Riess et al., 1998)

No	Isomer	Level before recycling	Level after recycling
1	2,3,7,8-TBDD	<0.009 µg/kg	<0.016 µg/kg
2	1,2,3,7,8-PeBDD	<0.027 µg/kg	<0.032 µg/kg
3	2,3,7,8-TBDF	0.407 µg/kg	0.431 µg/kg
4	2,3,4,7,8-PeBDF	5.45 µg/kg	4.05 µg/kg
5	1,2,3,4,7,8-HxBDD + 1,2,3,6,7,8-HxBDD	<0.11 µg/kg	<0.023 µg/kg
6	1,2,3,7,8,9-HxBDD	<0.11 µg/kg	<0.023 µg/kg
7	1,2,3,7,8-PeBDF	<0.019 µg/kg	<0.021 µg/kg
Sum 1-4		5.90 µg/kg	4.53 µg/kg
Sum 1-7		6.14 µg/kg	4.59 µg/kg

Meyer et al. (1993) studied the levels of polybrominated dibenzofurans and dibenzo-*p*-dioxins (as per the German Dioxin Regulations) in ABS containing a polybrominated diphenyl ether (not identified in the study) in newly moulded parts (first processing) and of old parts that were reground and subsequently reprocessed. The results are shown in **Table A23**. Although the results of the analysis indicate that the polybrominated dibenzofurans and dibenzo-*p*-dioxins were present at levels in excess of those given in the German Dioxin Regulations, there was no increase in these levels on subsequent recycling/reprocessing of the plastic. Similar results were obtained 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

Note: 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 175-210°C and injection moulded at 199-227°C	Deca alone (composite sample from three suppliers)	HIPS containing 12% deca and Sb_2O_3, extruded at 175-210°C and injection moulded at 199-227°C	HIPS containing 12% deca and Sb_2O_3, extruded at 175-210°C and injection moulded at 199-227°C, recycled 5 times by grinding and injection moulding
Polybrominated diphenyl ethers				
3,4,4'-tri	nd (<5)	nd (<55)	nd (<5)	nd (<5)
Total tri[a]	nd	102	8	9
2,4,4',6-tetra	nd (<8)	nd (<90)	nd (8)	nd (<8)
2,3',4',6-tetra	nd (<8)	nd (<90)	nd (<8)	nd (<8)
2,2',4,4'-tetra	nd (<8)	245	39	39
2,3',4,4'-tetra	nd (<8)	nd (<90)	nd (<8)	nd (<8)
3,3',4,4'-tetra	nd (<8)	nd (<90)	nd (<8)	nd (<8)
Total tetra	nd	245	39	39
2,3',4,4',6-penta	nd (<9)	nd (<85)	nd (<9)	nd (<9)
2,2',4,4',5-penta	nd (<9)	2,227	338	341
2,2',3,4,4'-penta	nd (<9)	nd (<192)	33	30
Total penta	nd	2,227	371	371
2,2',4,4',5,5'-hexa	nd (<10)	9,279	1,150	1,195
Total hexa[a]	nd	11,705	1,507	1,554
2,3,3',4,4',5,6-hepta	nd (<180)	nd (<1,400)	nd (<180)	nd (<180)
Total hepta[a]	nd	33,541	4,623	4,449
Polybrominated dibenzo-*p*-dioxins and furans				
2,3,7,8-TeBDD	nd (<0.02)	-	nd (<0.02)	nd (<0.02)
1,2,3,7,8-PeBDD	nd (<0.04)	-	nd (<0.04)	nd (<0.04)
2,3,7,8-TeBDF	nd (<0.03)	-	nd (<0.04)	nd (<0.03)
2,3,4,7,8-PeBDF	nd (<0.04)	-	nd (<0.05)	0.07[c]
Sum of the 4 PBDD/F (limit value 1 µg/kg[b])	nd	-	nd	0.07[c]
1,2,3,4,7,8-HxBDD + 1,2,3,6,7,8-HxBDD	nd (<0.2)	-	nd (<0.2)	nd (<0.2)
1,2,3,7,8,9-HxBDD	nd (<0.2)	-	nd (<0.3)	nd (<0.3)
1,2,3,7,8-PeBDF	nd (<0.04)	-	nd (<0.04)	0.06
Sum of the 8 PBDD/F (limit value 5 µg/kg[b])	nd	-	nd	0.06

Notes: 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 USEPA. The limits of quantitation varied from 0.1 μg/kg for 2,3,7,8-tetrabromo-p-dioxin to 1.0 μg/kg for 2,3,7,8-tetrabromodibenzofuran to 1,000 μg/kg for 1,2,3,4,6,7,8- and 1,2,3,4,7,8,9-heptabromodibenzofuran.

Similar results were also reported by Donnelly et al. (1989). The analytical method used was again based on GC-MS with extensive sample clean up before analysis. Checks were also carried out to ensure that polybrominated diphenyl ethers were not co-eluting with the PBDF peaks. Samples of octa- and decabromodiphenyl ether from commercial suppliers were analysed. In the case of octabromodiphenyl ether no brominated dibenzofurans were detected, but, since the clean up steps involve did not completely remove the potential interferences, the possibility remained that brominated dibenzofurans could still be present at very low levels. The decabromodiphenyl ether sample was found to contain very low levels of hexa- (2.3 μg/kg), hepta- (250 μg/kg) and octabromodibenzofuran (34 μg/kg). These results are consistent with the not detected results found by Ranken et al. (1994).

Hileman et al. (1989) also analysed several brominated diphenyl ether flame retardants for the presence of brominated dibenzofurans. Again extensive sample clean up was carried out before analysis to enable the brominated dibenzofurans to be quantified. For a flame retardant product composed of tetra- to hexabrominated diphenyl ethers (a commercial pentabromodiphenyl ether) tetrabromodibenzofurans were found at a level of approximately 2 ppm (mg/kg). The major tetrabromodibenzofuran isomers did not co-elute with either 1,2,7,8- or 2,3,7,8-tetrabromodibenzofuran. Penta- and hexabromodibenzofurans were present at 4 and 2 ppm (mg/kg) respectively. For a product composed of hexa- to nonabromodiphenyl ether (a commercial octabromobipenyl ether), no tetrabromodibenzofurans were seen above the detection limit of 0.2 mg/kg but penta- (2-4 mg/kg), hexa- (2-4 mg/kg) and heptabromodibenzofuran isomers (detected but not quantified) were found. In a commercial decabromodiphenyl ether, tetra- and pentabromodibenzofurans were not found above the detection limit of 0.2 mg/kg, hexabromodibenzofuran isomers were just detectable at the 0.2 mg/kg detection limit and heptabromodibenzofurans were detected but not quantified. The levels of brominated dibenzofurans detected were thought to be related to the presence of trace amounts of dibenzofuran (1.7-5.3 mg/kg) in the diphenyl ether used to manufacture the flame retardants.

In terms of the environmental risk assessment, as the effects data used in the assessment 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

In the EUSES model the use patterns refer to the following scenarios in the risk assessment:

USE Pattern 1 [production]	release from production site (default estimates)
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
USE Pattern 2 [formulation]	release from use in textiles: compounding
USE Pattern 2 [processing]	release from use in textiles: application
USE Pattern 2 [private use]	release over service life of textiles
USE Pattern 2 [recovery]	"waste remaining in the environment" from polymers
USE Pattern 3 [processing]	release from use in textiles: combined compounding and application site

Appendix C SAMS soil model for decabromodiphenyl ether

The SAMS soil model was run to give an indication of the likely leaching behaviour of decabromodiphenyl ether in soil. The model was run over 730 days at one day intervals. The initial concentration of decabromodiphenyl 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    = 1163-19-5
# CAS registry number (CAS: Chemical Abstract Services)
Name   = DECABROMODIPHENYL ETHER
# Substance name
SumFor = C12Br10O
# Chemical sum formula
MolW   =      959.2 # [g/mol] Molecular mass
SolW   =     1e-007 # [g/l] Solubility in water
VP     =  4.63e-006 # [Pascal] Vapor pressure at 20 centigrades
MP     =        373 # [Kelvin] Melting point
Koc    =  1.59e+006 # [cm3 H2O/g] Partition coefficient organic carbon -
water
logKow =       6.27
# Logarithm of the n-octanol - water - partition coefficient
BCF    =          4 # Bioconcentration factor in Fish
RPhoto =          0 # [1/day] Overall photodegradation rate in air
RWater =          0 # [1/day] Overall degradation rate in water
RSoil  =          0 # [1/day] Overall degradation rate in soil

Parameters for SOIL:
SOIL_Input  =          0 # [kg/mýd]
