IPCS

INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY

Environmental Health Criteria 162

Brominated Diphenyl Ethers

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ernational Labour Organisation, and the World Health Organization

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Environmental Health Criteria 162

BROMINATED DIPHENYL ETHERS

First draft prepared by Dr G.J. van Esch,
Bilthoven, Netherlands

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CONTENTS

GLOSSARY

PBDE	polybrominated diphenyl ethers
MBDE	monobromodiphenyl ethers
DiBDE	dibromodiphenyl ethers
TrBDE	tribromodiphenyl ethers
TeBDE	tetrabromodiphenyl ethers
PeBDE	pentabromodiphenyl ethers
HxBDE	hexabromodiphenyl ethers
HpBDE	heptabromodiphenyl ethers
OBDE	octabromodiphenyl ethers
NBDE	nonabromodiphenyl ethers
DeBDE	decabromodiphenyl ethers
PBDF	polybrominated dibenzofurans
TeBDF	tetrabromodibenzofurans
PeBDF	pentabromodibenzofurans
HxBDF	hexabromodibenzofurans
HpBDF	heptabromodibenzofurans
PBDD	polybrominated dibenzodioxins
TeBDD	tetrabromodibenzodioxins
PeBDD	pentabromodibenzodioxins
HxBDD	hexabromodibenzodioxins
HpBDD	heptabromodibenzodioxins
PBBz	polybrominated benzenes
PBP	polybrominated phenols
PBN	polybrominated naphthalenes
PBB	polybrominated biphenyls
PCB	polychlorinated biphenyls
THP	Tetrakis(hydroxymethyl)phosphonium salts
ABS	acrylonitrile-butadiene-styrene
BASF	Badische Anilin und Soda Fabrik
BFRIP	Brominated Flame Retardant Industry Panel
BOD	biochemical oxygen demand

CEFIC	Conseil Européen de l'Industrie Chimique (European Chemical Industry Council)
DTA	differential thermal analysis
EBFRIP	European Brominated Flame Retardant Industry Panel
EEC	European Economic Community
ER	epoxy resin
FY	Fiscal Year
GC/ECD	gas chromatography/electron capture detector
GC/MS	gas chromatography/mass spectrometry
HIPS	high impact polystyrene
HPLC	high pressure liquid chromatography
HRGC/MS	high resolution gas chromatography/mass spectrometry
IG	ignition loss
NCI	negative chemical ionization
NHATS	National Human Adipose Tissue Survey
NIOSH	National Institute of Occupational Safety and Health
PA	polyamide
PAN	polyacrylonitrile
PBT	polybutylene terephthalate
PE	polyethylene
PET	polyethylene terephthalate
PP	polypropylene
PR	phenolic resin
PS	polystyrene
PUR	polyurethane
PVC	polyvinylchloride
SIM	selective ion monitoring
TGA	thermal gravimetric analysis
UPE	unsaturated (Thermoset) polyesters
US EPA	United States Environmental Protection Agency
US NTP	United States National Toxicology Program
XPE	cross-linked polyethylene

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NOTE TO READERS OF THE CRITERIA DOCUMENTS

Every effort has been made to present information in the criteria documents as accurately as possible without unduly delaying their publication. In the interest of all users of the environmental health criteria documents, readers are kindly requested to communicate any errors that may have occurred to the Director of the International Programme on Chemical Safety, World Health Organization, Geneva, Switzerland, in order that they may be included in corrigenda, which will appear in subsequent volumes.

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A detailed data profile and a legal file can be obtained from the International Register of Potentially Toxic Chemicals, Case Postale 356, 1219 Châtelaine, Geneva, Switzerland (Telephone No. 9799111).

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NOTE: The proprietary information contained in this document cannot replace documentation for registration purposes, because the latter has to be closely linked to the source, the manufacturing route, and the purity/impurities of the substance to be registered. The data should be used in accordance with paragraphs 82-84 and recommendations paragraph 90 of the Second FAO Government Consultation (1982).

ENVIRONMENTAL HEALTH CRITERIA FOR BROMINATED DIPHENYL ETHERS

A WHO Task Group on Environmental Health Criteria for Brominated Diphenyl Ethers met at the World Health Organization, Geneva, from 28 June to 2 July 1993. Dr K.W. Jager, of the IPCS, welcomed the participants on behalf of Dr M. Mercier, Director IPCS, and the three cooperating organizations (UNEP/ILO/WHO). The Group reviewed and revised the draft criteria monograph and made an evaluation of the risks for human health and the environment from exposure to brominated diphenyl ethers.

The first draft of the monograph was prepared by Dr G.J. van Esch of the Netherlands, who also prepared the second draft, incorporating comments received following circulation of the first draft to the IPCS contact points for Environmental Health Criteria monographs.

Dr K.W. Jager of the IPCS Central Unit was responsible for the scientific content of the monograph, and Mrs M.O. Head of Oxford, England, for the editing.

The fact that industry made proprietary toxicological information available to the IPCS and the Task Group on the products under discussion is gratefully acknowledged. This allowed the Task Group to make its evaluation on a more complete data base.

The efforts of all who helped in the preparation and finalization of the document are gratefully acknowledged.

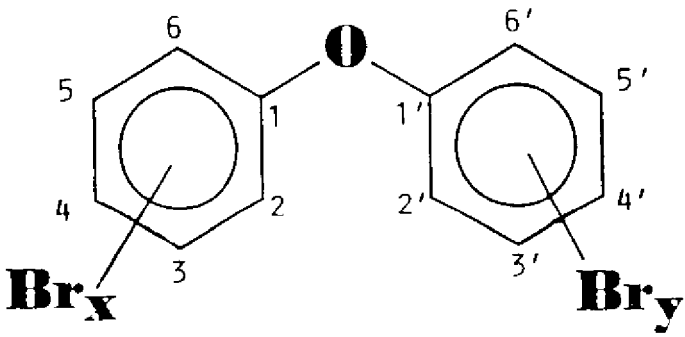
BROMINATED DIPHENYL ETHERS

GENERAL INTRODUCTION

1. GENERAL REMARKS

This Environmental Health Criteria monograph on brominated diphenyl ethers has been prepared as part of an overview on the impact of a number of flame retardants on human health and the environment. The group of polybrominated diphenyl ethers (PBDE) has been selected as a priority because of the recent interest in these substances. Only products based on penta-, octa-, and decabromodiphenyl ethers are of commercial interest.

The general chemical formula of brominated diphenyl ethers is:



Polybrominated diphenyl ethers (PBDE) have a large number of congeners, depending on the number and position of the bromine atoms on the two phenyl rings. The total number of possible congeners is 209, and the numbers of isomers for mono-, di-, tri- up to decabromodiphenyl ethers are: 3, 12, 24, 42, 46, 42, 24, 12, 3, and 1, respectively.

The commercial PBDE are produced by the bromination of diphenyl oxide under certain conditions, which result in products containing mixtures of brominated diphenyl ethers (see the individual PBDE). The compositions of commercial DeBDE, OBDE, and PeBDE are given in Table 1.

Table 1. Composition of commercial brominated diphenyl ethers

Product	Composition								
	PBDE[a]	TrBDE	TeBDE	PeBDE	HxBDE	HpBDE	OBDE	NBDE	DeBDE
DeBDE								0.3-3%	97-98%
OBDE					10-12%	43-44%	31-35%	9-11%	0-1%
PeBDE		0-1%	24-38%	50-62%	4-8%				
TeBDE[b]	7.6%	-	41-41.7%	44.4-45%	6-7%				

[a]Unknown structure.
[b]No longer commercially produced. Analysis of one single sample.

No, or virtually no, data are available on dibromo-, tribromo-, hexabromo-, heptabromo-, and nonabromodiphenyl ether (DiBDE, TrBDE, HxBDE, HpBDE, and NBDE, respectively). Flame retardants containing predominantly penta-, octa- and decabromodiphenyl ethers are commercially produced (with tetrabromodiphenyl ether as a major component of "pentabromodiphenyl ether", which is a mixture).

The commercial PBDE are rather stable compounds with boiling points ranging between 310 and 425 °C and with low vapour pressures, e.g., 3.85 up to 13.3 Pa at 20-25 °C; they are lipophilic substances. Their solubility in water is very poor, especially that of the higher brominated diphenyl ethers, and the *n*-octanol/water partition coefficients (log P_{ow}) range between 4.28 and 9.9.

Polybrominated diphenyl ethers have not been reported to occur naturally in the environment, but other types of brominated diphenyl ethers have been found in marine organisms (Carte & Faulkner, 1981; Faulkner, 1990).

The presence in the environment of some of the brominated diphenyl ethers has been documented, the highest concentration being 1 g/kg sediment in streams or ponds in the vicinity of a manufacturing facility.

Data on environmental fate, although limited to MBDE, DiBDE, and DeBDE, suggest that biodegradation is not an important degradation pathway for the PBDE, but that photodegradation may play a significant role.

Many reports have appeared in the literature describing the behaviour of brominated flame retardants under pyrolytic conditions. In general, these reports have indicated that maximum concentrations of PBDF and/or PBDD were observed at temperatures of 400-800 °C and that the 2,3,7,8-substituted compounds were seen only in very low concentrations.

Processing of the polymers under abusive or extreme conditions produced higher levels of PBDF, but the concentrations were significantly lower than the values previously reported from laboratory pyrolysis studies. 2,3,7,8-Brominated isomers were only found at low levels in a sample abusively processed. The 2,3,7,8-brominated isomers, which are of concern for toxicological

and regulatory reasons, were not detected under normal processing conditions. The results of the laboratory pyrolysis experiments with PBDE, showed that PBDF and/or PBDD were formed in various concentrations, depending on the type of PBDE, the polymer matrix, the specific processing conditions (temperature, presence of oxygen, etc.) and equipment used, and the presence of Sb_2O_3. Behaviour of PBDE is strongly dependent upon the polymer matrix and upon the specific processing conditions mentioned above, thus laboratory pyrolysis experiments can hardly be used as reliable models to predict behaviour in commercial moulding operations.

2. GENERAL INFORMATION ON BROMINATED DIPHENYL ETHERS

2.1 Analytical methods

Several methods to determine residues of PBDE in various media (air, sewage sludge, sediment, human adipose tissue, marine organisms, fish, and feed) as well as in commercial products have been reported. For details, see Table 2.

In general, sample extraction and clean-up techniques for the analysis of PBDE residues in biological samples are similar to those developed for PBB (see EHC 152: *Polybrominated biphenyls*), though the chromatographic conditions have to be modified in view of the long retention times of the highly brominated PBDE. Temperature programming and the use of capillary columns have been found to be very useful for the separation of the different congeners of PBDE. Recovery for the different PBDE is generally higher than 80%. Most methods are based on extraction with organic solvents, such as hexane/acetone, hexane/diphenyl ether, acetone, etc, purification of the extracts by gel permeation or adsorption chromatography, and determination mainly by gas chromatography, either with electron capture detection (ECD), or, coupled with mass spectrometry (MS). A multi-residue method has also been developed that includes a multi-step separation enabling the determination of several polychlorinated and polybrominated pollutants in biological samples (Jansson et al., 1991).

2.2 Production levels and processes

According to the information given by the European Brominated Flame Retardant Industry Panel (EBFRIP), eight manufacturers are currently producing polybrominated diphenyl ethers. They are: Dead Sea Bromines/Eurobrome (The Netherlands); Atochem (France); Ethyl Corporation (USA); Great Lakes Chemical Corporation (USA); Tosoh (Japan); Matsunaga (Japan); Nippo (Japan); Great Lakes Chemical Ltd (United Kingdom).

Table 2. Analytical methods for PBDE

Sample	Extraction and clean-up	Separation and detection	Limit of determination	Reference
Sewage	extract with chloroform; evaporate and dissolve residue in ethanol	GC/MS	0.06 mg/kg	Kaart & Kokk (1987)
Sediment	extract with acetone; clean-up on Florisil	NAA; GC/EC	< 5 µg/kg < 5 µg/kg	Watanabe et al. (1987b)
Fish	extract with acetone-hexane + hexane-ethyl ether; treatment with sulfuric acid or clean-up on alumina; chromatography on silica gel	GC/EC; GC/MS	limit of detection 0.1 mg/kg fat	Andersson & Blomkvist (1981)
Animal tissues (Multi-residue method)	homogenize; extract with *n*-hexane-acetone; treatment with sulfuric acid; gel permeation chromatography; chromatography or silica gel; chromatography or activated charcoal	GC/MS (NCI)	10 ng/kg	Jansson et al. (1991)
Rat liver	extract with tetrahydrofuran	HPLC		Rogers & Hill (1980)

Table 2 (continued)

Fish	extract freeze-dried powdered sample with pet. ether; gel permeation chromatography; clean-up on Florisil; elute with hexane	GC/MS (NCI/SIM)	< 5 μg/kg fat	Krüger (1988)
Cow's milk	centrifuge; gel permeation chromatography; clean-up on Florisil; elute with hexane	GC/MS (NCI/SIM)	< 2.5 μg/kg fat	Krüger (1988)
Human milk	extract with potassium oxalate/ethanol/diethyl ether/pentane; gel permeation chromatography; clean-up on Florisil; elute with hexane	GC/MS (NCI/SIM)	< 0.6 μg/kg fat	Krüger (1988)
Human adipose tissue	extract with methylene chloride; evaporate; clean-up on silica gel followed by clean-up on alumina and on a carbon/silica gel column	HRGC/HRMS[a]	limit of detection 0.73-120 ng/kg (different congeners)	Cramer et al. (1990a,b)
Commercial PBDE	homogenize and dissolve in tetrachloromethane for HPLC and GC/MS or *n*-hexane for TLC/UV	HPLC; GC/MS; TLC/UV	-	deKok et al. (1979)

[a]High resolution gas chromatography/high resolution mass spectrometry.

The annual global consumption of PBDE is 40 000 tonnes (30 000 tonnes of DeBDE; 6000 tonnes OBDE and 4000 tonnes PeBDE) (Arias, 1992).

It has been reported that the use of brominated flame retardants in Japan increased from 2500 tonnes in 1975 to 22 100 tonnes in 1987 (Watanabe & Tatsukawa, 1990).

The production and import figures for the European Economic Community (EEC) are given in Table 3.

Table 3. Production and import quantities of PBDE in metric tonnes in the EEC[a]

	1986	1987	1988	1989
Production	4276	3624	4066	3843
Import	4310	3492	4955	7103
Total	8586	7116	9021	10 946

[a]From: EBFRIP (1990).

Data on the usage of PBDE are available for some individual European countries. Germany uses 3000-5000 tonnes/year, Sweden 1400-2000 tonnes/year, and The Netherlands 3300-3700 tonnes/year (OECD, 1991; van Zorge, 1992), but Pijnenburg & Everts (1991) and Pijnenburg et al. (1992) reported a level of 2500 tonnes PBDE for the last country. In the United Kingdom, up to 2000 tonnes per year are used (UK DOE, 1993).

Because of the significant reduction in the fire hazard for the public achieved by the use of PBDE in a wide range of applications, particularly in the furniture industry, and electrical/computer components and housing, the consumption of PBDE has significantly increased over the last years (EBFRIP, 1990).