# Substance input rate into the upper soil layer
# This is the default value.
SOIL_Hori   =          3 # number of soil horizons
# This is the default value.
SOIL_Rain   =        2.1 # [mm/d] Precipitation
# This is the default value.
SOIL_Evap   =        1.6 # [mm/d] Evapotranspiration
# This is the default value.
SOIL_Runoff =        0.2 # [mm/d] Surface water runoff
# This is the default value.
SOIL_Time   =        730 # [d] Current time
# This value has been estimated
SOIL_TEnd   =        730 # [d] End of simulation period
SOIL_TStep  =          1 # [d] Time step for output action during simulation
# This is the default value.
SOIL_DT     =       0.01 # [d] Internal time step for simulation
# This is the default value.
SOIL_StartTime =          0 # [d] Starting time for mass balance
# This is the default value.
```

Boxes	Depth	Por	Disp	Dens	OrgC
	m	m3/m3	m	kg/m3	kg/kg
20	0.2	0.5	0.05	1309	0.015
20	0.6	0.5	0.05	1271	0.05
20	1.4	0.5	0.05	1271	0.05

OrgM	VolW	Temp	WFlux	pH	KD	RDeg
kg/kg	m3/m3 soil	K	mm/d		cm3 H2O/g	1/d
0.02586	0.3	293	0.3	6.8	23850	0
0.0862	0.3	293	0.3	6.8	79500	0
0.0862	0.3	293	0.3	6.8	79500	0

```
SOIL_ConcTop =      0.883 # [kg/m3] Concentration in top layer
# This value has been estimated
SOIL_ConcBot = 1.891e-216 # [kg/m3] Concentration in bottom layer
# This value has been estimated
SOIL_SumSorb =        541 # [kg/mý] Total of substance sorbed to soil matrix
# This value has been estimated
SOIL_SumSolv =    0.02268 # [kg/mý] Total of substance solved in soil water
# This value has been estimated
SOIL_SumAir =  0.0004135 # [kg/mý] Total of substance in soil air
# This value has been estimated
SOIL_SumTot =   0.009243 # [kg/mý] Total of substance remaining in soil
# This value has been estimated
```

	Flow	Balance
	kg/mý/d	kg/mý
Input	0	0.01
Runoff	0	0
Volatilisation	9.65e-007	0.0007567
Degradation	0	0
Leaching	5.61e-225	6.892e-224
Remaining	-9.65e-007	0.009243

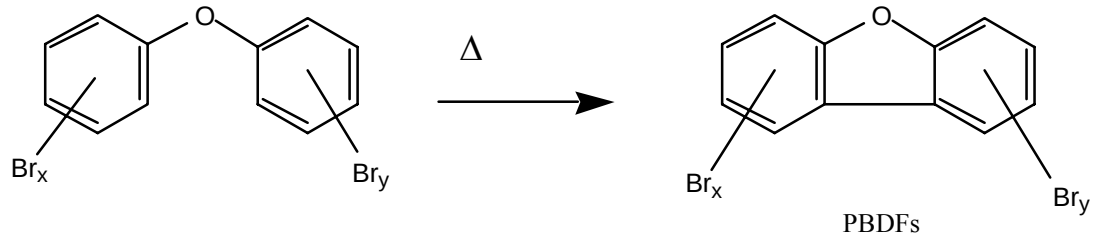
Depth	Conc	ConcA	ConcW	ConcS
m	kg/m3	kg/m3 air	kg/m3 H2O	kg/kg soil
0.01	0.883	5.157e-007	2.829e-005	0.0005154
0.02	0.04044	2.362e-008	1.295e-006	2.361e-005
0.03	0.0009151	5.344e-010	2.931e-008	5.342e-007
0.04	1.376e-005	8.038e-012	4.409e-010	8.034e-009
0.05	1.551e-007	9.057e-014	4.968e-012	9.053e-011
0.06	1.397e-009	8.159e-016	4.476e-014	8.156e-013
0.07	1.049e-011	6.124e-018	3.359e-016	6.121e-015
0.08	6.743e-014	3.938e-020	2.16e-018	3.936e-017
0.09	3.794e-016	2.216e-022	1.215e-020	2.215e-019
0.1	1.898e-018	1.108e-024	6.079e-023	1.108e-021
0.11	8.54e-021	4.988e-027	2.736e-025	4.985e-024
0.12	3.494e-023	2.041e-029	1.119e-027	2.04e-026
0.13	1.31e-025	7.652e-032	4.197e-030	7.649e-029
0.14	4.536e-028	2.649e-034	1.453e-032	2.648e-031
0.15	1.458e-030	8.514e-037	4.67e-035	8.51e-034
0.16	4.373e-033	2.554e-039	1.401e-037	2.553e-036
0.17	1.23e-035	7.183e-042	3.94e-040	7.18e-039
0.18	3.256e-038	1.901e-044	1.043e-042	1.9e-041
0.19	8.138e-041	4.753e-047	2.607e-045	4.751e-044
0.2	1.288e-043	7.521e-050	4.125e-048	7.517e-047
0.22	7.327e-047	1.322e-053	7.251e-052	4.535e-050
0.24	1.226e-050	2.212e-057	1.213e-055	7.589e-054
0.26	1.958e-054	3.533e-061	1.938e-059	1.212e-057
0.28	2.99e-058	5.395e-065	2.959e-063	1.851e-061
0.3	4.375e-062	7.893e-069	4.329e-067	2.708e-065
0.32	6.144e-066	1.108e-072	6.08e-071	3.802e-069
0.34	8.294e-070	1.496e-076	8.208e-075	5.133e-073
0.36	1.078e-073	1.945e-080	1.067e-078	6.672e-077
0.38	1.351e-077	2.437e-084	1.337e-082	8.362e-081

0.4	1.635e-081	2.949e-088	1.617e-086	1.012e-084
0.42	1.911e-085	3.448e-092	1.891e-090	1.183e-088
0.44	2.163e-089	3.902e-096	2.14e-094	1.338e-092
0.46	2.37e-093	4.276e-100	2.346e-098	1.467e-096
0.48	2.519e-097	4.544e-104	2.493e-102	1.559e-100
0.5	2.598e-101	4.687e-108	2.571e-106	1.608e-104
0.52	2.603e-105	4.696e-112	2.576e-110	1.611e-108
0.54	2.535e-109	4.573e-116	2.509e-114	1.569e-112
0.56	2.402e-113	4.333e-120	2.377e-118	1.487e-116
0.58	2.216e-117	3.998e-124	2.193e-122	1.371e-120
0.6	1.328e-121	2.396e-128	1.314e-126	8.219e-125
0.64	2.955e-126	5.332e-133	2.924e-131	1.829e-129
0.68	6.416e-131	1.157e-137	6.349e-136	3.971e-134
0.72	1.36e-135	2.453e-142	1.345e-140	8.414e-139
0.76	2.814e-140	5.077e-147	2.785e-145	1.742e-143
0.8	5.692e-145	1.027e-151	5.632e-150	3.523e-148
0.84	1.126e-149	2.031e-156	1.114e-154	6.966e-153
0.88	2.177e-154	3.928e-161	2.155e-159	1.348e-157
0.92	4.123e-159	7.438e-166	4.08e-164	2.552e-162
0.96	7.643e-164	1.379e-170	7.563e-169	4.73e-167
1	1.388e-168	2.504e-175	1.373e-173	8.589e-172
1.04	2.47e-173	4.456e-180	2.444e-178	1.529e-176
1.08	4.309e-178	7.773e-185	4.264e-183	2.667e-181
1.12	7.372e-183	1.33e-189	7.295e-188	4.563e-186
1.16	1.238e-187	2.233e-194	1.225e-192	7.659e-191
1.2	2.039e-192	3.678e-199	2.018e-197	1.262e-195
1.24	3.298e-197	5.95e-204	3.264e-202	2.041e-200
1.28	5.24e-202	9.453e-209	5.185e-207	3.243e-205
1.32	8.178e-207	1.475e-213	8.092e-212	5.061e-210
1.36	1.254e-211	2.263e-218	1.241e-216	7.763e-215
1.4	1.891e-216	3.412e-223	1.871e-221	1.17e-219

Appendix D Risk assessment associated with polybrominated dibenzodioxins (PBDDs) and -furans (PBDFs) during industrial use of OBDPO and DBDPO flame retardants

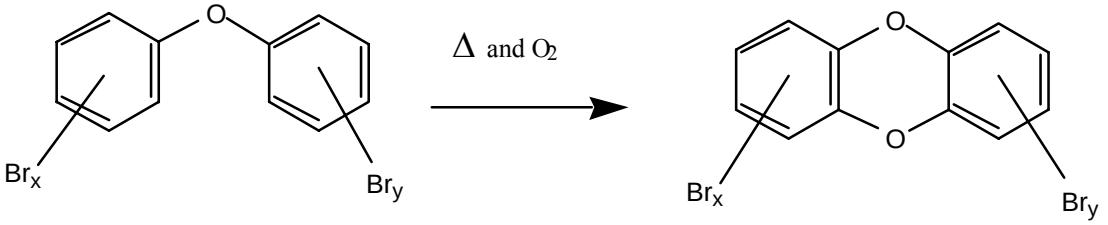
Exposure assessment of workers to PBDDs and PBDFs in the manufacture or use of polybrominated flame retardants

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 :



PBDFs

(1)



PBDDs

(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. The rapporteur 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 the rapporteur 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.