2.3 Resins, polymers, and substrates in which PBDE are used

The major uses of the polybrominated diphenyl ethers in descending order of importance are: high-impact polystyrene, ABS, flexible polyurethane foam, textile coatings (not clothing),

wire and cable insulation, electrical/electronic connectors and other interior parts. These applications account for at least 80-90% of the consumption of brominated diphenyl ethers in the USA.

Brominated diphenyl ethers are used as additive flame retardants. Additive flame retardants are incorporated into the plastic matrix like other additives, such as plasticizers. The ideal additive is inexpensive, colourless, easily blended, compatible, heat and light stable, efficient, permanent, and has no deleterious effect on the properties of the base polymer. The most important limitations are incompatibilities that affect the physical properties of the polymers and the tendency for additives to be fugitive. These additive flame retardants are much more prone to leaching or escape from the finished polymer product than the reactive flame retardants (Hutzinger et al., 1976; Hutzinger & Thoma, 1987; Larsen, 1980).

The uses of penta-, octa-, and decabromodiphenyl ethers in the different resins, polymers, and substrates are shown in Table 4. The principal applications of these PBDE-containing substances are shown in Table 5.

PBDE are used in the different resins, polymers, and substrates at levels ranging from 5 up to 30%. The quantities used for each application are not publicly available. In consumer products, resins containing PBDE are typically used in interior parts, minimizing the potential for exposure of the public. The incorporation of the PBDE into the polymer matrix further reduces the possibilities of exposure (EBFRIP, 1990).

Table 4. Use of penta- (PeBDE), octa- (OBDE), and decabromodiphenyl ethers (DeBDE) in resins, polymers, and substrates[a]

Resins/polymers/substrates	DeBDE	OBDE	PeBDE
ABS		X	
Epoxy-resins	X		
Phenolic resins	X		X
PAN	X		
PA	X	X	
PBT	X	X	
PE/XPE	X		
PET	X		
PP	X		
PS, HIPS	X	X	
PVC	X		X
PUR			X
UPE	X		X
Rubber	X		X
Paints/lacquers	X		X
Textiles	X		X

[a]From: EBFRIP (1990); UK Department of Environment (1992).

Table 5. The various applications of resins in which PBDE are used are listed below[a]

Polymer	Principal applications	Examples of final products
ABS	Moulded parts	TV-sets/business machines, computer housings, household appliances (hairdryer, curler), automotive parts, electronics, telecommunications
EPOXY	Circuit boards, protective coatings	Computers, ship interiors, electronic parts
PAINTS/ LACQUERS	Coatings	Marine and industry lacquers for protection of containers
PHENOLICS	Printed circuit boards	Paper laminates/glass prepregs for printed circuit boards
PAN	Panels, electrical components	Lighting panels for elevators and rooms, housing of electrical appliances
PA	Electrical connectors, automative interior parts	Computers, connectors, housing in electrical industry, board, electrical connectors, automotive industry, transportation
PBT	Electrical connectors and components	Switches, fuse, switch box, computer housings, switchboard electrical connectors, stereos, business machines, military electronics
PE/XPE	Cross-linked wire and cable, foam tubing, weather protection and moisture barriers	Major application: power cable with cross-linked low density PE; also used for conduit for building with high density PE; Final uses: portable apparatus building control, instrument, shipboard, automotive, marine appliances, insulation of heating tubes
PET	Electrical components	Boxes, relays, coils, bobbins

Table 5 (contd)

PP	Conduits, electronic devices	TV and electronic devices, such as yoke, housings, circuit board hangers, conduits; Final uses: electro-mechanical parts TV, hot waste water pipes, underground junction boxes
PS, HIPS	TV cabinets and back covers, electrical appliance housings	TV back panels, computer covers and housings of electrical appliances, office machines, smoke detectors
PVC	Cable sheets	Wire and cables, floor mats, industrial sheets
PUR	Cushioning materials, packaging, padding	Furniture, sound insulation panels, wood imitations, transportation
RUBBER	Transportation	Conveyor belts, foamed pipes for insulation
TEXTILES	Coatings	Back coatings, impregnation: carpets, automotive seating, furniture in homes and official buildings, aircraft, undergrounds, tents, trains, and military safety clothing
UPE	Circuit boards, coatings	Electrical equipment, coatings for chemical processing plants mouldings, military and marine applications: construction panels

[a]From: EBFRIP (1990).

3. FORMATION OF BROMINATED DIBENZOFURANS AND DIBENZODIOXINS FROM POLYBROMINATED DIPHENYL ETHERS

3.1 General

Polybrominated dibenzofurans (PBDF) and polybrominated dibenzodioxins (PBDD) can be formed from polybrominated diphenyl ethers, polybrominated phenols, and polybrominated biphenyls under different conditions, including heating (combustion). Laboratory experiments have also demonstrated the formation of PBDF and PBDD during the pyrolysis of certain other brominated flame retardants (see the EHC on *Brominated flame retardants*, in preparation). As discussed in EHC 88: *Polychlorinated dibenzo*-para-*dioxins and dibenzofurans*, there are hundreds of possible congeners of halogenated dibenzofurans and dibenzo-dioxins. However, only congeners with substituents in the 2,3,7,8-positions are of toxicological significance. In many reports, only the total levels of PBDF and PBDD are given, without regard to substitution pattern; such totals are of limited value in the estimation of possible risk.

Hutzinger & co-workers investigated the pyrolysis of brominated flame retardants and flame retardant polymer systems and several publications have appeared. In general, the results reported showed that brominated dibenzofurans were observed at 700-800 °C and that the 2,3,7,8-substituted compounds were seen in only low concentrations, if at all (Thoma et al., 1987a,b; Thoma & Hutzinger, 1987; Dumler et al., 1989).

Shortly after the initial reports of Buser and Hutzinger, BFRIP and German chemical companies (Bayer, BASF, and Hoechst) and American industries independently reported the results of combustion and pyrolysis experiments with flame retarded polymers (BFRIP, 1990).

Recently, brominated aromatic compounds have also attracted attention, since reports have appeared about emissions of PBDD and PBDF and other brominated and mixed halogenated aromatic compounds in accidental fires and from the combustion of waste (see section 4 of both DeBDE and OBDE).

For more information on these pyrolysis experiments, see the different sections relating to the individual brominated diphenyl ethers, e.g., PeBDE, OBDE, and DeBDE.

As an example, the formation of PBDF and PBDD from decabromodiphenyl ether is illustrated in Fig. 1.

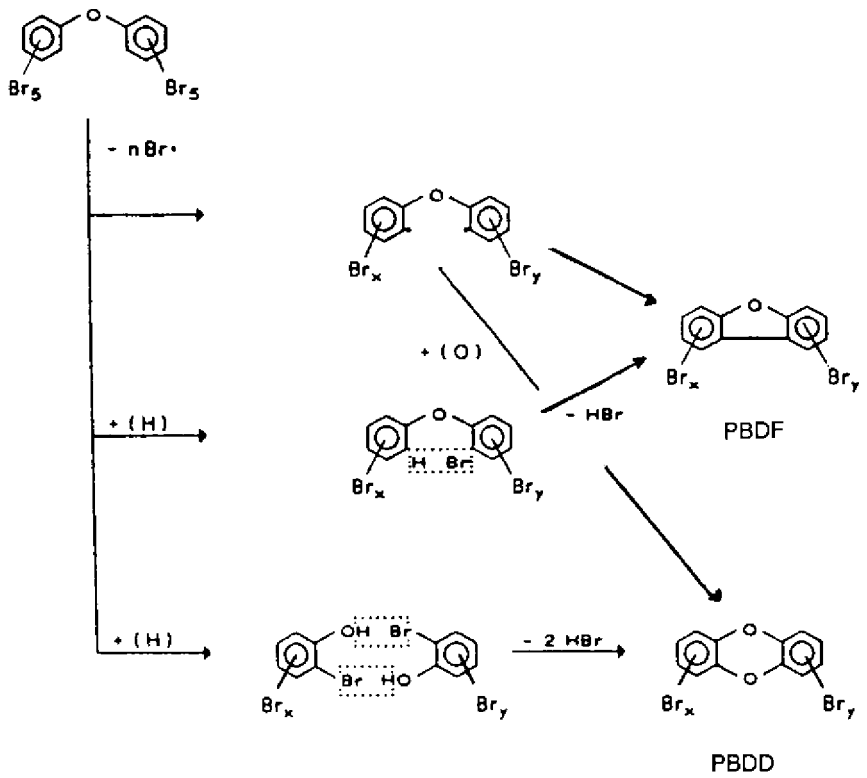


Fig. 1. Possible mechanisms for the formation of PBDF and PBDD from decabromodiphenyl ether. From: Bienek et al. (1989).

3.2 Additional data on the pyrolysis of non-specified PBDE and/or polymers containing non-specified PBDE

The earliest published work on the pyrolysis of brominated flame retardants was that of Buser, whose first paper appeared in 1986 (Buser, 1986). Buser pyrolysed three technical PBDE mixtures with different degrees of bromination from commercial sources (pentabromo-, 71% bromine; octabromo-, 79% bromine (predominantly hexa- to nonabrominated PBDE) and decabromo-, 83% bromine, 97% DeBDE) at 510-630 °C in small quartz vials. The vials were placed in a heated oven for about one minute, and the contents analysed.

A range of PBDD and PBDF was found with a total yield of up to 10%. HRGG/MS analysis revealed the formation of reasonably simple mixtures of reaction products with often one or two main PBDF- and PBDD-isomers. Debromination reactions lead to lower brominated PBDF and PBDD congeners. In general, the higher brominated PBDE lead to higher brominated PBDF and PBDD. Most likely, the PBDF and PBDD are formed in intramolecular cyclization reactions involving the attack by oxygen on the diphenyl ether system (Fig. 1) (Buser, 1986; Bieniek et al., 1989).

The next report to appear in the literature was also in 1986 from the laboratory of Hutzinger. Hutzinger's group pyrolysed penta- and decabromodiphenyl ethers at 700, 800, and 900 °C, in a quartz tube oven, for about 10 min. They did not provide any isomer-specific results, but they reported the formation of PBDF and PBDD. Hutzinger continued to investigate the pyrolysis of brominated flame retardants and brominated flame retardant polymer systems, and several publications appeared (Thoma et al., 1987a,b; Thoma & Hutzinger, 1987; Dumler et al., 1989a). In general, the results reported in these publications were consistent with those of earlier work in that maximum concentrations of PBDF were observed at 700-800 °C and 2,3,7,8-substituted compounds were seen only in very low concentrations, if at all.

Shortly after the initial reports of Buser and Hutzinger, BFRIP and German chemical companies (Bayer, BASF and Hoechst) independently reported the results of combustion and pyrolysis experiments with flame retarded polymers.

In the German work, pyrolysis studies were conducted with high-impact polystyrene/DeBDE, polypropylene/DeBDE, and ABS/OBDE (Neupert et al., 1989) (see also individual flame retardants). In all of these studies, the pyrolysis residues were analysed for the presence of PBDD and PBDF. While brominated PBDF were identified, only very small quantities of 2,3,7,8-TeBDF were observed (see Table 6) (BFRIP, 1990).

Table 6. Analytical results from the pyrolysis products of ABS/OBDE (Bayer)[a]

Compound	Concentration	
	Test 1 (ppm)	Test 2 (ppm)
Brominated dibenzodioxins	ND[b]	ND[b]
Brominated dibenzofurans:		
MBDF	115	60
DiBDF	10 000	7500
TrBDF	8000	2500
TeBDF	2000	2500
2,3,7,8-TeBDF	< 0.1	< 8
PeBDF	1700	2000
HxBDF	530	470
HpBDF	< 1.4	32
OBDF	< 3	< 2.5

[a]From: BFRIP (1990).
[b]ND = Not detectable.

Other brominated pyrolysis products of PBDE may be formed by cleavage and oxidation, including PBBz, phenol, and some naphthalenes. PBDF, however, may also be formed from small reactive species generated during PBDE cleavage (Umweltbundesamt, 1989; Buser, 1986) (see also the individual brominated diphenyl ethers).

Table 7. Thermal decomposition products from a mixture of two commercial PBDE (1:1 w/w)[a]

Product	Maximum yield (%)	
	Nitrogen (650 °C)	Air (625 °C)
Dibromobenzenes	0.35	ND[c]
Tribromobenzenes	0.64	0.92
Tetrabromobenzenes	0.43	0.95
Unknown (pentabromobenzenes?)	0.04	0.24
Brominated alkanes, alkenes, and other PICs[b]	1.40	0.77
DiBDF	0.03	ND[c]
TrDBF	0.03	0.03
TeBDF	0.03	0.03
DiBDD	ND[c]	0.04
TrBDD	ND[c]	0.04
TeBDD	ND[c]	0.01

[a]From: Striebich et al. (1991).
[b]PICs = Products of incomplete combustion.
[c]ND = Not detectable.

Striebich et al. (1991) examined gas phase oxidative and pyrolysis thermal decomposition of a 1:1 percentage weight mixture of two commercial polybrominated diphenyl ether products (tri- through deca-bromination). The gas phase material was quantitatively transported to a quartz thermal reactor and subjected to a series of controlled time/temperature exposures (300-800 °C for 2.0 seconds) in either air or a nitrogen atmosphere. Thermal decomposition products were identified. Isomers with higher levels of bromination were generally more stable than lower brominated diphenyl ethers, under both oxidative and pyrolytic conditions. Table 7 shows the approximate yields of products from brominated diphenyl ethers. At 800 °C, all products were decomposed to HBr or non-detectable products, in both air and nitrogen. Neither PBDF/PBDD nor any parent material could be detected at this temperature.

4. WORKPLACE EXPOSURE STUDIES

4.1 Exposure to PBDE

Inhalation exposure to brominated diphenyl ethers is expected to be low, since the vapour pressure of these chemicals is in the range of 10^{-7} mmHg. Particulates in the respirable range are expected to be formed during the grinding of solids. As inhalation of dust is possible, the use of dust respirators and gloves/goggles is recommended in areas of potential exposure.

Dermal exposure may occur during filtration, drying, drumming/bagging, size reduction, and maintenance (US EPA, 1986).

Exposure to these compounds can also take place during processing (incorporation into various polymers) and the use of the polymer blend to fabricate the final articles. After processing, the resin is generally in the form of pellets rather than powder. Exposure is expected to be low at fabrication sites because of the low vapour pressure and of ventilation controls (US EPA, 1986).

4.2 Exposure to PBDF/PBDD

Workers may be exposed to PBDF/PBDD during the production and processing of plastics containing PBDE as flame retardants and of products made from them. In addition, workers and the general population may be exposed to PBDF/PBDD when products, particularly from the electrical, electronic, and computer industries, emit PBDF/PBDD during normal operations (see section 4 of both DeBDE and OBDE).

The PBDF/PBDD contents of component parts taken from 6 electrical appliances (including printers, TV sets, and computer terminals) as well as two casings were determined. PBDF/PBDD were detected in 16 of the materials; mainly higher brominated PBDF at concentrations of between 0.007 and 4.2 mg/kg (sum of MBDF to HxBDF/MBDD to HxBDD) were found (Hamm & Thiesen, 1992).