The rapporteur will also use the value of 10 pg TEQ[5]/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[6] value) of 50 pg/m^3 on the basis of 10 m^3 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/m^3 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.

[5] TEQ = Toxicity Equivalent vs. 2,3,7,8 TCDD

[6] 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
						∑ 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/m3 at the workplace	I-TEF	TEQ (ng/m3)
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
			∑ TEQ: 1.2 or 1.8 ng/m3

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/m³ (40, 10 and 550 pg/m³).

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	Tetrabromo	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	4.51×10^{-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, $7.9\cdot10^{-3}$	10.6	849	$1.99\cdot10^{3}$, $1.58\cdot10^{8}$, >44.4, $>5\cdot10^{-4}$	>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
$Kp_{sed\text{-}water}$ (l/kg)												
Measured		28,293	49,167	49,167		62,727					79,433	
Koc (l/kg)												
Measured/ experimental[c]		565,860	983,340	983,340		$1.25\cdot10^{6}$					$1.59\cdot10^{6}$	
Estimated from log Kow[b]	3,180; 2,400	71,560-122,900; 383,440	215,080-556,800; $2.02\cdot10^{6}$	215,080-556,800; $2.02\cdot10^{6}$	264,060	453,520-$3.27\cdot10^{6}$; $1.06\cdot10^{7}$	5.58×10^{7}	$7.30\cdot10^{6}$-$2.03\cdot10^{7}$; $2.93\cdot10^{8}$	156,640	1.54×10^{9}	150,900; $1.50\cdot10^{8}$; $8.11\cdot10^{9}$	150,300

Notes 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, $Kp_{sed\text{-}water}$ (and Koc) and BCF were constructed.

Based on the plots below, the following relationships were found:

$$\log Kow_{measure,HPLC} = 0.718 \cdot \log Kow_{estimated} + 1.236 \quad [N=6, R^2=0.99]$$

$$\log (\text{water solubility } \{\mu g/l\}) = -0.611 \cdot \log Kow_{estimated} + 5.896 \quad [N=5, R^2 = 0.87]$$

$$\log (\text{vapour pressure } \{Pa\}) = -1.109 \cdot \log Kow_{estimated} + 4.225 \quad [N=5, R^2 = 0.92]$$

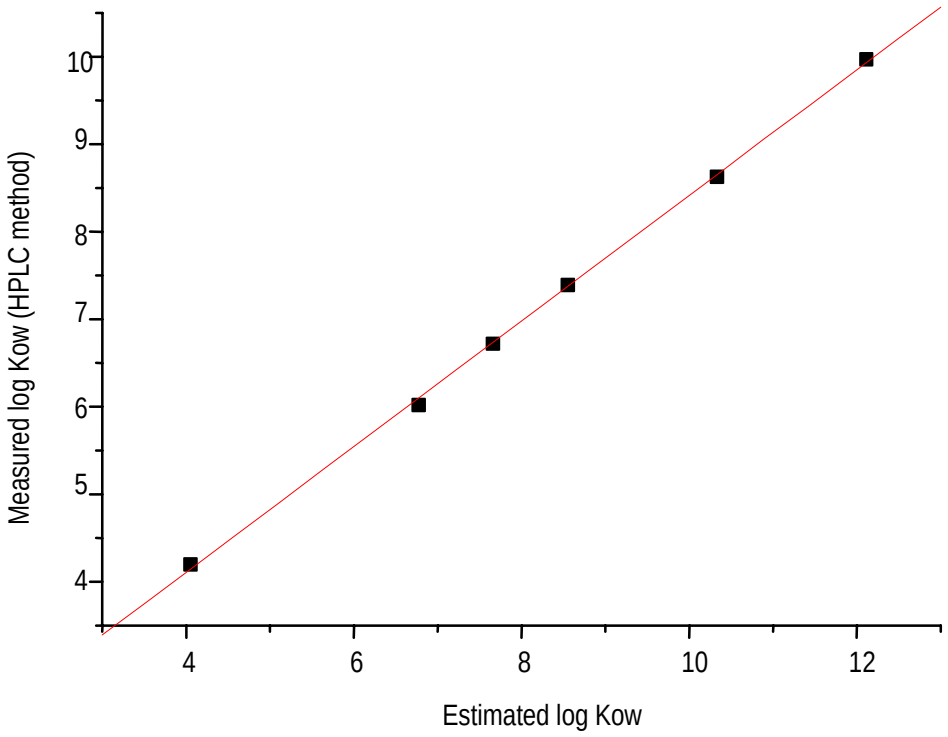
$$\log (Kp_{sed\text{-}water} \ \{l/kg\}) = 8{,}505 \cdot \log Kow_{estimated} - 19{,}709 \quad [N=4, R^2 = 0.85]$$

$$\log (Koc \ \{l/kg\}) = 170{,}108 \cdot \log Kow_{estimated} - 394{,}177 \quad [N=4, R^2 = 0.85]$$

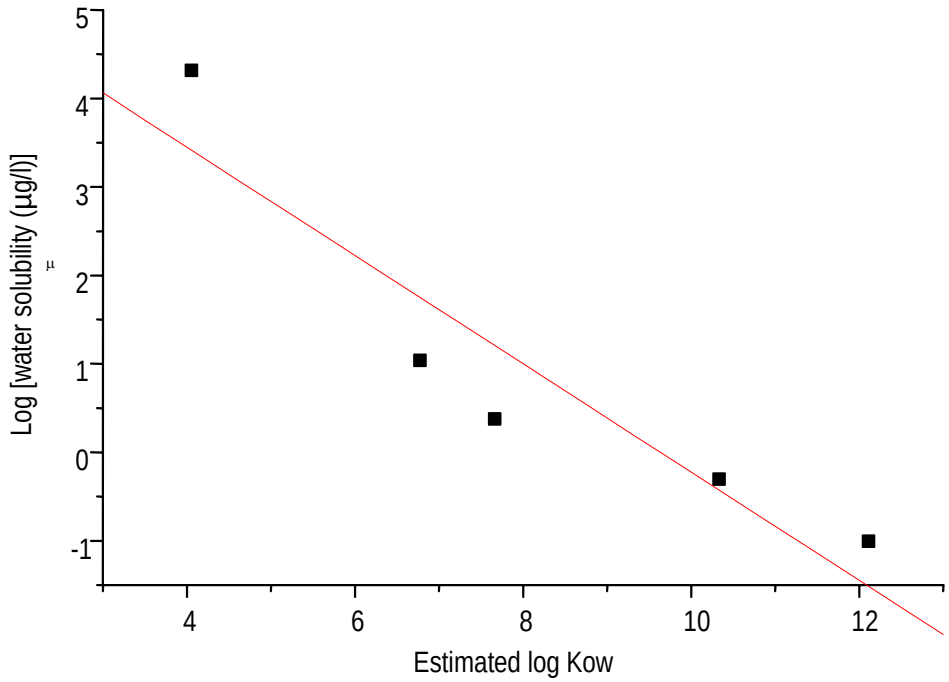
For the measured bioconcentration factors, a simple linear relationship between the BCF and estimated log Kow could not be derived and so approximate values have to be estimated from the graph.

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.

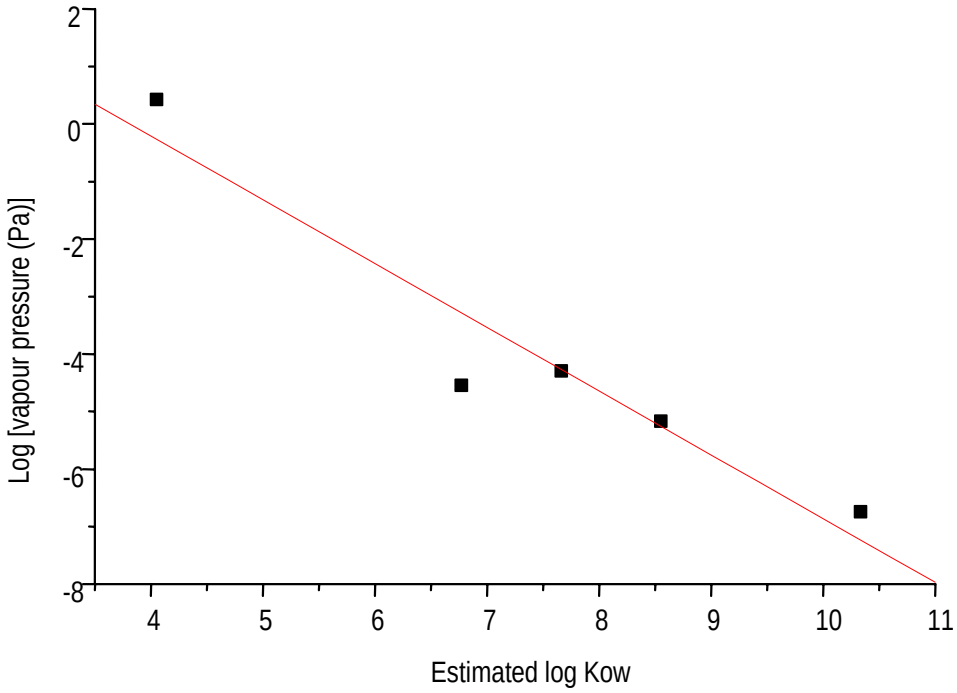
Plot 1: Relationship between measured log Kow (HPLC method) and estimated log Kow



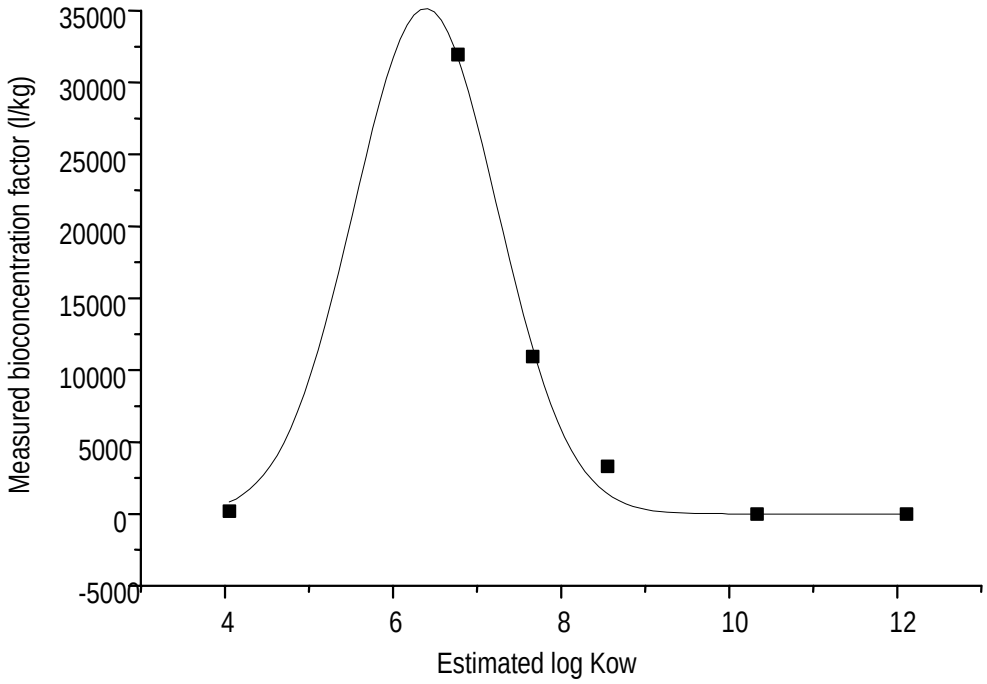
Plot 2: Relationship between log Kow and water



Plot 3: Relationship between estimated log Kow value and measured (GC method) vapour presure



Plot 4: Relationship between bioconcentration factor and log



Plot 5: Relationship between estimated log Kow and measured sediment-water partition coefficient

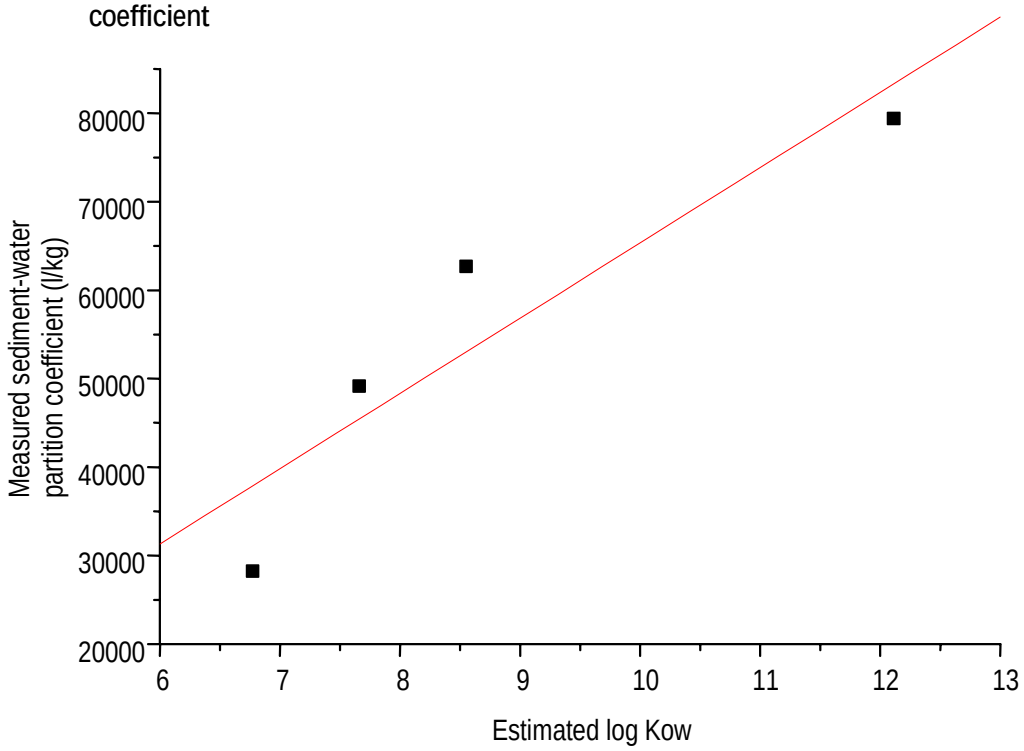


Table E3 shows the basic physico-chemical data for the brominated diphenyl ethers. The values have been derived from the equations given above using the EPI log Kow estimate, except where reliable measured data were available for specific congeners (e.g. water solubility, BCFs). These values will be 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} $molecule^{-1}$

Note 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.

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

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

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

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

Notes: 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

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/m^3	4.2 ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	6.3 µg/l	6.2 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	227 mg/kg wet wt.	216 mg/kg wet wt.
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	85.5 mg/kg wet wt.	84.9 mg/kg wet wt.
	Conc. in fish[a]	n/a	n/a	n/a	n/a	4.3 µg/kg wet wt.	3.7 µg/kg wet wt.
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	340 mg/kg wet wt.	149 mg/kg wet wt.
	Local daily human intake via food	n/a	n/a	n/a	n/a	567 mg/kg wet wt.	0.22 mg/kg bw/day
Decabromo: polymers: compounding and conversion	Air concentration (emission episode)	n/a	n/a	n/a	n/a	53 ng/m^3	52.2 ng/m^3
	PEC_{local} (water)	n/a	n/a	n/a	n/a	0.50 µg/l	0.31 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	17.6 mg/kg wet wt.	10.8 mg/kg wet wt.
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	3.6 mg/kg wet wt.	3.26 mg/kg wet wt.
	Conc. in fish[a]	n/a	n/a	n/a	n/a	1.3 µg/kg wet wt.	0.66 µg/kg wet wt.
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	164 mg/kg wet wt.	40.3 mg/kg wet wt.