Determination of PBDE and PBDF concentrations in air and dust samples were made in offices having a large number of TV or computer monitors in operation: the police traffic control office in Hamburg (47 monitors; room 100 m^2, 6 m high, 23 °C) and three rooms of a television company with monitors (20 °C).

In the police traffic control office, air samples were taken for 3 days at a level of 1.5 m above the floor, a total of 84 m^3 air being drawn, and analysed. Dust samples were taken from the monitors from a total surface of 3 × 10 m (39 g).

In the first room of a television company (50 m^2), where 58 monitors were in use, a total of 129 m^3 air was taken over 5 days. In the second room (40 m^2),where 38 monitors were in use, 126 m^3 air was taken, while in the third room (30 m^2), where 42 monitors were in use, 145 m^3 air was taken. Dust samples were also collected once a day from all rooms using a vacuum cleaner.

The concentrations in air of the police station and the television company ranged between 0.29 and 1.27 pg PBDF/m^3 and 97 pg PBDE/m^3. Indoor dust contained PBDF at low ppb and PBDE at high ppb levels. 2,3,7,8-substituted PBDF were not detected (limit of determination between 0.3 and 0.1 pg/m^3) (Ball et al., 1992).

5. EXPOSURE OF THE GENERAL POPULATION

5.1 General population

Limited information is available on the exposure of the general population to brominated diphenyl ethers. Uptake of TeBDE and PeBDE may occur in humans via the foodchain, e.g., by consuming fish. In Germany, PBDE has been detected in human and cow's milk at levels of 2.6 and 3 μg/kg fat, respectively (Krüger, 1988).

Remmers et al. (1990) found evidence of the occurrence of polychlorinated diphenyl ethers (PCDE) and PBDE in human adipose tissue specimens from the USA, during the analysis of these tissues for dioxins and furans. The results showed the presence of HxBDE/HxCDE through to DeBDE/DeCDE in the tissues analysed.

The presence of brominated diphenyl ethers was indicated in all of the 47 samples analysed (Cramer et al., 1990a,b). The human samples were composites derived from all parts of the USA and covering ages ranging from birth to > 45 years. Additional work is needed to confirm the presence of these compounds, which have been found provisionally in the following frequencies and concentrations; HxBDE (72%; nd-1000 ng/kg); HpBDE (100%; 1-2000 ng/kg) and OBDE (60%; nd-8000 ng/kg). DeBDE was found in only a few samples at concentrations of 0.4-0.7 ng/kg.

Exposure may also mainly occur through skin contact (flame retardants in polymers used in textiles), but also via inhalation (release of flame retardants from the polymer matrix) (US EPA, 1986).

5.2 Possible exposure to PBDE and PBDF/PBDD

5.2.1 Television sets

Studies were carried out to determine whether PBDF escape from TV sets. Four air samples (2 parallel to each other) were taken over 3 days in a closed room (volume 26.8 m^3), where a new TV set was operating for 17 h/day. The surface temperature

of the TV set (back panel) was 38-40 °C. One sampling was performed above the TV set, while the others were carried out in the centre of the room (2.2 m from the TV set). The levels in the centre of the room of tri-, tetra-, penta-, and hexabromodibenzofurans were 25, 2.7, 0.5, and 0.1 pg/m^3, respectively (levels in outdoor air ranged from < 0.05 to 0.16 pg/m^3). Above the TV set, the concentrations of the 4 PBDF were 143, 11, 0.5, and < 0.1 pg/m^3. Hepta- and octabromodibenzofuran, and polybrominated dibenzodioxins were not found (limits of determination 0.1 and 0.2 pg/m^3, respectively) (Bruckmann et al., 1990).

An investigation was conducted to determine the emissions of PBDE and PBDF from plastics in two TV sets, one colour and one monochrome, two computer monitors, and three printers, under conditions of use. Analytical methods were refined to obtain a reliable determination of PBDF. Each appliance was placed, under conditions of use, in a test chamber. The volume of the steel chamber was 1.17 m^3 (1.5×1.07×0.82 m). For three days, pure air was continuously drawn through the chambers at a rate of 1.5 m^3/h; the emitted compounds were absorbed on a sampler for the subsequent extraction and determination of PBDE and PBDF with 4 or more bromines. PBDF concentrations were found to vary between not detected (limit of detection 3-10 pg) and 1799 pg per appliance tested and PBDE concentrations, between 0.4 and 889 ng/appliance; 2,3,7,8 isomers (1070 pg/appliance) were detected only from the colour TV set (Ball et al., 1991).

Three new television sets were placed in a 1.81 m^3 test chamber. Two of the cabinets were made from polystyrene, which was flame retarded with 11.5% DeBDE. The third television set was made of high-impact polystyrene, treated with DeBDE/Sb_2O_3 as a flame retardant. PBDF and PBDD concentrations were determined in air collected over 3 days while the two television sets were operating and during one day when the third TV set was operating. The concentrations of TeBDD, PeBDD, TeBDF, and PeBDF ranged between 0.09 and 1.52 pg/m^3 (Ranken et al.,1990).

5.2.2 *Fire tests and fire accidents*

Six appliances and 2 casings were burned in a fire test room (floor area 21 m^2, volume 48 m^3), which was kept closed during the fire tests and slowly ventilated after extinguishing the fires

(worst case conditions). After the fire test, samples of combustion residues and smoke condensate were taken. Smoke was collected in 5 tests. The combustion residues showed the presence of PBDF and PBDD in concentrations ranging between 1 and 1930 mg/kg and from the casing components almost 1%. Smoke condensate from contaminated surfaces contained levels of between 6 and 1610 μg monobromo- up to hexabromodibenzofuran/dibenzodioxin per m^2. Smoke contained 11-1700 μg monobromo- up to hexabromo- dibenzofuran/dibenzodioxin per m^3 (see Table 8) (Hamm & Theisen, 1992).

Residues and smoke condensates resulting from actual fire accidents with 9 TV sets were examined. PBDF/PBDD concentrations in the residues were mainly in the μg/kg range, one value being 107 mg/kg. Close to the fire site, the PBDF/PBDD area contamination concentrations were between 0.1 and 13.1 $\mu g/m^3$ (see Table 9) (Hamm & Theisen, 1992).

It was concluded that the levels of PBDF/PBDD produced in real fires are much lower than those produced under fire-test conditions.

Table 8. PBDF/D concentrations in original components of electrical appliances and in samples from fire tests with these appliances or with their casings[a]

Object of investigation	Original components		Fire test samples		
	Casings	Printed circuit boards	Combustion residues	Smoke condensate	Smoke
	Total mono- to hexaBDF/D µg/g (ppm)	Total mono- to hexaBDF/D µg/g (ppm)	Total mono- to hexaBDF/D µg/g (ppm)	Total mono- to hexaBDF/D µg/m³	Total mono-to hexaBDF/D µg/m³
Casing of electrical appliance 1	0.63	-[b]	8700	177	-[b]
Casing of electrical appliance 2	0.64	-[b]	7750	1610	-[b]
Electrical appliance 3	-[c]	1.77	468	106	456
Electrical appliance 4	0.06	3.44	43	260	355
Electrical appliance 5	0.81	1.98	18	396	1700
Electrical appliance 6	4.20	0.35	1930	234	1350
Electrical appliance 7	-[c]	0.13	1	6	11
Electrical appliance 8	1.26	0.007	24	323	-[b]

[a]From: Hamm & Thiesen (1992).
[b] = Not determined.
[c] = Not detectable.

Table 9. PBDF/D-concentrations in residues and smoke condensates from real fire accidents with television sets[a]

Fire accident (Case number)	Combustion residues	Smoke condensates	
		Close to fire site	At some distance from fire site
	Total mono- to hexaBDF/D µg/g (ppm)	Total mono- to hexaBDF/D µg/m²	Total mono- to hexaBDF/D µg/m²
I	0.235	10.7	0.665
II	0.004	0.134	0.102
III	0.209	13.1	0.382
IV	0.009	ND[b]	ND[b]
V	0.001	4.82	1.39
VI	0.017	0.759	0.425
VII	0.001	0.021	0.008
VIII	0.001	10.5	5.37
IX	107	7.47	0.847

[a]From: Hamm & Thiesen (1992).
[b]ND = Not detectable.

6. ENVIRONMENTAL POLLUTION BY PBDE

6.1 Ultimate fate following use

Products containing PBDE are disposed of in the normal domestic waste stream (landfill and incineration).

No studies are available on the fate of PBDE-containing products in landfills, but there is concern that the PBDE may eventually leach out. Bearing in mind that PBDE, at least the congeners with more than 3 bromine atoms, are persistent in the environment, the introduction of such chemicals into widespread products may be a considerable long-term diffuse source of emissions of these compounds to the environment. This type of source is difficult to control and the unnecessary use of persistent organic compounds should be avoided.

Formation of PBDF and/or PBDD as a result of landfill fires is also a possibility, though no data are available on the scale of this source. The results of pyrolysis experiments showed that PBDE can form PBDF and PBDD (in much smaller quantities) under a wide range of heating conditions (see General Introduction sections 3.1 and 3.2). If chlorine is present, mixed halogenated furans/dioxins can also be generated (Oberg et al., 1987; Zier et al., 1991). Unless sufficiently high temperatures and long residence times are maintained, PBDF/PBDD can be generated during the incineration of products containing PBDE. They can also result from poorly-controlled combustion gas cooling. Modern, properly operated municipal waste incineration (MWI) should not emit significant quantities of PBDF/PBDD, regardless of the composition of the municipal waste.

Lahl et al. (1991) reported increases in dibenzofuran and dibenzodioxin levels in filter dust, when products containing PBDE were added to the feed-stock. Riggs et al. (1990) reported PBDF generation when a flame retarded resin was burnt under simulated MWI conditions. However, Oberg et al. (1987) reported no increased emissions of dibenzodioxins when the bromine content of an incineration feed-stock was increased. Monobromodichloro-dibenzofuran levels were slightly increased. Oberg & Bergström (1990) conducted further experiments with a hazardous waste

incinerator, to study the relationship between bromine levels in municipal waste and incinerator dibenzodioxin and dibenzofuran emissions. They concluded that no unacceptable environmental risks were associated with the incineration of brominated compounds in plants with good combustion conditions equipped with efficient flue gas cleaning. They further noted that only 0.0125% of the feed to Swedish MWIs was brominated waste.

6.2 Air

Watanabe et al. (1992) reported on the presence of PBDE in the air in Taiwan and Japan. The concentrations in the air samples collected in Taiwan from a recycling plant in January 1991 were, in general, higher than those in Japan; 3 samples were analysed in Taiwan, and 5 in Japan. Tribromo-, tetrabromo-, pentabromo-, and hexabromodiphenyl ethers were present in the following mean concentrations: Taiwan, 32, 52, 23, and 31 pg/m^3, and, Japan, 7.1, 21, 8.9, and 21 pg/m^3, respectively.

6.3 Soil

Two ash and two soil samples were collected in Taiwan from a recycling plant in January 1991 and analysed for the presence of PBDE. Tri-, tetra-, penta-, hexa-, and decabromodiphenyl ethers were present in ash in the following concentrations 20-20, 130, 78-110, 47-54, and 510-2500 μg/kg, respectively; the concentrations in soil were 38-40, 75-104, 41-84, 20-23 and 260-330 μg/kg, respectively. Hepta- and octabromodiphenyl ether were not found (Watanabe et al., undated).

6.4 Water

Marine, estuarine, and river water samples were analysed for the presence of the different PBDE. Except for monobromodiphenyl ether, levels of all the higher brominated PBDE were below the detection limit. MBDE was mainly found in the surroundings of manufacturing plants in the USA (US EPA, 1986).

6.5 Sediments and sewage sludge

In Japan, Spain, Sweden, and the USA, studies were carried out to determine the presence of the different PBDE in marine, estuarine, or river sediment. PBDE were mainly found in river sediment. In general, the levels were below 100 μg/kg dry weight, except in rivers in the vicinity of manufacturing plants. In these cases, the concentrations were much higher. In a river in Sweden, concentrations of 11.5 mg DeBDE, 0.8 mg TeBDE, and 2.8 mg PeBDE/kg dry weight were found. In the USA, at a manufacturing plant, as much as 1 g DeBDE/kg was found (Zweidinger et al., 1978; DeCarlo, 1979; Environment Agency Japan, 1983, 1989, 1991; Watanabe et al., 1986, 1987b; Fernandez et al., 1992).

The upper layers in a laminated sediment core from the Baltic Sea (Bornholm Deep) contained higher levels of TeBDE and PeBDE than the deeper layers, indicating an increasing burden of these compounds (Nylund et al., 1992).

A series of samples of sewage sludges from municipal waste water treatment plants in Germany were analysed for poly-halogenated compounds, such as halogenated diphenyl ethers. Tribromo- to heptabromodiphenyl ethers were found at relatively high concentrations (Hagenmaier et al., 1991). Sewage sludge was analysed in Sweden for the presence of TeBDE and PeBDE. Concentrations of 15 and 19 μg/kg, respectively, were found (Sellström et al., 1990a,b).

6.6 Aquatic vertebrates

The presence of PBDE depends mainly on the degree of bromination. DeBDE, OBDE, and HxBDE were not found in mussel and fish samples collected in Japan. No data are available for HpBDE. However, PeBDE was found in mussel and fish species in concentrations of < 3 μg/kg wet weight in Japan. Concentrations of 22 μg 2,2′,4,4′,5-PeBDE/kg wet weight were found in cod liver collected in the North Sea, and concentrations of up to 64 μg/kg on a fat basis were found in fish collected in Sweden. The concentrations were much higher in fish collected in the vicinity of industrial areas, e.g., up to 9.4 mg/kg on a fat basis (Jansson et al., in press). Levels for TeBDE, mainly 2,2′,4,4′-

TeBDE, were comparable but generally higher. Mussels and fish in Japan contained up to 14.6 μg/kg wet weight, cod liver collected in the North Sea, 360 μg/kg, and eel from the Netherlands, up to 1700 μg/kg fat. Different species of fish collected in Sweden contained up to 88 mg/kg fat (Andersson & Blomkvist, 1981; Watanabe, 1987; Watanabe et al., 1987b; De Boer, 1989, 1990). An increasing trend was observed in PeBDE and TeBDE levels in freshwater fish in Sweden. Only limited data are available concerning lower brominated PBDE (Jansson et al., in press).

Thirty-five samples of 18 freshwater fish collected in German rivers, and 17 samples collected from the Baltic Sea and the North Sea contained 18.2-983.6 and 0.6-119.9 μg PBDE/kg fat (determined as Bromkal 70-5DE), respectively (Kruger, 1988).

6.7 Aquatic mammals

Three bottle-nose dolphins (*Tursiops truncatus*), collected during the 1987/88 mass mortality event along the central and south Atlantic coast of the USA, were analysed for brominated diphenyl ethers. The concentrations of PBDE were 200, 220, and 180 μg/kg lipid (Kuehl et al., 1991).