	Local daily human intake via food	n/a	n/a	n/a	n/a	23.7 mg/kg bw/day	$9.5 \cdot 10^{-3}$ mg/kg bw/day

Table E13 continued overleaf

Table E13 continued

Scenario	Compartment/ endpoint	Sum of penta components (tetra-hexa: Table 12)	Commercial 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/m³	1.7 ng/m³
	PEC_{local} (water)	n/a	n/a	n/a	n/a	2.6 µg/l	2.5 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	93.1 mg/kg wet wt.	87.9 mg/kg wet wt.
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	34.4 mg/kg wet wt.	34 mg/kg wet wt.
	Conc. in fish[a]	n/a	n/a	n/a	n/a	4.7 µg/kg wet wt.	4.4 µg/kg wet wt.
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	179 mg/kg wet wt.	81.1 mg/kg wet wt.
	Local daily human intake via food	n/a	n/a	n/a	n/a	228 mg/kg bw/day	0.088 mg/kg bw/day
Decabromo: textiles - application	Air concentration (emission episode)	n/a	n/a	n/a	n/a	5×10^{-4} ng/m³	0.8 ng/m³
	PEC_{local} (water)	n/a	n/a	n/a	n/a	1.4 µg/l	1.3 µg/l
	PEC_{local} (sediment)	n/a	n/a	n/a	n/a	50 mg/kg wet wt.	131 mg/kg wet wt.
	PEC_{local} (agr. soil)	n/a	n/a	n/a	n/a	17.3 mg/kg wet wt.	17 mg/kg wet wt.
	Conc. in fish[a]	n/a	n/a	n/a	n/a	2.7 µg/kg wet wt.	2.4 µg/kg wet wt.
	Conc. in earthworms[a]	n/a	n/a	n/a	n/a	142 mg/kg wet wt.	58.6 mg/kg wet wt.
	Local daily human intake via food	n/a	n/a	n/a	n/a	115 mg/kg bw/day	0.044 mg/kg bw/day
All regional sources	$PEC_{regional}$ (air)	0.34 ng/m³	0.27 ng/m³	0.26 ng/m³	0.11 ng/m³	0.015 ng/m³	4.1 ng/m³
	$PEC_{regional}$ (water)	$2.6 \cdot 10^{-4}$ µg/l	$1.5 \cdot 10^{-3}$ µg/l	0.26 µg/l	$3.8 \cdot 10^{-4}$ µg/l	0.18 µg/l	0.081 µg/l
	$PEC_{regional}$ (sediment)	10.0 µg/kg wet wt.	32.5 µg/kg wet wt.	16.6 mg/kg	0.019 mg/kg wet wt.	11.1 mg/kg wet wt.	4.94 mg/kg wet wt.
	$PEC_{regional}$ (agr. soil)	27.8 µg/kg wet wt.	132 µg/kg wet wt.	72.3 mg/kg wet wt.	0.073 mg/kg wet wt.	48.4 mg/kg wet wt.	27.1 mg/kg wet wt.
	Regional daily human intake via food	0.78 µg/kg bw/day [0.79 µg/kg bw/day][b]	1.93 µg/kg bw/day [1.96 µg/kg bw/day][b]	482 mg/kg bw/day [482 mg/kg bw/day][b]	$2.4 \cdot 10^{-4}$ mg/kg bw/day	321 mg/kg bw/day	0.073 mg/kg bw/day

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	$1.363 \cdot 106$	0.094%	8.46%	91.4%
7.29	10.6	$1.363 \cdot 106$	0.094%	8.46%	91.4%
8.29	10.6	$1.363 \cdot 106$	0.094%	8.46%	91.4%
9.29	10.6	$1.363 \cdot 106$	0.094%	8.46%	91.4%
6.29	1.06	$1.363 \cdot 106$	0.011%	8.48%	91.5%
6.29	0.106	$1.363 \cdot 106$	0.0010%	8.49%	91.5%
6.29	0.0106	$1.363 \cdot 106$	0.00011%	8.49%	91.5%
6.29	106	$1.363 \cdot 106$	0.81%	8.27%	90.9%
b) Koc estimated from Kow					
6.29	10.6	$1.57 \cdot 105$	0.77%	11.8%	87.5%
7.29	10.6	$1.01 \cdot 106$	0.10%	8.62%	91.3%
8.29	10.6	$6.54 \cdot 106$	0.020%	8.10%	91.9%
9.29	10.6	$4.22 \cdot 107$	0.0031%	8.02%	92.0%
6.29	1.06	$1.57 \cdot 105$	0.091%	12.0%	87.9%
6.29	0.106	$1.57 \cdot 105$	0.0094%	12.1%	87.9%
6.29	0.0106	$1.57 \cdot 105$	0.00094%	12.1%	87.9%
6.29	106	$1.57 \cdot 105$	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 humans 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^{o}C in the dark. Analysis of the degradation products was carried out by gas chromatography with electron capture detection (GC-ECD) using authentic standards of individual polybrominated biphenyl isomers, or standards purified from the commercial mixture used. However, several new peaks were seen in the chromatograph. For these compounds the number of bromine atoms present/molecule was determined by mass spectrometry and the most probable identity of the compound was determined by the relative retention times and the assumption that

the corresponding polybrominated biphenyl and polychlorinated biphenyl congeners have the same relative retention times and response factors.

In the experiments using the inocula derived from Aroclor 1242-contaminated sediment, 29% of the *meta*- and *para*-bromines present in the polybrominated biphenyl mixture (Firemaster) were removed during 40 weeks incubation at a concentration of 500 µg/g sediment. The same sediment system had previously been shown to dechlorinate polychlorinated biphenyls and 59% of the *meta*- and *para*-chlorines of added Aroclor 1242 were removed under the same conditions. No asymptote was reached in the degradation curve for the polybrominated biphenyl mixture, indicating that further debromination could have occurred over a longer incubation period. No debromination of the polybrominated biphenyl mixture was seen with the inocula derived from Aroclor 1260 (when Aroclor 1260 itself was incubated at 500 µg/g sediment 18% removal of *meta*- and *para*-chlorines was seen over 40 weeks incubation, but a 24-week acclimation period was seen before dechlorination occurred).

In a second series of experiments, 32% removal of *meta*- and *para*-bromines using the inocula from polybrominated biphenyl-contaminated sediment, 12% removal of *meta*- and *para*-bromines using inocula from Aroclor 1242-contaminated sediment and 3% removal of *meta*- and *para*-bromines using inocula from Aroclor 1260-contaminated sediment was seen over 32 weeks. In these experiments, the polybrominated biphenyl mixture (Firemaster) was incubated at a concentration of 500 µg/g sediment. No debromination was seen in incubations at a polybrominated biphenyl concentration of 50 µg/g sediment. A similar pattern was seen when the pure compound 2,4,5,2',4',5'-hexabromobiphenyl was incubated in the same system.

The authors concluded that debromination or dechlorination was greatest in those systems that had previously been exposed to the brominated or chlorinated biphenyl under investigation. The results indicated that adaptation of the microorganisms present (enzyme induction) was needed for debromination to occur, and this was further supported by the fact that no debromination was seen at lower polybrominated biphenyl concentrations of 50 µg/g. A similar concentration dependence for the reductive dechlorination of polychlorinated biphenyls had previously been seen (Morris et al., 1992).

Other relevant chlorinated substances

The reductive dechlorination of polychlorinated biphenyls has been studied using two freshwater sediments and an estuarine sediment under both methanogenic and sulfidogenic conditions. All sediments had been previously contaminated with polychlorinated biphenyls. A 35% (v/v) sediment inoculum was used in the experiments and incubations were carried out at 30^{o}C in the dark over a 17 month period. The polychlorinated biphenyls (PCB) used in the experiments were either Aroclor 1242 at 100 mg/kg or Aroclor 1260 at 400 mg/kg (these correspond to the contamination levels found in the sediments). In general, reductive dechlorination started within 1-2 months in the experiments carried out under methanogenic conditions, with a decrease in the concentrations of tri-, tetra- and pentachlorobiphenyls and a corresponding increase in the mono- and dichlorobiphenyls (dechlorination of the ortho chlorine atoms did not occur). The half-life for the reaction was found to be slow in the laboratory experiments (of the order of several months). No dechlorination was seen under sulfidogenic conditions (Alder et al., 1993).