Limited data are available on the presence of PBDE in aquatic mammals. 2,2'4,4'5-PeBDE was found in ringed and grey seals, collected in Sweden, in concentrations of 1.7 and 40 μg/kg fat, respectively. TeBDE, mainly 2,2',4,4'-TeBDE, was also found in the blubber of these 2 species in concentrations of 47 and 650 μg/kg fat, respectively (Jansson et al., in press). Seals collected at Spitzbergen contained approximatey 10 μg PBDE/kg fat, determined as Bromkal 75DE (Kruger, 1988).

6.8 Terrestrial vertebrates

Pooled samples of rabbits, moose, and reindeer, collected in Sweden, contained PeBDE and TeBDE in concentrations of < 0.3, 0.64, and 0.26 μg 2,2',4,4',5-PeBDE/kg and < 2, 0.82, and 0.18 μg 2,2',4,4'-TeBDE/kg lipid, respectively (Jansson et al., in press).

Four samples of cow's milk were analysed in Germany for the presence of PBDE. The average concentration was 3.572 μg/kg fat (range 2.536-4.539 μg/kg) determined as Bromkal 70-5DE. The main component was HxBDE (Krüger, 1988).

6.8.1 Birds

Limited data are available on the presence of PBDE in birds. In Sweden, 2,2',4,4',5-PeBDE was found in the muscle tissue of osprey, in newborn starlings, and in guillemot eggs in concentrations of 140, 2.3-4.2, and 24-260 μg/kg lipid, respectively. A trend towards increasing concentrations of PeBDE and TeBDE in guillemot eggs from the Baltic Sea was observed. 2,2',4,4'-TeBDE was found in the muscle tissue of osprey in concentrations of up to 1800 μg/kg. Guillemots collected from the Baltic Sea, the North Sea, and Spitzbergen contained 370, 80, and 130 μg/kg on a fat basis, respectively (Jansson et al., 1987, 1993).

In the USA, indications were found that dibromodiphenyl ether was present in the eggs of fish-eating birds, but it was not quantified (Stafford, 1983).

6.8.2 Humans

In Germany, 25 samples of breast milk were analysed for the presence of PBDE. The ages of the women ranged between 24 and 36 years and most of them were breast-feeding their first or second child. The samples contained 0.6-11.1 μg PBDE/kg fat, determined as Bromkal 70-5DE. The main component was HxBDE. One sample from a Chinese woman showed 7.7 μg PBDE/kg fat; a sample from another woman, exposed occupationally to hydraulic fluids and tranformer oils, contained 50 μg PBDE/kg fat. This last value was excluded from the given range and average. (Krüger, 1988).

DECABROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS, AND RECOMMENDATIONS

1.1 Summary and evaluation

1.1.1 Identity, physical and chemical properties

Typically, commercial DeBDE has a purity of 97-98%, with 0.3-3.0% of nona- and/or octabrominated diphenyl ethers. Nonabromodiphenyl ether (NBDE) is the major impurity. In contrast to the other polybrominated diphenyl ethers there is only one isomer of DeBDE.

The melting point of DeBDE is approximately 300 °C and decomposition occurs above 400 °C. Solubility in water is 20-30 μg/litre and the log of the *n*-octanol/water partition coefficient is greater than 5. Vapour pressure is $< 10^{-6}$ mmHg at 20 °C.

1.1.2 Production and uses

Among the brominated diphenyl ethers (mono- to deca-), decabromodiphenyl ether is the most important commercial product with regard to production and use.

Commercial DeBDE has been produced in increasing degrees of purity since the late 1970s. The global production of DeBDE is approximately 30 000 tonnes/year. It is used as an additive flame retardant in many plastics, especially high-impact polystyrene, and in the treatment of textiles used in soft furnishing, automobile fabrics, and tents.

1.1.3 Environmental transport, distribution, and transformation

Photodegradation of DeBDE occurs in organic solvents under ultraviolet radiation (UVR) or sunlight; lower brominated diphenyl ethers and brominated dibenzofurans are formed. Photodegradation also occurs, to a lesser extent, in water with sunlight; however, lower brominated diphenyl ethers and brominated dibenzofurans have not been found.

Levels of DeBDE extracted from polymers are close to, or below, the limit of detection, depending on the polymer type and extraction solvent.

Because of its extremely low water solubility and vapour pressure, DeBDE is likely to be transported primarily by adsorption to particulate matter. It is persistent and likely to accumulate in sediment and soil.

No data are available on its bioavailability from sediment and soil. A study on rainbow trout did not show any bioaccumulation in flesh, skin, or viscera, over 48 h. DeBDE is unlikely to bioaccumulate because of its high relative molecular mass.

Products containing commercial DeBDE will eventually be disposed of by landfill or incineration. DeBDE may eventually leach from landfills. Polybrominated dibenzofurans (PBDF) and mixed halogen-dibenzofurans and -dibenzodioxins may result from landfill fires and inefficient incineration. Products containing commercial DeBDE may contribute to these emissions.

Pyrolysis of both commercial DeBDE itself and polymers (HIPS, PBT, industrial polypropylene) containing DeBDE, in the presence of oxygen, produced PBDF, polybrominated dibenzodioxins (PBDD) being found to a lesser extent. The maximum formation of PBDF occurs at 400-500 °C, but it can occur at temperatures up to 800 °C, and Sb_2O_3 plays a catalytic role in the formation of PBDF and PBDD.

The formation, and amounts found, of PBDF and PBDD depend on temperature, oxygen content, and length of pyrolysis. In the absence of oxygen, mainly polybromobenzenes and polybromonaphthalenes are formed.

1.1.4 Environmental levels and human exposure

DeBDE has been identified in air in the vicinity of manufacturing plants at concentrations of up to 25 $\mu g/m^3$. DeBDE was not detected in water samples collected in Japan in the period 1977-91. However, it was detected in river and estuarine sediment, collected in Japan in the same period, at concentrations of up to approximately 12 mg/kg dry weight. DeBDE (up to 1 g/kg) was also found in the USA in river sediment close to one manufacturing plant. DeBDE was not detected in fish samples

collected in Japan, but, in one mussel sample, a level just above the level of detection was found. DeBDE was not detected in human adipose tissue samples collected in Japan, but, in the USA, DeBDE was found in 3 out of 5 samples of human adipose tissue.

Human exposure to DeBDE can occur in the course of manufacture and formulation into polymers. Exposure of the general population to DeBDE is insignificant.

Determination of occupational exposure to the breakdown products of DeBDE during manufacture, formulation, or use, showed that air samples close to the extruder head contained high concentrations of PBDF. Lower levels were found in the air of the workroom. PBDF was also found in wipe samples. The application of good engineering techniques has been shown to reduce occupational exposure to PBDF.

Exposure of the general population to PBDF impurities in flame retarded polymers is unlikely to be of significance.

1.1.5 Kinetics and metabolism in laboratory animals and humans

DeBDE is poorly absorbed from the gastrointestinal tract and is rapidly excreted following injection.

The results of metabolic studies on the rat, using ^{14}C labelled DeBDE, indicated a half-life for the disappearance from the body of less than 24 h and that the principal route of elimination following oral ingestion was via the faeces. No appreciable ^{14}C activity (less than 1%) was found in either urine or expired air.

Rats fed 0.1 mg/kg body weight per day, for up to two years, showed no accumulation of DeBDE in serum, kidneys, muscle, or testes, as estimated from total bromine determination. Bromine accumulation in the liver plateaued at 30 days and was cleared within 10 days following treatment. After 180 days of treatment, the bromine level in the liver of treated rats was no greater than that in control rats. Adipose tissue accumulated low levels of total bromine, which remained after 90 days of clean diet; the nature of the retained "bromine" is not known. Since DeBDE accounted for only 77% of the commercial mixture used, "bromine" could have been derived from NBDE or OBDE.

1.1.6 Effects on laboratory mammals and in vitro test systems

The acute toxicity of DeBDE for laboratory animals is low. The substance is not an irritant to the skin or eyes of rabbits. It is not chloracnegenic on the skin of rabbits and is not a human skin sensitizer.

The combustion products of flame retarded polystyrene containing DeBDE and Sb_2O_3 were tested for acute toxicity and comedogenicity. The rat oral LD_{50} of the soot and char was > 2000 mg/kg body weight.

In short-term toxicity studies on rats and mice, DeBDE (purity > 97%) at dietary levels of 100 g/kg (4 weeks) or 50 g/kg (13 weeks; equivalent to 2500 mg/kg body weight for the rat) did not induce adverse effects. A one-generation reproduction study on rats showed no adverse effects with dose levels of 100 mg/kg body weight. DeBDE did not cause any teratogenic effects in the fetuses of rats administered a dose level of 100 mg/kg body weight. With 1000 mg/kg body weight, malformations, such as delayed ossification, were seen. DeBDE was not shown to be mutagenic in a number of tests.

In a carcinogenicity study on rats and mice, DeBDE (purity 94-99%) was administered at dietary levels of up to 50 g/kg. An increase in the incidence of adenomas (but not carcinomas) was found in the livers of male rats receiving 25 g/kg and female rats receiving 50 g DeBDE/kg. In male mice, increased incidences of hepatocellular adenomas and/or carcinomas (combined) were found at 25 g/kg and an increase in thyroid follicular cell adenomas/carcinomas (combined) at both dose levels. Female mice did not show any increase in tumour incidence. There was equivocal evidence for carcinogenicity in male and female rats and male mice only at dose levels of 25-50 g DeBDE/kg diet. As the results of all mutagenicity tests have been negative, it can be concluded that DeBDE is not a genotoxic carcinogen. IARC (1990) concluded that there was limited evidence for the carcinogenicity of DeBDE in experimental animals. The very high dose levels, lack of genotoxicity, and minimal evidence for carcinogenicity indicate that DeBDE, at the present exposure levels, does not present a carcinogenic risk for humans.

1.1.7 Effects on humans

No evidence for skin sensitization was found in 200 human subjects exposed to DeBDE in a sensitization test.

A morbidity study of extruder personnel blending polybutyleneterephthalate containing DeBDE, with consequently potential exposure to PBDD and PBDF for 13 years, did not reveal any deleterious effects, even though 2,3,7,8-TeBDF and -TeBDD were detected in the blood. Results of immunological studies showed that the immune system of the exposed persons was not adversely affected in 13 years.

1.1.8 Effects on other organisms in the laboratory and field

The EC_{50}s for the growth of 3 marine unicellular algae were greater than 1 mg DeBDE/litre. No further information is available on the effects of DeBDE on other organisms in the laboratory and field.

1.2 Conclusions

1.2.1 DeBDE

DeBDE is widely used incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure is very low since the DeBDE is not readily extracted from polymers. The acute toxicity of DeBDE is very low and there is minimal absorption from the gastrointestinal tract. Thus, risk to the general population from DeBDE is considered to be insignificant.

Occupational exposure is to DeBDE in particulate form. The control of dust during manufacture and use will adequately reduce the risk for workers.

DeBDE is persistent and binds to particulate matter in the environment; it is likely to accumulate in sediment. It is unlikely to bioaccumulate. Current evidence suggests that environmental photodegradation in water does not lead to the formation of lower brominated diphenylethers or brominated dibenzofurans, but little is known about degradation in other media.

There is minimal information on the toxicity of DeBDE for organisms in the environment.

1.2.2 Breakdown products

Formation of PBDF and, to some extent, PBDD may occur when DeBDE, or products containing it, are heated to 300-800 °C. The possible hazards associated with this have to be addressed.

Properly controlled incineration does not lead to the emission of significant quantities of brominated dioxins and -furans. Any uncontrolled combustion of products containing DeBDE can lead to an unquantified generation of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future Environmental Health Criteria on PBDF/PBDD.

PBDF have been found in the blood of workers involved in the production of plastics containing DeBDE. No adverse health effects have been associated with this exposure. Good engineering controls can prevent worker exposure to PBDF.

1.3 Recommendations

1.3.1 General

- Workers involved in the manufacture of DeBDE and products containing the compound should be protected from exposure through the application of appropriate industrial hygiene measures, the monitoring of occupational exposure, and engineering controls.

- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled, to minimize environmental contamination with this persistent material and its breakdown products.

- Manufacturers should minimize levels of impurities in commercial DeBDE products, using the best available techniques. A purity of 97% or higher is recommended.

- Incineration should only be carried out in properly constituted incinerators, running at consistently optimal conditions. Burning by any other means may lead to the production of PBDF and/or PBDD.

1.3.2 Further studies

- Further studies on the bioavailability and toxicity of sediment-bound DeBDE should be performed on relevant organisms.

- Continued monitoring of environmental levels is required.

- The generation of PBDF under real fire conditions should be further investigated.

- Environmental biodegradation, and photodegradation in compartments other than water, should be further studied.

- Investigation into possible methods and consequences of recycling of DeBDE-containing polymers should be made.

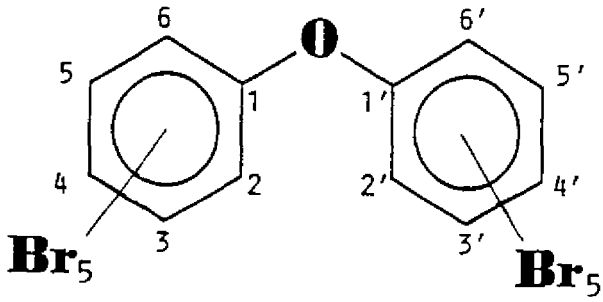
- Analytical methods for DeBDE in various matrices should be validated.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

2.1.1 Pure substance

Chemical structure:



Chemical formula:	$C_{12}Br_{10}O$
Relative molecular mass:	959.22
Chemical name:	decabromodiphenyl ether (DeBDE); decabromodiphenyl oxide
CAS registry number:	1163-19-5 (61345-53-7, mixture of decabromodiphenyl oxide and Sb_2O_3)
CAS name:	1,1′-oxybis[2,3,4,5,6-pentabromo]-benzene
IUPAC name:	bis(pentabromophenyl) ether
EINECS registry number:	214604

MITI number:	3-2846
Synonyms:	decabromobiphenyl ether; decabromobiphenyl oxide; Decabrom; ether, bis(pentabromophenyl); ether, decabromodiphenyl

From: US EPA (1984); Ethyl Corp. (1992a).

On the basis of the chemical structure, decabromodiphenyl ether is fully brominated and there is only one congener.

2.1.2 Technical product

Trade names:	FR-300 BA; DE-83-RTM; Saytex 102; Saytex 102E; FR-1210; Adine 505; AFR 1021; Berkflam B10E; BR55N; Bromkal 81; Bromkal 82-ODE; Bromkal 83-10 DE; Caliban F/R-P 39P; Caliban F/R-P 44; Chemflam 011; DE 83; DP 10F; EB 10FP; EBR 700; Flame Cut BR 100; FR 300BA; FR P-39; FRP 53; FR-PE; FR-PE(H); Planelon DB 100; Tardex 100; NC-1085; HFO-102; Hexcel PF1; Phoscon Br-250; NCI-C55287 Caliban-F/RP-44 is a DeBDE mixture with antimony oxide, and, F/RP-53 contains 60% DeBDE, which is used in conjunction with THP-salts finishes and an acrylic binder.

Commercial DeBDE is typically composed of 97-98% decabromodiphenyl ether with 0.3-3.0% other brominated diphenyl ethers (BFRIP, 1990) (see Table 1). Nonabromodiphenyl ether isomers are the major impurities. The commercial product typically contains a minimum of 81-83% bromine (IARC, 1990) (83% theoretical; Ethyl Corp. 1992a).

Differences in manufacturing processes affect the nature and amounts of impurities in the product (Larsen, 1980). Today's commercial product is considerably purer than that manufactured in the past. Isomers of nonabromodiphenyl ether and octabromodiphenyl ether have been reported as impurities in DeBDE (Timmons & Brown, 1988). FR-300-BA, produced in the early 1970s (no longer a commercial product), was composed of 77.4% DeBDE, 21.8% NBDE, and 0.8% OBDE (Norris et al., 1975c). Later production of DeBDE, by the same manufacturer, ranged in composition from 94 to 99% DeBDE with 0.3-4.5% impurities (NBDE isomers were identified as the major impurities) (NTP, 1986). Other DeBDE products, e.g., DE-83, Saytex 102E, and Bromkal 82-0DE have a purity of approximately 93 to 98.5% with different quantities of impurities (Dow Chem. Comp., 1978; De Kok et al., 1979; Davidson & Ariano, 1986).

The availability of a technical product (possibly FR-1208) of 88.1% purity containing 11% nona-, and 0.5% octabromodiphenyl ether, and 0.1% hexabromobenzene has been reported (Klusmeier et al., 1988).

In Japan, a DeBDE is produced containing about 3% of nonabromodiphenyl ether as an impurity (Watanabe & Tatsukawa, 1987).

2.2 Physical and chemical properties

Commercial DeBDE is a free-flowing, odourless, off-white powder, with a bromine content of 81-83% and a high melting point.

Melting point:	290-306 °C	
Decomposition point, DTA	> 320, > 400, and 425 °C (different products)	
Volatility: TGA (% weight loss)	1%	319 °C
	5%	353 °C
	10%	370 °C
	50%	414 °C
	90%	436 °C
Specific gravity:	3.0, 3.25	at 20 °C

Vapour pressure:	$< 10^{-6}$	20 °C
(mmHg)	< 1	250 °C
	2.03	278 °C
	5.03	306 °C
Solubility:	water	20-30 μg/litre
(at 25 °C)	cottonseed oil	600 mg/litre
	saturated copra oil	920 mg/litre
	acetone	0.5, 1.0 g/litre
	benzene	1.0, 4.8 g/litre
	chlorobenzene	6.0 g/litre
	methylene bromide	4.2 g/litre
	methylene chloride	1.0, 4.9 g/litre
	o-xylene	8.7 g/litre
	methanol	1 g/litre
	toluene	2 g/litre
	methyl ethyl ketone	1 g/litre
	pentane	< 1 g/litre
	styrene	< 1 g/litre
Stability:	stable under normal temperatures and pressures	
Flash-point:	none	
Flammability:	non-flammable	
Autoignition point:	not applicable	
n-Octanol/water partition coefficient (log P_{ow}):	5.24; 9.97*	

From: Norris et al. (1973, 1974, 1975a,c); Tabor & Bergman (1975); US EPA (1986); Chemag. (1988); Great Lakes Chemical Corporation (1990b); IARC (1990); Kopp (1990); Watanabe & Tatsukawa (1990)*; Bromine Compounds Ltd. (1992); Ethyl Corp. (1992a).

2.3 Analytical methods

The detection and quantification of DeBDE have been investigated by several authors. The methods are based on gas-liquid chromatographic separation using different detection methods, such as electron capture detection and mass spectrometry (see General Introduction, section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

DeBDE has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

DeBDE is produced by the bromination of diphenyl oxide in the presence of a Friedel-Crafts catalyst (Larsen, 1978). It is manufactured in a batch process in enclosed vessels during both the reaction and the drying cycle (US EPA, 1988; IARC, 1990).

Commercial production of DeBDE in the USA began in 1976. Among brominated flame retardants, the quantities produced rank second only to the quantities of tetrabromobisphenol A. There are 2 manufacturers in the USA (BFRIP, 1992). IARC (1990) reported 2 manufacturers in Belgium, 1 each in Switzerland, the United Kingdom, and Israel, and 5 in Japan (US EPA, 1988).

About 30 000 tonnes of DeBDE are used annually throughout the world. About 40% of this total is used (in combination with antimony trioxide) in high-impact polystyrene applications, such as television and radio cabinets. Textile applications, such as a polyester fibre additives and coatings for automobile fabric, tarpaulins, and tents account for about 900 tonnes (IARC, 1990; OECD, 1991; Arias, 1992).

The annual consumption of DeBDE in Japan was 1000 tonnes in 1976, 2900 tonnes in 1984, 4000 tonnes in 1987, and 9800 tonnes in 1991, mainly used for polystyrene, polyester, and polypropylene (Watanabe, 1987; Watanabe et al., 1987b; Watanabe et al., undated). Recently published figures from a Japanese study showed that the consumption of PBDE (mainly DeBDE) in Japan was about 20-30% of the total consumption of brominated flame retardants (OECD, 1991).

In the Federal Republic of Germany, 1800-2000 tonnes were used in plastics in 1988. DeBDE mixed with antimony trioxide and DeBDE used in conjunction with tetrakis (hydroxymethyl) phosphonium (THP) salt finishes and an acrylic binder are used to blend 50/50 and 65/35 with polyester/cotton (Ulsamer et al., 1980).

An estimation of the use of decabromodiphenyl ether in the Netherlands in 1988 was 1100-1300 tonnes (Anon, 1989).

3.2.2 Uses

DeBDE is a non-reactive, additive flame retardant widely used for its high bromine content, thermal stability, and cost effectiveness. It is used in thermoplastic resins, thermoset resins, textiles, adhesives, and coatings. The major applications are for high-impact polystyrene, cross-linked polyethylene polybutyl-eneterephthalate, glass-reinforced thermoset and thermoplastic polyester moulding resins, low density polyethylene extrusion coatings, non-drip polypropylene (homo and copolymers), acrylo-nitrile-butadiene-styrene rubber (ABS), nylon, adhesives, epoxy resins, polyvinylchloride, and elastomers. The concentrations of DeBDE in the polymers range from 6 to 22% (Tabor & Bergman, 1975; Flick, 1986; NTP, 1986; Kaart & Kokk, 1987; IARC 1990).

A mixture of DeBDE and antimony trioxide has been used to treat nylon and polyester/cotton fabrics for industrial safety apparel and tents (LeBlanc, 1979). DeBDE is also used in the insulating materials for wire and electrical cable (IARC, 1990).

In the United Kingdom, approximately 1000-1200 tonnes DeBDE is used per year in the textile industry (back coatings on synthetic fibres) (United Kingdom Department of Environment, 1992).

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

4.1 Transport and distribution between media

4.1.1 Extraction from polymers

Pellets of ABS (acrylonitrile-butadiene-styrene) terpolymer and polystyrene containing 10% DeBDE, were placed in 2 litres of water and shaken mechanically. Total bromine in water was estimated after 3 h and up to 187 h. Extraction of bromine took place from the ABS, during the first 43 h, in concentrations ranging from < 1.0 to 3.7 mg/litre. No bromine was extracted from polystyrene (limit of determination < 0.5 mg/litre). Because there was no increase in bromine concentration with time, it was suggested by the authors that the levels found were due to erosion and not to extraction. Extraction studies were also carried out under static conditions with pellets of ABS containing 4.25% DeBDE. Water, acetic acid, and cottonseed oil were used as extraction solvents at temperatures of approximately 50 or 60 °C, during 1 or 7 days. Extraction occurred only with cottonseed oil (7 days, 60 °C) at 1 mg DeBDE/litre (limit of determination 0.075 mg/litre) (Norris et al., 1973, 1974, 1975a).

4.2 Biotransformation

No data are available.

4.3 Abiotic degradation

4.3.1 Photodegradation

Studies have been performed on the photodegradation of DeBDE in organic solvents and water. Organic solvents were used in the initial photodegradation studies because of the extremely low water solubility of DeBDE. In xylene, DeBDE was photodegraded by reductive debromination with a half-life of 15 h (Norris et al., 1973, 1975a).

A commercial mixture of DeBDE containing traces of a nonabromodiphenyl ether, was irradiated in hexane solution with UVR and sunlight. A complicated mixture of tri- to octabromodiphenyl ether congeners was detected. Furthermore, a large number of PBDF containing 1-6 bromo atoms was formed. The yield of the PBDF under the experimental conditions was approximately 20% of the total amount of DeBDE, after 16 h of irradiation by UVR and approximately 10% by sunlight. The formation and distribution of photoproducts by sunlight were similar to those of UVR, though a few differences could be recognized in both, i.e., the decomposition rate of DeBDE and the total amount of, and kinds of, PBDF formed. Polybromobenzenes were also found in minor quantities in this experiment. The formation of PBDF appeared to occur secondarily from debrominated diphenyl ethers as photoproducts of DeBDE, but not directly from DeBDE (Watanabe & Tatsukawa, 1987).

The xylene studies showed that DeBDE photodegraded readily, but did not provide any indication of the nature of the stability of the decomposition products of DeBDE in an aqueous environment. The proposed stepwise photoreduction of DeBDE in xylene could lead to the formation of lower brominated diphenyl ethers, which might be more stable to UVR. However, in water, photohydroxylation would be the favoured route and the hydroxyl substituted degradation products would decompose rapidly via increased UV absorption. This was demonstrated when DeBDE in water was exposed to actual sunlight over a 3-month period (10 g DeBDE in 8 litres of water). This study was conducted to determine whether stable lower brominated diphenyl ethers were formed that would show increased persistence over DeBDE. Analysis (by GC/MS) of the exposed water solution after 31, 66, and 98 days showed a significant increase in bromine concentration relative to the unexposed 98-day sample. After 98 days, the bromine concentration corresponded to the breakdown of about 300 times the initial amount of DeBDE soluble in water. Xylene extracts of the water phase of both 98-day samples were analysed using electron capture gas chromatography. Levels of 4-monobromodiphenyl ether and 4,4′-dibromodiphenyl ether were quantified and found to be < 5 and < 2 ppb, respectively. In no case did the exposed sample show an increase in any peak, with

retention times similar to those of the lower brominated diphenyl ethers.

The products of the photodegradation of DeBDE in water are not lower brominated diphenyl ethers (Norris et al., 1973, 1975a).

4.3.2 Pyrolysis

A commercial DeBDE, FR 300 BA (77% DeBDE), was heated in a quartz tube at 700, 800, and 900 °C and the concentrations of PBDD and PBDF determined. The residues contained tetra- to octabromodibenzofurans together with hepta- and octabromo-dioxins; the optimal formation temperatures were 800 and 900 °C (Thoma et al., 1987a; Zacharewski et al., 1988).

FR 300 BA (77%) was pyrolysed at 600, 700, 800, and 900 °C in the absence of oxygen in a SGE pyrojector and the residues were analysed using GC/MS in an on-line operation. Polybromobenzenes (PBB), polybromonaphthalenes (PBN), and polybrominated dibenzofurans were detected in the pyrolysate. Sixty percent of the starting products were decomposed at 600 °C, hexabromobenzene being formed as the main component together with traces of pentabromobenzenes and nonabromodiphenyl ether. At a higher temperature (700 °C), the pentabromobenzene concentration increased and tetrabromobenzenes were also formed. Maximum amounts of hepta- and octabromodibenzofurans and hexabromonaphthalenes were produced at this temperature. At 800 °C and higher, an increase in levels of tetra- and pentabromobenzenes was observed. During these reactions, the C-O bond is cleaved followed by the attachment of a bromine atom. C-C ring closure leading to dibenzofuran formation is very strongly suppressed by DeBDE (Thoma & Hutzinger, 1987, 1989).

In the case of decabromodiphenyl ether (DeBDE), a total amount of 1-2% PBDF and PBDD was formed on thermolysis of DeBDE. At a temperature of 630 °C, 90% of DeBDE was decomposed. The major products were PBBz (tri- to hexabrominated). A heptabromodibenzofuran was a main product, though tetra- to heptabromodibenzofurans and tetra- to octabromodibenzodioxins were also found. In these experiments, PBDF and PBDD were formed, which contained at least one or

two, respectively, bromine substituents less than the PBDE in the technical product; often the same major isomers were present (Buser, 1986).

4.3.3 Combustion of polymers containing DeBDE

4.3.3.1 Pyrolysis studies

Clausen et al. (1987), Bieniek et al. (1989), and Lahaniatis (1989) studied the influence of the combustion temperature on the formation of PBDD and PBDF from plastics containing DeBDE. The results of the experiments with PBT with 10% DeBDE/6% Sb_2O_3 at temperatures of 400, 500, 600, 700, and 800 °C in the presence of air, showed the formation of PBDFs at mg/kg (ppm) concentrations. 2,3,7,8-TeBDD was not found with a limit of determination of 10 mg/kg. Maximum formation of TeBDF (4000 mg/kg) occurred at 400 °C, and, with increasing temperature, concentrations decreased. No PBDF were formed in the thermolysis of PBT with DeBDE but without Sb_2O_3. The results are summarized in Table 10.

Comparable experiments were reported by Lahaniatis et al. (1991). The formation of 2,3,7,8-tetrabromodibenzodioxin and -furan from various polymers with DeBDE or PBDE were studied in thermolysis experiments at 400, 600, and 800 °C. The polymers studied were PBT with 10% DeBDE with, or without, 6% Sb_2O_3, epoxide resin (ER) with 3-6% DeBDE, and phenol resin (PR) with 3-6% of PBDE and copper. The concentrations of the TeBDD and TeBDF at the 3 temperatures are given in Table 11. The 2,3,7,8-TeBDD concentrations ranged from 0.01 to 7 mg/kg and the 2,3,7,8-TeBDF concentrations from 0.01 to 52 mg/kg. The concentrations decreased with increasing temperature, and were low at 800 °C.