A similar experiment has been carried out by Sokol (1998). Here the ability of polychlorinated biphenyl-contaminated sediments to dechlorinate PCBs was investigated in laboratory incubations over a 39 month period. The sediment used had an average PCB concentration of 300 mg/kg dry weight and these, along with PCB-free sediments spiked with Aroclor 1248 at 300 mg/kg were used to prepare inocula for the experiments. The results indicated that the

majority of the dechlorination occurred during the first 4 months of incubation, but there was some indication of further dechlorination of the initial products after a further lag period. The results agreed with those of earlier studies in that dechlorination appears to be congener specific, with *meta*- and *para*-chlorines being removed more easily than ortho-chlorines. The results also indicated that a threshold concentration may exist, below which no dechlorination of PCBs is observed.

Factors affecting anaerobic dehalogenation

Several factors have been put forward as being important in considering the dehalogenation of aromatic compounds under anaerobic conditions. These include:

- microbial populations present (position of dehalogenation may be population specific)
- adsorption of the substrate to sediment/soil
- availability of co-metabolites/electron donors/carbon source
- concentration of substance.

Peijnenburg et al. (1991) carried out a series of tests on the rate of both biotic and abiotic transformation of halogenated hydrocarbons in anoxic sediments. The object of the tests was to provide a database in order to assess the factors that were important in determining the rate of degradation. Reductive dehalogenation was seen to occur for halogenated aromatic compounds but the rate and selectivity of the reaction was found to depend on both compound specific factors and environmental factors (such as nature and location of the substituents on the carbon skeleton, redox potential of the system, temperature, sediment composition and microbial habitat). For most compounds considered in the study the rate of degradation was seen to increase after a lag period. This was thought to be due to acclimation as treatment with γ-radiation reduced the rate back to that seen at the start. The results were interpreted in terms of an underlying abiotic process occurring at the start of the experiment (although the nature of the actual reducing agent in the sediment was unknown), then, after a lag phase, biodegradation becoming the dominant removal process. For halogenated aromatic compounds, the abiotic process was found to be a minor removal process compared to biotic dehalogenation. The rates of dehalogenation were found to correlate with molecular structural parameters such as bond strength, Hammett σ-constants (a descriptor of charge distribution within the molecule), inductive effects of substituents and steric parameters.

In an experiment with PCBs, dechlorination has been demonstrated under methanogenic but not sulfidogenic conditions. Methanogenic conditions in sediments are usually associated with the deeper layers of the sediment, where direct exchange with the aerobic upper layers is minimal. Sulfidogenic aerobic conditions usually exist between the aerobic surface layers and the methanogenic lower layers and some exchange between the sulfidogenic and aerobic surface layers can occur. Thus, if anaerobic debromination of the polybrominated diphenyl ethers occurs in the environment under similar conditions to the dechlorination of PCBs, any products formed are more likely to be present in the deeper methanogenic layers of the sediment, and rapid exchange between this layer and the aerobic sediment and water phases would be expected to be limited (Ten Berge, 1995).

Conclusion on anaerobic biodegradation regarding brominated diphenyl ethers

The available data for halogenated aromatic compounds indicate that reductive dehalogenation can occur under some anaerobic conditions. The rate of reaction is generally found to be slow, with the rate depending on several factors, one of which appears to be carbon-halogen bond

strength. Most of the data reported above is for chlorinated organics, with a moderate degree of chlorination. Given that the C-Br bond is weaker than the C-Cl bond, then dehalogenation of brominated diphenyl ethers in the environment under anaerobic conditions is a possibility, and indeed has been seen with other brominated aromatic compounds (e.g. polybrominated biphenyls). It is not clear from the available information whether dehalogenation would occur for fully halogenated substances (such as decabromodiphenyl ether), as little experimental data 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^{o}C using 300 nm lamps on a range of halogenated benzene derivatives in water and used the results obtained to identify the parameters that were important in the reactions involved. In most cases, photohydrolysis was the only reaction pathway observed. They identified that photohydrolysis occurred in two steps. After light adsorption and excitation of the molecule to the excited state, the first rate determining step was cleavage of the carbon-halogen bond having the lowest bond strength, which was then followed by formation of the corresponding hydroxylated derivative. Both the carbon-halogen bond strength and steric factors in the molecule were considered to be important in determining the site of photohydrolysis.

Many other photolysis studies have been carried out with halogenated aromatic compounds under a variety of conditions and a selection of these are summarised in **Table F1**.

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_2O_3, and ZnO)	simulated sunlight - xenon lamp with a 340 nm cut-off filter.	Catalytic activity was TiO_2>WO_3>ZnO, with CdS and Fe_2O_3 being poor catalysts. Suggests mineralized into CO_2 and HCl. A reaction pathway involving hydroxy intermediates is given based on results from other chloroaromatic compounds.	Pelizzetti et al., 1988.
Pentachlorobenzene and methoxychlor	various types of purified water with and without humic acid	eight 350 nm lamps	In unpurified water, rate faster in presence of humic acid. In pure water, pentabromobenzene does not disappear - this was expected since does not absorb at 350 nm and reaction was put down to presence of photosensitising trace impurity. Decrease in pentabromobenzene was apparently second order. Methoxychlor appeared to be stable under the conditions used. No details of products formed	van Noort et al., 1988

Table F1 continued overleaf

Table F1 continued

Substance	Solvent	Radiation	Comments	Reference
Bromo- and bromo/chloro tetra- and penta-halogenated dibenzo-*p*-dioxins	i-octane or as a thin solid film (no solvent)	natural sunlight	Fast photochemical decomposition of the bromo- and bromo/chloro-derivatives in solution, much slower in the solid phase experiments. Reductive dehalogenation was occurring in solution but there was evidence of other degradation routes in the solid phase experiments (not identified).	Buser, 1988
3,4-Dichlorobiphenyl	aqueous suspensions of TiO_2	Xenon/mercury lamp (λ 300-380 nm)	Degrades but no information on products is given.	Tunesi and Anderson, 1987
Brominated biphenyls	90% acetonitrile/water with and without sodium borohydride	λ = 254 nm	Rate of degradation enhanced by sodium borohydride. Reductive debromination occurring. A chain mechanism is thought to occur in presence of borohydride.	Epling et al., 1987
Chlorinated dioxins, biphenyls, phenols and benzenes	aqueous suspensions of semiconductor materials (TiO_2)	λ 310-830 nm	Decomposition occurs. No details of products formed, although reported to be CO_2 and HCl for chlorophenols.	Barbeni et al., 1986
Polychlorodibenzo-*p*-dioxins	water/acetonitrile (2:3 v/v)	λ 290-310	Degradation occurs, no details of products formed.	Choudhry and Webster, 1986
Polychlorinated biphenyls	-	-	Explains photolysis rates in terms of preferential photodissociation of chlorine from a lateral vs. a non-lateral position to yield the corresponding aryl radical and/or aryl cation-aryl carbene intermediate.	Mamantov, 1985a
Polychlorinated diphenyl ethers and chloroanisoles	-	-	Postulates that photolysis of polychlorinated diphenyl ethers to give chlorinated dibenzofurans may proceed via a carbene insertion reaction. Also photosubstitution of chloroanisoles and diphenyl ethers may proceed via an aryl carbene/aryl cation, whereas the photoreduction may proceed via an aryl radical.	Mamantov, 1985b
Polychlorinated dibenzo-*p*-dioxins	-	-	Photolysis rates of tetrachlorodibenzo-*p*-dioxins are explained by the preferential photodissociation of chlorine from a lateral vs. non-lateral position to yield the corresponding aryl radical and/or aryl cation-aryl carbene intermediate.	Mamantov, 1985c.