Pure DeBDE and commercial polybutyleneterephthalate polymer samples containing DeBDE and antimony trioxide have been pyrolysed at temperatures ranging from 300 to 800 °C. The experiments were carried out in a vertical combustion apparatus. The polymer/DeBDE samples were: polybutylene-terephthalate (PBT) with 11% DeBDE and 5.5% Sb_2O_3, PBT with 9% DeBDE and 7% Sb_2O_3, and PBT with 11% DeBDE and 2.7% Sb_2O_3 (Dumler et al., 1989a,b). The results of the pyrolysis studies are

Table 10. Thermolysis products of PBT with 10% decabromodiphenyl ether and 6% Sb_2O_3[a]

	400 °C	500 °C	600 °C	700 °C	800 °C
Bromodiphenyl ether					
MBDE	10	50	-	-	-
DiBDE	30	100	-	-	-
TrBDE	100	200	50	-	-
TeBDE	500	300	-	-	-
PeBDE	800	400	-	-	-
HeBDE	1000	400	-	-	-
HpBDE	500	400	-	-	-
OBDE	(500)	-	-	-	-
Bromodibenzofuran					
MBDF	100	300	100	50	-
DiBDF	500	400	200	10	-
TrBDF	3000	2000	400	-	-
TeBDF	4000	3000	600	-	-
PeBDF	4000	1000	200	-	-
HxBDF	1000	200	-	-	-
HpBDF	(500)	-	-	-	-

[a] From: Clausen et al. (1987); Bieniek et al. (1989).
Semiquantitative values in mg/kg based on the sample - not confirmed.
2,3,7,8-Tetrabromodibenzofuran was not found (limit of determination 20 mg/kg).
2,3,7,8-Tetrabromodibenzodioxin was not found (limit of determination 10 mg/kg).

given in Table 12. TeBDF were formed, with yields of up to 16%, from the 3 polymer samples. PBDF were mainly formed during pyrolysis in the presence of DeBDE and Sb_2O_3. At 300 °C, the conversion of DeBDE to PBDF was low, while highly brominated compounds were formed. By increasing the temperature, the yield of polybrominated compounds increased and

Table 11. Generation of 2,3,7,8-TeBDD/TeBDF by thermolysis of plastics with flame retardants as additives in mg/kg[a,b]

Compound	2,3,7,8-TeBDD			2,3,7,8-TeBDF		
Sample	400 °C	600 °C	800 °C	400 °C	600 °C	800 °C
PBT/DeBDE/Sb_2O_3	0.02	0.01	-[c]	52	5.7	-
PBT/DeBDE	-[c]	-[c]	-[c]	2.5	4.2	0.08
Five samples of ER/DeBDE						
minimum	0.05	0.3	0.01	0.4	0.6	0.01
maximum	0.3	0.8	0.03	1.0	2.5	0.04
PR/DeBDE/Cu	-[d]	7	-[d]	-[d]	5.7	-[d]

[a]From: Lahaniatis et al. (1991).
[b]The mg/kg values are based on the material used.
[c]Non-detected, detection limit 0.01 mg/kg.
[d]= Not determined.

Table 12. Results of pyrolysis studies

A. Polymer Sample A: Polybutyleneterephthalate with 11% decabromodiphenyl ether and 5.5% antimony (III) oxide (yields in mg/kg, relative to the flame retardant)[a]

	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
MBDF	-	754	3012	5551	3513	3076
DiBDF	9	2357	10 219	15 343	8445	1547
TrBDF	9	10 747	37 911	32 751	28 592	1274
TeBDF	9	14 979	52 634	37 437	35 963	1511
PeBDF	55	2293	18 391	20 666	13 504	555
HxBDF	703	127	3713	10 438	2639	109
HpBDF	1320	-	246	946	491	-
OBDF	-	-	-	-	-	-

Table 12 (continued)

B. Polymer Sample B: Polybutyleneterephthalate with 9% decabromodiphenyl ether and 7% antimony (III) oxide (yields in mg/kg, relative to the flame retardant)

	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
MBDF	-	-	13 088	7633	8510	1144
DiBDF	-	-	15 754	10 643	9721	244
TrBDF	47	456	34 408	24 842	19 276	44
TeBDF	1472	4544	48 762	35 230	23 353	367
PeBDF	5560	18 132	24 753	16 154	6988	156
HxBDF	2886	24446	18 587	8832	1633	22
HpBDF	420	6910	2877	922	100	-
OBDF	-	-	-	-	-	-

Table 12 (continued)

C. Polymer Sample C: Polybutyleneterephthalate with 11% decabromodiphenyl ether and 2,7% antimony (III) oxide (yields in mg/kg, relative to the flame retardant)

	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
MBDF	-	2202	3413	2129	610	18
DiBDF	-	5187	6124	1674	82	-
TrBDF	-	15 033	15 952	1738	36	15
TeBDF	-	17 836	17 463	901	9	12
PeBDF	-	9127	3349	391	-	-
HxBDF	464	2457	901	82	-	-
HpBDF	2375	1329	246	36	-	-
OBDF	traces	traces	-	-	-	-

Table 12 (continued)

D. Decabromodiphenyl ether (yields in mg/kg)

	300 °c	400 °c	500 °c	600 °c	700 °c	800 °c
MBDF	-	-	-	-	-	2
DiBDF	4	8	-	3	2	1
TrBDF	4	13	-	4	25	3
TeBDF	-	15	11	-	100	102
PeBDF	-	16	218	380	591	218
HxBDF	-	42	109	61	1965	988
HpBDF	-	-	1081	1734	4539	418
OBDF	-	-	-	-	-	-

[a]From: Dumler et al. (1989b).

more lower brominated PBDF were formed. The maximum formation of PBDF occurred between 400 and 500 °C. With increasing temperature, not only ring-closure reactions but also debromination reactions with the predominant formation of tri- and tetra- brominated PBDF may occur. The same reactions probably occur at 600 °C. At these elevated temperatures, PBDD were also detected to a minor extent. The polymers with the lowest amount of Sb_2O_3 gave the lowest PBDF concentrations. With increasing amounts of Sb_2O_3, the concentration of PBDF increased, which suggests that antimony trioxide plays a catalytic role. Pure DeBDE, pyrolysed under the same conditions, produced significantly lower PBDF concentrations than polymers with the flame retardants. In the case of pure DeBDE, the temperature for the maximum formation of PBDF shifted to 700 °C.

A sample (1 g) of industrial polypropylene containing 125 g DeBDE/kg and 75 g Sb_2O_3/kg, and a pure DeBDE sample, without additives, were pyrolysed in a DIN-oven or in a sealed quartz ampoule at temperatures of 400, 600, or 800 °C. Combustion products obtained with the pyrolysis of pure DeBDE (50 mg) in the DIN-oven were mainly hexabromobenzenes and the yields at 400, 600, and 800 °C, were 123, 568, and 6 g/kg, respectively. PBDF/PBDD were found in concentrations of 1, 3, and 2 g/kg at 400, 600, and 800 °C, respectively. At 400 and 600 °C, HxBDF up to OBDF were found in concentrations of between 96 and 1449 mg/kg. At 800 °C, lower PBDF, e.g., TrBDF, TeBDF, and PeBDF, were also present in concentrations ranging between 11 and 35 mg/kg. The concentrations of HxBDF and HpBDF were 81 mg and 959 mg/kg, respectively, but no OBDF was found. The concentrations of PBDD at 400-600 °C for HxBDD up to OBDD were between 6 and 329 mg/kg; at 800 °C, lower brominated compounds, e.g., TrBDD, TeBDD, and PeBDD were also found at concentrations of between 8 and 35 mg/kg. HxBDD up to OBDD were present in concentrations of between 74 and 452 mg/kg. The combustion products of the samples of polypropylene containing DeBDE/Sb_2O_3 were mainly PBDF and PBDD and the concentrations were much higher than from the combustion of the pure DeBDE. MBDF up to HpBDF were present at concentrations of between 4762 and 107 517 mg/kg, 1033 and 49 677 mg/kg, and 353 and 29 147 mg/kg at 400, 600, and 800 °C, respectively. At all 3 temperatures,

TeBDF were found in the highest concentrations. The results with polypropylene containing DeBDE/Sb_2O_3, pyrolysed in a sealed quartz ampoule at 600 °C, showed only MBDF up to PeBDF at concentrations ranging between 8860 and 142 940 mg/kg. The highest concentrations were found for TrBDF and TeBDF. PBDD were not found. From this study, it is clear that pure DeBDE gives much lower PBDF values than polypropylene containing DeBDE/Sb_2O_3 (Dumler et al., 1990).

The formation of PBDD and PBDF during the pyrolysis of PBT containing DeBDE was studied at different temperatures and carrier gas compositions. PBDF were formed at ppm levels. Even when oxygen was available in the carrier gas, PBDD were formed at a much lower level than PBDF. In the presence of 10% oxygen, the maximum yield of tetra- to octabromodibenzofurans was 70 ppm at 600 °C. The yields of 2,3,7,8-TeBDF and 1,2,3,7,8-PeBDF were less than 4.5 ppm. The thermal degradation processes of the polymer were investigated using thermogravimetric analysis. The flame retardant did not exert any influence on the elementary chemical degradation processes. The flame retardant activity of DeBDE consists of the emission of brominated species in the gas phase, which scavenge the propagation radicals and reduce flammability. The mechanisms of formation of PBDD and PBDF from DeBDE in PBT consist of a combination of a condensed phase and a gas phase mechanism (Luijk & Govers, 1992).

Macro-pyrolysis experiments were performed in a quartz tube reactor. The polymer sample, PBT, was inserted in the pre-heated tube and exposed at 400-700 °C for 20 min. The carrier gas was nitrogen, or nitrogen combined with 5% or 10% oxygen. The results are given in Tables 13 and 14. PBDF were formed in all tests with the different carrier gases, but the yield of PBDD was at least two orders of magnitude lower than that of the PBDF. In a nitrogen atmosphere, no PBDD were detected (Luijk & Govers, 1992).

Using GC/MS, Sovocool et al. (1990) analysed pyrolysates of PBT resins (flame retarded with DeBDE) which had been exposed to temperatures of 400 and 600 °C in the presence of oxygen. They found brominated dioxins, brominated dibenzofurans, brominated naphthalenes, brominated benzenes and brominated

Table 13. The yield of PBDF during the pyrolysis of PBT/DeBDE in ppm relative to blend, under different carrier gas conditions[a]

Temperature [°C]	TrBDF	TeBDF	2,3,7,8-TeBDF	PeBDF	1,2,3,7,8-PeBDF	HxBDF	HpBDF	NBDF
				Nitrogen				
400	6.7 (0.8)	3.9 (2.4)	0.15 (0.09)	8.7 (0.5)	0.2 (NS)[b]	10.6 (1.9)	3.7 (0.4)	0.05 (0.00)
500	15.9 (2.8)	14.5 (0.8)	0.6 (0.1)	13.3 (2.5)	0.1 (NS)[b]	9.8 (1.1)	4.8 (0.9)	0.1 (0.1)
600	6.8 (0.4)	4.9 (0.2)	0.2 (0.0)	4.5 (1.8)	0.1 (NS)[b]	2.9 (0.5)	0.7 (0.2)	ND[c]
700	4.2 (0.8)	1.2 (0.1)	0.1 (NS)	0.5 (0.0)	(NS)[b]	0.2 (0.0)	0.06 (0.02)	ND[c]
				Nitrogen + 5% oxygen				
400	4.7 (1.4)	3.6 (1.1)	0.2 (0.1)	3.6 (1.1)	0.1 (NS)[b]	2.9 (1.2)	0.7 (0.3)	ND[c]
500	7.7 (0.7)	6.4 (0.4)	0.4 (0.1)	5.3 (0.1)	0.1 (0.0)	5.3 (0.1)	1.1 (0.0)	ND[c]
600	22.1 (2.7)	17.2 (1.8)	2.4 (0.3)	17.7 (3.2)	0.8 (0.2)	16.8 (1.3)	4.8 (0.3)	0.3 (0.0)
700	15.7 (0.3)	7.6 (0.1)	1.2 (0.0)	6.6 (1.2)	0.4 (0.1)	5.7 (0.2)	1.3 (0.3)	0.08 (0.03)
				Nitrogen + 10% oxygen				
400	9.6 (0.7)	7.5 (1.0)	0.3 (0.1)	7.7 (1.5)	(NS)[b]	5.9 (3.0)	1.8 (1.0)	ND[c]
500	11.0 (0.3)	8.7 (0.5)	0.6 (0.1)	8.8 (0.4)	0.2 (0.0)	8.7 (0.8)	3.7 (0.3)	ND[c]
600	28.8 (3.2)	20.8 (1.8)	3.4 (0.5)	21.6 (3.4)	1.2 (0.2)	17.8 (1.3)	7.6 (1.1)	0.8 (0.1)
700	17.5 (0.7)	10.3 (1.4)	2.0 (0.2)	8.9 (0.3)	0.6 (0.0)	5.3 (0.3)	2.1 (0.3)	0.02 (0.02)

[a]From: Luijk & Govers (1992).
[b]NS = not separable, due to interferences.
[c]ND = not detected (below detection limit).

Table 14. The yield of PBDD during the pyrolysis of PBT/DeBDE in ppb relative to blend, under different carrier gas conditions[a]

Temperature [°C]	TrBDD	TeBDD	2,3,7,8-TeBDD	PeBDD	1,2,3,7,8-PeBDD	HxBDD	HpBDD	NBDD
				Nitrogen + 5% oxygen				
400	NS[b]	NS[b]	NS[b]	NS[b]	NS[b]	ND[c]	ND[c]	ND[c]
500	NS[b]	NS[b]	NS[b]	NS[b]	NS[b]	NS[b]	7 (2)	4 (4)
600	NS[b]	8 (NS[b])	NS[b]	44 (6)	NS[b]	110 (10)	43 (0)	13 (1)
700	NS[b]	5 (1)	NS[b]	19 (6)	NS[b]	40 (5)	8 (2)	ND[c]
				Nitrogen + 10% oxygen				
400	NS[b]	NS[b]	NS[b]	NS[b]	NS[b]	ND[c]	ND[c]	ND[c]
500	6 (NS[b])	NS[b]	NS[b]	3 (NS[b])	NS[b]	48 (NS[b])	16 (NS[b])	ND[c]
600	44 (NS[b])	29 (7)	NS[b]	75 (NS[b])	NS[b]	106 (11)	46 (4)	16 (0)
700	32 (18)	24 (NS[b])	NS[b]	21 (NS[b])	NS[b]	19 (3)	4 (4)	ND[c]

[a]From: Luijk & Govers (1992).
[b]NS = Not separable, due to interferences.
[c]ND = Not detected (below detection limit).

toluenes, brominated biphenyls, and brominated methyldibenzofurans (Me-PBDF). Besides the methyldibenzofurans, other (C2 and C3) alkyl-PBDF were found in the pyrolysates. Numerous congeners of ethyl- (and/or dimethyl)-PBDF and a few propyl (and/or trimethyl or ethylmethyl)-PBDF were detected.

The C2- and C3-alkyl-PBDF found in the pyrolysates exhibited relatively intense (M-CH3)+ fragments, supporting the argument for ethyl-and propyl or ethyl-methyl substitutions rather than dimethyl and trimethyl substitution patterns.

Early in 1987, the General Electric Company (GE) began to investigate the pyrolysis of polybutyleneterephthalate (PBT) flame retardant systems. The initial work was carried out at temperatures of 600-900 °C, but subsequent efforts were at processing temperatures in the range of 200-500 °C. The results showed little or no formation of PBDD at temperatures of 250-400 °C; concentrations of PBDF in the pyrolysed products were as high as about 6000 mg/kg. The concentrations of 2,3,7,8-substituted dibenzofurans were much lower, not exceeding a maximum of 150 mg/kg. The results for PBDD and PBDF were much higher than would be expected, based on the previous work by Buser and Hutzinger. The results were also inconsistent with what was observed in combustion experiments. The explanation was that the exposure times and conditions used did not represent a good model of what would actually occur in moulding equipment (BFRIP, 1990).

In the GE experiments at the Fresenius Institute, an apparatus was used in which a small sample of the polymer in the form of a finely ground powder was exposed to the pyrolysis temperature in a flowing air stream. The pyrolysis time for these samples varied from 10 min at the high temperatures to as much as 1.5 h at the low temperatures. This is in contrast to extrusion and moulding operations in which the polymer is in the form of a molten mass, air is largely excluded, and exposure lasts less than 1 min.