1,2,3,4,7-pentachloro- and 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	water/acetonitrile (4:6 v/v)	λ = 313 nm	Degradation but no information on products.	Choudhry and Webster, 1985

Table F1 continued overleaf

Table F1 continued

Substance	Solvent	Radiation	Comments	Reference
Chlorobenzene	water	λ = 254 nm and around 300 nm	Phenol is the product. Previously photoreduction was seen in cyclohexane, isopropanol and methanol (photosubstitution competes with photoreduction in methanol). Reaction photosensitized by acetone.	Tissot et al., 1984
Biphenyl, 2-chlorobiphenyl and 4,4'-dichlorobiphenyl	adsorbed onto silica gel	λ>290	Hydroxylated products formed.	Kotzias et al., 1984
Aroclor 1254	aqueous 2-propanol	λ>300 nm or natural sunlight	Dechlorination enhanced by presence of photosensitiser (hydroquinone), increasing aqueous solvent (1:1 water:alcohol) and maintaining neutral pH. Some evidence for photonucleophilic displacement by 2-propyl groups	Chaudhary et al., 1984
Tetrachlorodibenzofurans	tetradecane or hexane	λ = 254 nm	Trichlorodibenzofurans formed. General rules: 1) chlorines on the same aromatic ring tend to stabilise the loss of chlorine from that ring; 2) vicinal chlorines stabilise the loss of a particular chlorine (i.e. the greater the number of adjacent chlorines about a given chlorine, the greater the likelihood of initially losing that particular chlorine; 3) given an equal number of vicinal chlorines, the 3-chlorine will be lost before the 2-chlorine.	Mazer and Hileman, 1982
Decachlorobiphenyl	hexane, methanol, acetone or benzene	30 different wavelengths between 199 and 358 nm	Observed reductive dechlorination in methanol and hexane. In benzene the product was a terphenyl derivative of decachlorobiphenyl, where a chlorine atom was replaced by a benzene molecule.	Koshioka et al. 1987
Chlorobenzene, 2- and 4-chlorobiphenyl and 2- and 4-chlorodiphenyl ether	water	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	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/	Approx. total	(product basis)			
River Tweed at Tweedmouth	Background site	0.4	<0.6	<0.4	0.4	<0.38	<0.44	<0.6	µg/kg dry wt.
River Tweed at Berwick on Tweed bridges	Background site	<0.3	0.6	<0.4	0.6	<0.38	<0.44	<0.6	µg/kg dry wt.
River Nith, upstream of wwtp	Near rubber producer	<0.3	<0.6	<0.4	nd	<0.38	<0.44	<0.6	µg/kg dry wt.
River Nith, downstream of wwtp	Near rubber producer	1.7	3.5	<0.4	5.2	0.6	<0.44	<0.6	µg/kg dry wt.
River Nith at Glencaple	Near rubber producer	0.7	1	<0.4	1.7	<0.38	2	<0.6	µg/kg dry wt.
Avonmouth	Near flame retardant producer/user	2.4-3.6	2.9-4.7	<0.4-9.2	7.1-16.6	0.6-1.0	<0.44	<0.6-7	µg/kg dry wt.
River Tees, upstream of confluence with River Skerne	Near a producer of penta/octabromodiphenyl ether	<0.3	<0.6	<0.4	nd	<0.38		<0.6	µg/kg dry wt.
River Tees, downstream of confluence with River Skerne	Near a producer of penta/octabromodiphenyl ether	8	11	2.9	21.9	35	<0.44-25	<0.6	µg/kg dry wt.
River Skerne at Croft-on-Tees	Near a producer of penta/octabromodiphenyl ether	51	85	3.5	139.5	34	129	7	µg/kg dry wt.
River Skerne at Newton Aycliffe	Near a producer of penta/octabromodiphenyl ether	239	319	2.7	560.7	130	397	64	µg/kg dry wt.
Howden Beck	Near a producer of penta/octabromodiphenyl ether	86	111	1.8	198.8	45	264	23	µg/kg dry wt.
River Skerne, upstream of Howden Beck	Near a producer of penta/octabromodiphenyl ether	68	126	0.7	194.7	51	333	294	µg/kg dry wt.
River Skerne, downstream of Howden Beck	Near a producer of penta/octabromodiphenyl ether	112	159	<0.4	271	68	1,405	95	µg/kg dry wt.
River Calder at Cock Bridge	Near a foam manufacturer	2.3	0.6	4.2	7.1	<0.38	9	399	µg/kg dry wt.
Hyndburn Brook, upstream of wwtp	Near to foam manufacturer	7.6	16	<0.4	23.6	6.1	3	<0.6	µg/kg dry wt.
River Calder, downstream of wwtp	Near to foam manufacturer	24	46	0.5	94.1	18	17	3,190	µg/kg dry wt.
Elstow landfill	Landfill receiving brominated wastes	0.8-2.4	2.9-5.7	<0.4	5.3-6.5	<0.38-1.5	<0.44-13	<0.6	µg/kg dry wt.
Elstow Brook	Downstream of landfill site	0.4	<0.6	1.2	1.6	<0.38	1	<0.6	µg/kg dry wt.
Tees Estuary	Portrack wwtp	8.9	16	9.1	34	19	29	5	µg/kg dry wt.
	Bamlett's Bight	368	898	4.8	1,271	366	164	<0.6	µg/kg dry wt.
	No. 23 buoy	49	99	14	162	77	263	9	µg/kg dry wt.
	Phillips approach buoy	103	201	72	372	81	1,348	8	µg/kg dry wt.
Great Ouse at Kings Lynn	Downstream of landfill site	4.2	4.6	<0.4	8.8	<0.38	7.9	<0.6	µg/kg dry wt.
River Ribble at Freckleton saltings	Near foam manufacturing site	1.2	1.7	<0.4	2.9	<0.38	4.4	111	µg/kg dry wt.
River Humber at Paull		21	36	<0.4	57	6.6	29	17	µg/kg dry wt.
Upstream of a plastics processor.	Decabromodiphenyl ether used					<50	<200	<200	µg/kg dry wt.
Downstream of a plastics processor.	Decabromodiphenyl ether used					<50	<200	<200	µg/kg dry wt.
Upstream of warehouse.	Decabromodiphenyl ether stored					<100	1,480	<500	µg/kg dry wt.
Downstream of warehouse.	Decabromodiphenyl ether stored					<100	3,030	<500	µg/kg dry wt.
Industrial area.	Upstream of site possibly using pentabromodiphenyl ether					<100	<500	<500	µg/kg dry wt.
Industrial area.	Downstream of site possibly using pentabromodiphenyl ether					<100	<500	<500	µg/kg dry wt.
Mersey estuary.	Industrial area, upstream of polymer processing site					<100	<500	<500	µg/kg dry wt.
Mersey estuary.	Downstream of polymer processing site.					<100	<500	<500	µg/kg dry wt.

Table F2 continued overleaf

Table F2 continued

Location	Comments	Pentabromodiphenyl ether components				Penta	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/	Approx. total	(product basis)			
Upstream of a plastic compounder.	Decabromodiphenyl ether used.					5.9	<200	<200	µg/kg dry wt.
Downstream of a plastic compounder.	Decabromodiphenyl ether used.					<5	<200		µg/kg dry wt.
Landfill site.	Pentabromodiphenyl ether waste disposed on-site					<100	<500	<500	µg/kg dry wt.
Haringvliet-east	River sediment from 1992	6.7	7.3		14				µg/kg wet wt.
Nieuwe Merwede	River sediment from 1992	17			17				µg/kg wet wt.
Meuse	River sediment from 1992	6.9	8.2		15.1				µg/kg wet wt.
Waal	River sediment from 1992	23	21		44				µg/kg wet wt.
Sediments from near a factory	Upstream	3.5	8.2		11.7				µg/kg 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

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/	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.

Note: 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/				
Dab liver	Off River Tees; 12% lipid	129	9.4	<1	13	325	<1.2	µg/kg wet wt.
	Off Wash; 31% lipid	117	23	<1	34	18	<1.2	µg/kg wet wt.
	Tees Bay; 23.6% lipid	601	29	55	236	179	<1.2	µg/kg wet wt.
	Bideford Bay; 33.6% lipid	37	11	11	33	<1	<1.2	µg/kg wet wt.
Dab muscle	Bideford Bay; 1% lipid	<1	<1	<1	1	9.7	<1.2	µg/kg wet wt.
	Tees Bay; 1.2% lipid	7	1	1.6	11	6	<1.2	µg/kg wet wt.
Whiting liver	Bristol Channel; 45% lipid	102	21	<1	48	<1	<1.2	µg/kg wet wt.
Flounder liver	Off Lune/Wyre; 12% lipid	49	6.5	<1	12	14	<1.2	µg/kg wet wt.
	Off River Humber; 14% lipid	217	22	<1	16	126	<1.2	µg/kg wet wt.
	Nith Estuary; 18.8% lipid	19	3.6	<1	9	<1	<1.2	µg/kg wet wt.
	Nith Estuary; 19.2% lipid	14	3.1	<1	9	16	<1.2	µg/kg wet wt.
	Bideford Bay; 18.8% lipid	69	4.9	22	22	19	<1.2	µg/kg wet wt.
	Tees Bay; 13.6% lipid	1,294	108	130	169	115	<1.2	µg/kg wet wt.
Flounder muscle	Nith Estuary; 1% lipid	1.4	<1	<1	1.2	<1	<1.2	µg/kg wet wt.