Dumler et al. (1989b) have recently published data from studies on the pyrolysis of PBT/DeBDE resins. This work was conducted in apparatus identical to that used by GE, thus, the results can be compared. In the report by Hutzinger and co-workers, concentrations of PBDF were calculated relative to the flame retardant only. Recalculation of the results by BFRIP

(1990), on the basis of the total polymer, showed general agreement with the GE results (Table 15).

Hutzinger's recent work was summarized in a report by Pohle of the Umwelbundesamt (Umweltbundesamt, 1989). In this work, the tube furnace (DIN Apparatus) and the vertical quartz oven (VCI Apparatus; as used by the Fresenius Institute) were used to pyrolyse polymers containing PBDE at temperatures ranging from 600 to 750 °C. The results showed that PBDF were formed under these conditions, but that 2,3,7,8-TeBDF was only a small fraction of the total. In general, the results were similar to those reported earlier by Hutzinger and GE.

Because of the lack of good data collected under actual operating conditions, BFRIP met with 6 major polymer producers in 1988, to design a series of experiments to investigate the behaviour of DeBDE and OBDE in HIPS, ABS, and PBT under controlled moulding or extrusion conditions. The experiments are outlined in Tables 16 and 25 (in OBDE section 4.2.3). For the three polymer systems, HIPS/DeBDE, ABS/OBDE, and PBT/DeBDE, samples were moulded in the application laboratories of polymer producers. For the moulding operations, the severity of operations ranged from normal to extreme. Normal conditions were those in the middle range recommended by the resin manufacturers for processing. The abusive conditions were at, or slightly above, the maximum recommended exposure time and temperature. The extreme conditions were well above those recommended by the resin manufacturer and resulted in samples with severely degraded physical properties and/or colour.

After moulding, all the samples were analysed by Triangle Laboratories, Research Triangle Park, NC (TLI). Samples were also sent to the US EPA Laboratory in Las Vegas for confirming analyses. The results of these analyses are summarized in Tables 17 and 26 (in OBDE section 4.2.3) and are discussed more fully in the report of this study made at Dioxin'90 (McAllister et al., 1990; BFRIP, 1990). With the exception of a single sample, PBDD were not identified in any of the samples and 2,3,7,8-TeBDF were seen only in this one sample at very low concentrations. In general, the Triangle Park and US EPA results agreed fairly well for the TBDF and TBDD.

Table 15. Comparison of GE and Hutzinger results on pyrolysis of PBT/DeBDE Resin (PBT/11% DeBDE/2.7% antimony trioxide)
All concentrations in mg/kg relative to total polymer[a]

	300 °C		400 °C		500 °C		600 °C		700 °C		800 °C	
Compound	General Electric USA	Dumler et al. (1989)	General Electric USA	Dumler et al. (1989)	General Electric USA	Dumler et al. (1989)	General Electric USA	Dumler et al. (1989)	General Electric USA	Dumler et al (1989)	General Electric USA	Dumler et al. (1989)
MBDF	NA[b]	-		240		370		230		70		ND[c]
DiBDF	-	-		570		673		180		9		-
TrBDF	-	-		1650		1750		190		36		ND[c]
TeBDF	5200	-	2000	1960	1200	1920	490	100	24	4	0.03	NA[b]
2,3,7,8-TeBDF	150	-	64	-	120	-	19	-	0.4	-	0.005	-
PeBDF	5900	-	1200	1003	1300	370	350	40	8	-	0.006	-
1,2,3,7,8-PeBDF	ND[c]	-	ND[c]	-	ND[c]	-	ND[c]	-	ND[c]	-	ND[c]	-
HpBDF	ND[c]	260	ND[c]	150	50	40	3	4	0.1	-	ND[c]	-
OBDF	-	Tr	-	Tr	-	ND[c]	-	ND[c]	-	-	-	-
Total TeBDF-HpBDF	13 450	310	4100	3383	3220	2430	943	234	35	4	0.04	NA[b]

[a]From: BFRIP (1990).
[b]NA = not analysed.
[c]ND = not detected.

Table 16. Moulding studies with two polymer/FR systems at different processing temperatures[a]

Polymer/FR[b]	Severity	Conditions
HIPS/DeBDE	None	Base resin, not moulded
	Normal	215-220 °C, 30- second cycle
	Abusive	235-245 °C, 5-min cycle
	Extreme	265-270 °C, 7-min cycle
PBT/DeBDE	Normal	255 °C, 23-second cycle
	Abusive	255 °C, 5-min cycle
	Extreme	255 °C, 10-min cycle

[a]From: McAllister et al. (1990).

[b] HIPS/DeBDE High impact polystyrene/ 84.3%
DeBDE + 12.0%
antimony trioxide 3.7%
PBT/DeBDE Polybutyleneterepthalate/ 88.0%
DeBDE + 6.5%
antimony trioxide 5.5%

Different interpretations of the analytical results of the 2 laboratories resulted in larger differences in values for hexa- through octa-brominated furans. These data showed that the processing of the resin systems under normal conditions did not change the composition compared with that of the base resin formulation. Even under abusive conditions, there was little generation of PBDF or PBDD. In fact, PBDD were observed in only 2 of the samples under abusive or extreme exposures. 2,3,7,8-Substituted dibenzofurans were not observed, except in one sample in which very low ppb levels were seen (Tables 17 and 26 in OBDE section 4.2.3).

Table 17. Comparison of Triangle Laboratories Inc. (TLI) (Research Triangle Park) and US EPA Laboratory (Las Vegas) results on moulded polymer samples containing various flame retardants. (All concentrations are in mg/kg)[a]

High impact polystyrene with decabromodiphenyl ether								
	Base resin 1222-16-0		Normal 1222-16-1		Abusive 1222-16-2		Extreme 1222-16-3	
Compound	TLI	US EPA	TLI	US EPA[c]	TLI	US EPA[d]	TLI	EPA
Total TBDF	0.01	ND	0.01		0.01	0.002	0.02	ND
PeBDF	0.04	0.004	0.05		0.06	0.02	0.2	0.009
HxBDF	< 5.3	0.95	< 14.3		< 5.5	0.11	< 34.1	0.2
HpBDF[b]	< 0.6	0.72	< 3.5		< 2.1	0.08	< 10.6	2.1
PBDF[b]	< 4.1	0.15	< 9.3		< 7.0	ND	< 35.7	3.2

Table 17 (continued)

PBT with decabromodiphenyl ether

	Base resin		Normal 1222-16-6		Abusive 1222-16-7		Extreme 1222-16-8	
Compound	TLI	US EPA	TLI	US EPA[d]	TLI	US EPA	TLI	US EPA[e]
Total TeBDD		< 0.001	< 0.0002	< 0.002	0.001			
Total PeBDD		< 0.001	< 0.0002	< 0.013	0.006			
Total TeBDF		0.003	0.003	0.007	0.03	0.2	1.0	
Total PeBDF		0.02	0.002	0.09	> 7.8	> 25	> 54	
Total HxBDF		0.11	0.013	1.1	> 16.1	> 120	> 7.0	
Total HpBDF[b]		0.31	< 4.3	3.0	< 4.6	58.5	< 12.1	
Total OBDF[b]		0.95	< 16.9	3.2	< 9.9	7.5	< 68.8	

[a]From: BFRIP (1990). Values preceeded by < are maximum possible. Analytical signals met identification criteria, but may include contribution from interferences. US EPA and TLI used different identification criteria, resulting in differences in reported values.

[b]Concentrations of HpBDF and OBDF from TLI are not validated because of lack of standards. Concentrations are reported for comparison only.

[c]Sample 1222-16-1 was spilled during workup.

[d]Average of 2 analyses of same sample.

[e]US EPA results not validated.

4.3.3.2 Workplace exposure studies

The occurrence of PBDF and PBDD during the thermal processing of glass-filled PBT resin containing DeBDE at 70 g/kg and Sb_2O_3 at 62 g/kg or no flame retardant was studied. No PBDD (limit of determination 2 ng) were found. PBDF were present and isomers containing bromine at the 2,3,7,8-position represented less than 10% of the total PBDF. Fumes evolved during thermal processing of the resins were collected at the die-head during extrusion.

The temperature in the 4 temperature zones was between 216 and 250 °C. It was found that thermal processing of resin with DeBDE/Sb_2O_3 yielded higher concentrations of PBDF in the fumes than that of resin without the flame retardants. The concentrations found in two samples of resin with flame retardant and one sample without flame retardant are given in Table 18.

In addition to these pyrolysis and moulding experiments, studies have been performed to determine the possibility of the workplace exposure to PBDF and PBDD of workers in extrusion or moulding facilities. The first of these studies was a simulation sponsored by General Electric (GE) at Battelle Laboratories in Columbus, OH (BFRIP, 1990). For this work, an experimental extrusion apparatus was used in which the total volatiles from the extruder could be collected and analysed. A typical commercial PBT/DeBDE resin was extruded, the volatiles were collected and analysed at the Fresenius Institute. The results of the analysis were used to estimate a probable workplace concentration of 0.76 ng/m^3 as TCDD equivalents.

The following experiment was carried out to determine the risks to employees working in the actual production of PBT resin, flame retarded with DeBDE, at Hoechst Celanese facility at Bishop, Texas (Hoechst Celanese Corp., 1988). High-volume samples were taken above the extruder die-head, the extruder vent port, the fibreglass addition port, and the raw material feeder, because these were the areas where off-gassing was most likely to occur and where employees could be exposed to the off-gases from extrusion. Source samples can be considered as worst-case situations, as samplers were placed directly in the off-gas streams.

Table 18. Concentrations of PBDF in resins in ng per sample component[a]

Substance	Two samples with flame retardant		One sample without flame retardant
TeBDF	201	1310	76
2,3,7,8-TeBDF	15	114	6
PeBDF	131	820	43
1,2,3,7,8-PeBDF	ND (< 2)	ND (< 5)	ND (< 2)
HxBDF	80	425	23
1,2,3,4,7,8-HxBDF	< 6	49	2
HpBDF	< 11	51	2
Total PBDF	423	2606	144

[a]From: (Vinci & Craig, 1988).
The values are the total quantity of PBDF (in ng) found in the 2 sample components, while the values of the specific isomers are given as values present in the total PBDF. For example: 15 ng of 2,3,7,8-TeBDF present in 201 ng total PBDF.
No PBDD was detected in any of these samples (limit of determination, 2 ng).

[b]ND = not detected.

A fifth sample was taken in an unused guard house, 90 m from the extruder building, as a field control. Full-shift personal samples were taken on all operators and helpers on each shift to determine the actual employee exposure. Each sampler was worn by employees for the entire 24-h period. The operating temperature was 240-260 °C. Personal samples are regarded as more representative than the area/source samples, since they were worn by employees during the production run.

The concentrations (expressed as TCDD equivalents) in ng/m^3 in the different air samples were:

Fibreglass port	0.027
Extruder die-head	3.589
Extruder vent port	0.191
Raw material feeder	0.015
Guard house	0.0004
Personal (three) samples	0.019, 0.011, 0.122.

BFRIP sponsored a study at a commercial PBT extrusion facility in 1988. This study was designed and conducted with input from the National Institute of Occupational Safety and Health (NIOSH) and the US EPA. In this study, both area samples and personnel monitors were used to collect information on potential exposures. Area samples were collected from locations expected to show maximum levels of volatile components. Personnel samples were collected with pumps worn by workers, and represented the average levels to which workers were exposed. In all cases, exposures were calculated in terms of TeCDD equivalents, using the concept of "Toxicity Equivalent Factors" (TEF) (the concentration of a particular chlorinated (brominated) dibenzo-dioxin or dibenzofuran is converted to an equivalent concentration of 2,3,7,8-TeCDD by multiplying by the appropriate factor). It should be noted that this conversion of exposure values for PBDF to TeCDD toxicity equivalents is only an estimate and is by no means generally accepted. The results from the area samples are summarized in Table 19 and from personnel samples in Table 20. The maximum worker exposure for PBDF was 0.1 ng/m^3, expressed as TeCDD toxicity equivalents (BFR/CEM Working Group, 1989; BFRIP, 1990; EBFRIP, 1990).

Determination of the occupational exposure during extrusion of PBT containing DeBDE at 90 g/kg and antimony trioxide at 80 mg/kg, was carried out by BASF, in Germany. In air, the total PBDF concentration close to the extruder head was 72.9 μg/m^3 and that in the rooms ranged from 0.169-0.989 μg/m^3. Concentrations of hexabromo- and heptabromodibenzofurans were the highest, followed by penta- and octabromodibenzofuran. The total PBDD concentration in the room was 28.12 ng/m^3, being mainly

Table 19. Results from BFRIP air sampling tests[a]

Compound	Toxicity equivalent factor	Area Samples									
		Fibreglass port		Extruder die head		Extruder vent port		Feed hopper		Guard gate	
		CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]
2,3,7,8-TeBDD	1.00000	0.0001	0.0001	0.0033	0.0033	0.0016	0.0016	0.0000	0.0000	0.0001	0.0001
1,2,3,7,8-PeBDD	0.50000	0.0001	0.0000	0.0059	0.0030	0.003	0.0016	0.0006	0.0003	0.0001	0.0001
1,2,3,4,7,8-HxBDD	0.10000	0.0002	0.0000	0.6220	0.0622	0.202	0.0202	0.0002	0.0000	0.0006	0.0001
1,2,3,6,7,8-HxBDD	0.10000	0.0002	0.0000	0.6221	0.0622	0.202	0.0202	0.0002	0.0000	0.0006	0.0001
OBDD	0.00100	0.0006	0.0000	0.0382	0.0000	0.020	0.0000	0.0009	0.0000	0.0023	0.0000
2,3,7,8-TeBDF	0.10000	0.0118	0.0012	0.0017	0.0002	0.104	0.0104	0.0055	0.0005	0.0001	0.0000
1,2,3,7,8-PeBDF	0.05000	0.0154	0.0008	0.0072	0.0004	0.005	0.0002	0.0092	0.0005	0.0002	0.0000
1,2,3,4,7,8-HxBDF	0.10000	1.0770	0.1077	126.8512	12.6851	1.962	0.1962	0.6036	0.0604	0.0006	0.0001
Total TeBDD	0.00000	0.0356	0.0000	1.9360	0.0000	2.199	0.0000	0.0412	0.0000	0.0001	0.0000
Total PeBDD	0.00000	0.0067	0.0000	0.3079	0.0000	0.003	0.0000	0.0048	0.0000	0.0001	0.0000
Total HxBDD	0.00000	0.0073	0.0000	36.9172	0.0000	0.448	0.0000	0.0084	0.0000	0.0006	0.0000
Total TeBDF	0.00000	3.4764	0.0000	394.2480	0.0000	13.735	0.0000	1.4432	0.0000	0.0620	0.0000
Total PeDBF	0.00000	7.4785	0.0000	1412.8761	0.0000	55.384	0.0000	3.5971	0.0000	0.0000	0.0000
Total HxBDF	0.00000	2.6888	0.0000	4544.6098	0.0000	146.321	0.0000	0.5275	0.0000	0.0000	0.0000
Air concentration ng/m^3			0.1098		12.8163		0.2503		0.0618		0.0004

[a]From: EBFRIP (1990).
[b]All concentrations are expressed as ng/m^3.
[c]Toxicity equivalent factors are the international values adopted by the US EPA in 1989.