	Nith Estuary; 1% lipid	1.2	<1	<1	1	<1	<1.2	µg/kg wet wt.
	Bideford Bay; 0.8% lipid	1.4	<1	<1	0.8	<1	<1.2	µg/kg wet wt.
	Tees Bay; 1.2% lipid	22	4.4	1.1	13	7	<1.2	µg/kg wet wt.
Plaice muscle	Bideford Bay; 0.6% lipid	0.6	<1	<1	1	3.3	<1.2	µg/kg wet wt.
	Tees Bay; 1.6% lipid	8.3	1.6	2.2	15	12	<1.2	µg/kg wet wt.
Plaice liver	Bideford Bay; 16% lipid	15	3	3.6	15	<1	<1.2	µg/kg wet wt.
	Tees Bay; 3.3% lipid	161	12	14	35	41	<1.2	µg/kg wet wt.
Winkles	River Tweed; 2.6% lipid	1.9	1.8	1.5	25	<1	<1.2	µg/kg wet wt.
Mussels	Gat Sand/Hunstanton, the Wash; 1.8% lipid	3.5	3.9	2	18	16	<1.2	µg/kg wet wt.
Rabbit	Pooled muscle samples, 1986	<1.8	<0.34	<0.21				µg/kg lipid
Moose	Pooled muscle samples, 1985-1986	0.82	0.64	0.24				µg/kg lipid
Reindeer	Pooled suet samples, 1986	0.17	0.26	0.04				µg/kg lipid
Whitefish	Pooled muscle samples, 1986	15	7.2	3.9				µg/kg lipid
Arctic char	Pooled muscle samples, 1987	400	64	51				µg/kg lipid
Herring	Pooled and individual samples, 1986-1987	12-450	3.4-46	1.6-32				µg/kg lipid
Ringed seal	Pooled blubber samples, 1981	47	1.7	2.3				µg/kg lipid
Grey seal	Pooled blubber samples, 1979-1985	650	40	38				µg/kg lipid
Osprey	Pooled muscle samples, 1982-1986	1,800	140	200				µg/kg lipid
Starling	Muscle samples, 1988	2.7-7.8	2.3-4.2	0.62-1.1				µg/kg lipid
Guillemot eggs	Pooled and individual samples, 1970-1989	130-1,500	24-330	4.2-79				µg/kg lipid
Bream	Muscle samples, 1987	250-750	2.3-2.4	11-37				µg/kg lipid

Table F3 continued overleaf

Table F3 continued

Species	Location/Comment	Pentabromodiphenyl ether components			Penta (product basis)	Octa	Deca	Units
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	2,2',3,4,4'-PeBDPE/				
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

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/				
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

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/				
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

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/				
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

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/				
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

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/				
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

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/				
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

Note: a) Other penta isomer is probably 2,2'4,4',6-pentabromodiphenyl ether (Sellström et al., 1998).

Conclusion

The available information indicates that the brominated diphenyl ethers have the potential to undergo biodegradation by reductive dehalogenation to form lower brominated congeners under anaerobic conditions. Photolysis may also occur but the products formed are most likely to be hydroxylated products which may react further. The environmental significance of these processes is unknown but the available monitoring data would suggest that reductive dehalogenation of decabromodiphenyl ether or octabromodiphenyl ether in the environment is only a minor source of the lower brominated congeners (e.g. tetra- and pentabromodiphenyl ether). However, such data is only suggestive and not conclusive. 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

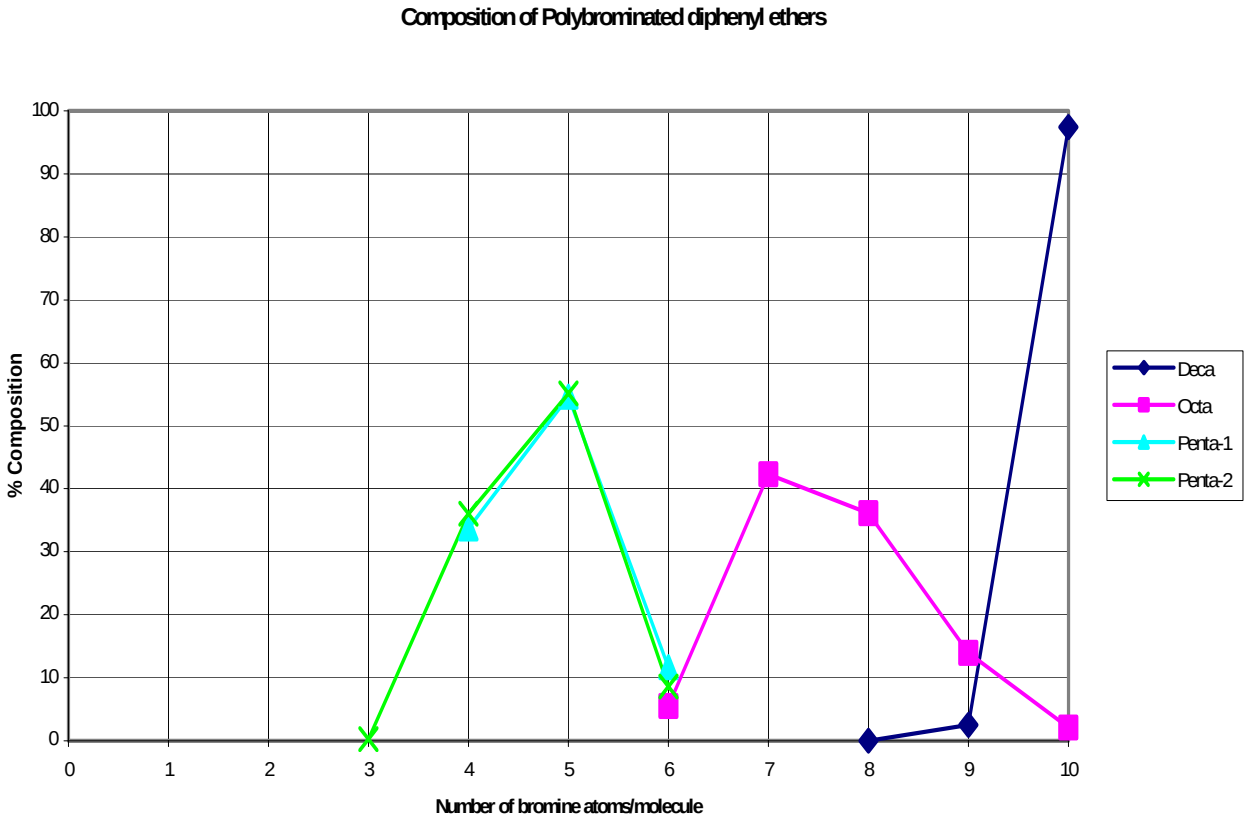
The three commercial polybrominated diphenyl ethers are all mixtures of congeners. This results from the fact that the production process involves a step-wise addition of bromine to the biphenyl ether ring and so each product has to pass through a series of lower brominated congeners until the required 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



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	1.02×10^{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	2.45×10^{-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	2.23×10^{-3}%	22.2 kg
2,2',4,4',5,5'-hexa	9,279		
Total hexa[a]	11,705	1.17×10^{-3}%	117.05 kg
2,3,3',4,4',5,6-hepta	nd (<1,400)		
Total hepta[a]	33,541	3.35×10^{-3}%	335.41 kg
Total (tri-hepta)			487.2 kg

Notes: 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	12
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	tribromodiphenyl ether	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'	tetrabromodiphenyl ether	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	pentabromodiphenyl ether	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

Isomer	Congener	Identity
2,2',3,4,4',5',6	heptabromodiphenyl ether	183
	heptabromodiphenyl ether	189
2,3,3',4,4',5,6	heptabromodiphenyl ether	190
2,2',3,4,4',5,5',6	octabromodiphenyl ether	203
2,2',3,3',4,4',5,5',6,6'	decabromodiphenyl ether	209

European Commission

EUR 20402 EN - European Union Risk Assessment Report
Bis(pentabromophenyl) ether, Volume 17

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Environment and quality of life series

The report provides the comprehensive risk assessment of the substance bis(pentabromophenyl) ether. 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 bis(pentabromophenyl) ether concludes that there is at present no concern for workers, consumers or humans exposed via the environment. The risk assessment for the environment concludes that there is a need for further information to characterise the risks for top predators via accumulation up the food chain (secondary poisoning). There is at present no concern for the atmosphere, aquatic ecosystem, terrestrial ecosystem or for microorganisms in the sewage treatment plant.

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