Table 20. Results from BFRIP air sampling tests[a]

Compound	Toxicity equivalent factor	Personnel monitors					
		6559		12524		49834	
		CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]
2,3,7,8-TeBDD	1.00000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1,2,3,7,8-PeBDD	0.50000	0.0000	0.0000	0.0005	0.0002	0.0000	0.0000
1,2,3,4,7,8-HxBDD	0.10000	0.0000	0.0000	0.0025	0.0002	0.0000	0.0000
1,2,3,6,7,8-HxBDD	0.10000	0.0000	0.0000	0.0025	0.0002	0.0000	0.0000
OBDD	0.00100	0.0000	0.0000	0.0093	0.0000	0.0000	0.0000
2,3,7,8-TeBDF	0.10000	0.0132	0.0013	0.0000	0.0000	0.0000	0.0000
1,2,3,7,8-PeBDF	0.05000	0.0365	0.0018	0.0012	0.0001	0.1855	0.0093
1,2,3,4,7,8-HxBDF	0.10000	0.3543	0.0354	0.1405	0.0140	5.4102	0.5410
Total TeBDD	0.00000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total PeBDD	0.00000	0.0000	0.0000	0.0005	0.0000	0.0000	0.0000
Total HxBDD	0.00000	0.0000	0.0000	0.0025	0.0000	0.0000	0.0000
Total TeBDF	0.00000	1.4065	0.0000	1.1929	0.0000	7.6914	0.0000
Total PeDBF	0.00000	5.0801	0.0000	5.9643	0.0000	38.8162	0.0000
Total HxBDF	0.00000	6.5995	0.0000	61.9528	0.0000	70.1965	0.0000
Air concentration ng/m^3			0.0386		0.0149		0.5503

[a]From: EBFRIP (1990).
[b]All concentrations are expressed as ng/m^3.
[c]Toxicity equivalent factors are the international values adopted by the US EPA in 1989.

octa- and hexabromodibenzodioxins. The tetrabromodibenzodioxin concentration was 2.04 ng/m^3 (Kraus, 1990).

Umweltbundesamt (1989) reported the results from the workplace study conducted by BASF in a PBT extrusion facility. The results from the BASF study are summarized in Table 21. The higher level observed in the vicinity of the extruder head was removed from the workplace by local ventilation. According to the BASF report, workers spent most of their time in the "Production room" or at the "Bagging station". Only if there were problems with the equipment did they work near the extruder. The actual worker exposure would be approximately the levels observed in the production room or at the bagging station.

The results of the BASF and BFRIP studies are summarized in Table 22. With the exception of the BASF sample collected at the extruder head, the results are generally consistent between the two studies. The higher value for this sample, compared with that from the extruder die-head from the BFRIP, could be a result of a difference in the placement of the sampler (BFRIP, 1990).

An occupational exposure limit has not been established for any PBDD or PBDF, but a recent paper by Leung et al. (1988) provides guidance. Applying a 100-fold safety factor to the no-observed-effect level in animal studies, an occupational exposure limit of 0.2 ng/m^3 is obtained. For other compounds that behave similarly to TeCDD in animals tests, safety factors from 2 to 10 have been used to establish the occupational exposure limit. Using a safety factor of 10, the occupational exposure limit for TeCDD becomes 2 ng/m^3. With the exception of the two samples from the extruder die-heads, all of the values from the BASF and BFRIP studies were below 2 ng/m^3. The studies also indicate that workers are unlikely to be routinely exposed to levels higher than 0.2 ng/m^3.

BASF has submitted to the US EPA a report of the biological monitoring of 5 workers, who were employed in the extrusion of PBT containing DeBDE as a flame retardant (BFRIP, 1990). The results indicated blood concentrations of 2,3,7,8-TeBDF and 2,3,7,8-TeBDD of 100-500 ng/litre. All workers appeared in good health. The finding of 2,3,7,8-TeBDD in the workers was particularly surprising, since air samples had not revealed the

Table 21. Results from BASF air sampling tests

Compound	Toxicity equivalent factor	Extruder							
		Production room		Work station		Bagging station		Extruder head	
		CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]	CONC[b]	TCDD equivalent[c]
2,3,7,8-TeBDD	1.00000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000
1,2,3,7,8-PeBDD	0.50000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000
1,2,3,4,7,8-HxBDD	0.10000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000
1,2,3,6,7,8-HxBDD	0.10000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000
OBDD	0.00100	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000
2,3,7,8-TeBDF	0.10000	0.0	0.0000	0.0	0.0000	0.0	0.0000		0.0000
1,2,3,7,8-PeBDF	0.05000	0.0	0.0000	1.3	0.0650	0.0	0.0000	87.0	4.3500
1,2,3,4,7,8-HxBDF	0.10000	0.0	0.0000	2.6	0.2600	0.3	0.0300	1186.0	118.6000
Total TeBDD	0.00000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000
Total PeBDD	0.00000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000

Table 21 (continued)

Total HxBDD	0.00000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000
Total DiBDF	0.00000	1.1	0.0000	1.3	0.0000	0.2	0.0000	322.0	0.0000
Total TriBDF	0.00000	13.0	0.0000	7.4	0.0000	1.1	0.0000	705.0	0.0000
Total TeBDF	0.00000	20.0	0.0000	33.7	0.0000	5.1	0.0000	980.0	0.0000
Total PeBDF	0.00000	98.0	0.0000	7143.0	0.0000	8.6	0.0000	3910.0	0.0000
Total HxBDF	0.00000	594.0	0.0000	554.0	0.0000	13.0	0.0000	22 162.0	0.0000
Total HpBDF	0.00000	260.0	0.0000	200.0	0.0000	88.0	0.0000	39 550.0	0.0000
Total OBDF	0.00100	0.0	0.0000	0.0	0.0000	7.0	0.0070	5275.0	5.2750
Air concentration ng/m^3			0.0000		0.3250		0.0370		128.2250

[a]From: EBFRIP (1990).
[b]All concentrations are expressed as ng/m^3.
[c]Toxicity equivalent factors are the international values adopted by the US EPA in 1989.

Table 22. Summary of BASF and BFRIP air sampling tests[a]

Location	Study	Concentration (ng/m^3 air) TCDD equivalent
Personnel-1	BFRIP	0.039
Personnel-2	BFRIP	0.015
Personnel-3	BFRIP	0.550
Room air	BASF	0.000
Work station	BASF	0.325
Bagging station	BASF	0.037
Extruder head	BASF	128.225
Fibre glass addition port	BFRIP	0.110
Extruder die head	BFRIP	12.816
Extruder vent port	BFRIP	0.250
Feed hopper	BFRIP	0.062
Guard gate	BFRIP	0.000

[a]From: EBFRIP (1990).

presence of brominated dioxins. These findings have not yet been confirmed, but a follow-up study is in progress.

Investigations by plastic producers have shown that PBDF and PBDD can be formed, not only on combustion of plastics containing PBDE, but also during the blending of the flame retardant into a polymer. This has been substantiated by BASF, who measured the workplace atmosphere around extruders.

4.4 Ultimate fate following use

4.4.1 General

For the ultimate fate of DeBDE following use, and its effects on the environment, see section 6.1. of the General Introduction.

4.4.2 Exposure of the general population

No data are available concerning the direct exposure of the general population to DeBDE.

In a study by Ranken et al. (1990) to investigate the possibility of exposure to PBDD/PBDF from TV sets, three new TV sets were placed in an 8.81 m^3 test chamber. Sets A and B were purchased locally, while set C was provided by the manufacturer. The rear portion of each television set cabinet was constructed from polystyrene. The purchased televisions were flame retarded with 11.5% DeBDE. Set C was made of high-impact polystyrene, flame retarded with DeBDE/Sb_2O_3. In order to determine background levels of PBDD/PBDF, air was pulled through the empty chamber and through a sampler for 8 h/day, for 3 days. Two purchased sets were placed in the chamber. Air was pulled through the chamber for 8 h/day, for 3 days. The experiment was repeated for another 3 days. The television set (C) was placed in the room for 3 days, but the television was not in operation. In all the described experiments, no PBDD/PBDF were found. Finally, the air was monitored for 24 h while the television set C was operating. No PBDD/PBDF were found. On the basis of the limits of determination, PBDD/PBDF emissions from the operating television sets can be calculated to be less than 0.17-1.52 pg TeBDD/m^3, 0.35-0.39 pg PeBDD/m^3, 0.09-0.33 pg TeBDF/m^3, and 0.14-0.19 pg PeBDF/m^3 of air. The authors concluded that, in actual practice, these values would be lower by a factor of 10-100 because of the dilution effect of a normal room size and the expected air turnover.

4.5 Fire accident

Bruckmann et al. (1989) reported about an accidental fire in a stock-house in which, according to an inventory file, 2.5 tonnes of flame retardants (a mixture of DeBDE and antimony trioxide (Traflam PO 80)) was stored. Four wipe samples and 6 solid samples of partly burnt material were taken several hours after the fire. At the time of sampling, it was discovered that only a minor quantity of the bags with the flame retardant had been in contact with the fire. The 4 wipe samples contained tetra-, penta-, hexa-, hepta-, and octabromodi-benzofurans in the following

concentrations; 4.0-123, 0.82-77.6, 4.5-51.7, 0.25-12.8, and 0.53-8.5 ng/m^2. PBDD were not found (limit of determination 1 ng/m^2 per isomer). The PBDF contents of the solid samples were low with the highest concentration at 1 μg/kg.

4.6 Simulated fire conditions

In the experiments conducted by the BFRIP, samples of high-impact polystyrene (HIPS) and HIPS/DeBDE/Sb_2O_3 were burned in a Mass Burning Rate Apparatus with 21% oxygen to simulate a real fire scenario. The temperatures ranged from 500 to 800 °C. Soot and char were collected and analysed for PBDD and PBDF (Table 23).

Table 23. Analytical results from combustion products of HIPS/DeBDE[a]

Compound	Concentration	
	Char (mg/kg)	Soot (mg/kg)
Brominated dibenzodioxins	ND[b]	ND[b]
Brominated dibenzofurans:		
MBDF	0.64	556
DiBDF	0.54	641
TrBDF	0.23	352
TeBDF	< 0.1	73
2,3,7,8-TeBDF	< 0.1	1.8
PeBDF	< 0.1	3.5
HxBDF-OBDF	< 0.1	< 0.1

[a]From: McAllister et al. (1990); Pinkerton et al. (1989).
[b]ND = Not detected.
A single study on a mixed range of PBDE, between HxBDE and DeBDE, indicated little bioconcentration in carp with a bioconcentration factor of < 4 after 8 weeks of exposure (CBC, 1982).

No PBDD or PBDF were found in the HIPS without flame retardant. Low levels of bromodibenzofurans were found in the char of the flame-retarded HIPS, however, the levels of brominated furans ranged from 3.5 mg penta- to 641 mg dibromodibenzofurans/kg. No PBDD were found in char and soot. A maximum of 1.8 mg/kg of 2,3,7,8-TeBDF was present in soot (Pinkerton et al., 1989; McAllister et al., 1990).

4.7 Bioaccumulation

A bioconcentration study was carried out with rainbow trout under static conditions. The concentration in the water was 20 μg ^{14}C-DeBDE/litre. Fish were exposed for 0, 1/2, 1, 2, 4, 6, 12, 24, or 48 h. There was no measurable accumulation of DeBDE in flesh, skin, or viscera (Brosier et al., 1972; Norris et al., 1973, 1974, 1975a).

A single study on mixed PBDE between HxBDE and DeBDE indicated little bioconcentration in carp with a bioconcentration factor of < 4 after 8 weeks of exposure (CBC, 1982).

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 Environmental levels

5.1.1 Air

Decabromodiphenyl ether was identified in 10 samples of air collected in the vicinity of two manufacturing facilities in concentrations ranging from 0.016 to 25 $\mu g/m^3$. The compound was present in air in the form of particulates (Zweidinger et al., 1977).

5.1.2 Water

DeBDE was determined in 15 water samples collected in Japan in 1977. DeBDE was not present in any of the samples (limit of determination 0.2-2.5 μg/litre) (Environment Agency Japan, 1983). DeBDE was not detected in 75 water samples (limit of determination 0.1 μg/litre) in 1987 and was not detected in 141 samples collected at 47 locations (limit of determination 0.06 μg/litre) in 1988-89 in Japan (Environment Agency Japan, 1989, 1991).

Yamamoto et al. (1991) analysed water from the Kino River basin for the presence of DeBDE. In 12 samples of river water, the concentrations of DeBDE were all below 0.1 μg/litre water.

5.1.3 Aquatic sediments

DeBDE was determined in 15 sediment samples collected in Japan in 1977. DeBDE was not found in any of the samples (limit of determination 25-870 μg/kg dry weight) (Environment Agency Japan, 1983).

Marine, estuarine, and river sediment samples were collected at different places in Japan in the years 1981-83 and analysed for DeBDE. The DeBDE occurred in 6 river and 1 estuarine sediment sample (7 out of 15 samples) in the range of 20-375 μg/kg, during this period (Watanabe et al., 1987b).

DeBDE was identified at 20 μg/kg (dry weight) in one sample of 3 estuarine sediment samples from Osaka but was not detected in samples from Tokyo, Matsuyama, or Hiroshima (Watanabe et al., 1987b).

In 1987, an environmental survey was conducted concerning DeBDE in sediment in Japan. DeBDE was detected in 16 out of 60 samples at concentrations ranging from 10 to 1370 μg/kg (limit of determination 7 μg/kg dry weight) in 1987 and was detected in 39 out of 129 samples collected at 43 locations at concentrations ranging from 4 to 6000 μg/kg (limit of determination 4 μg/kg dry weight) in 1988-89 (Environment Agency Japan, 1989, 1991).

A sample was collected using a dredger, from the upper sediment layer of the Second Neya River in Osaka, Japan, in 1983. The sample contained approximately 0.2 mg DeBDE/kg dry weight (Watanabe et al. (1986).

Yamamoto et al. (1991) analysed 20 sediment samples collected from the Kino River in Japan and found that DeBDE was present in all the samples. The concentrations ranged from 0.003 to 11.6 mg/kg dry weight.

Zweidinger et al. (1978) found DeBDE at levels ranging from not detectable to 1 g/kg in sediment samples in the vicinity of a flame retardant manufacturing facility in the USA.

DeBDE (limit of determination < 10 μg/kg) was found in sediment in the vicinity of bromine facilities in El Dorado and Magnolia, Arkansas (DeCarlo, 1979) and also in sludge samples from a discharge-treatment zone of a DeBDE facility in Bayonne, New Jersey (US EPA, 1988; IARC, 1990).

5.1.4 Aquatic and terrestrial organisms

One of 3 mussel samples, collected in 1981-85, from Osaka Bay, Japan, contained 1.4 μg DeBDE/kg (wet weight basis) (Watanabe, 1987; Watanabe et al., 1987a,b). DeBDE was not found in mullet, goby, sea bass, horse mackerel, sardine, mackerel, or hairtail from this area or in mussel, mullet, goby, sardine, mackerel, or hairtail from other locations (limit of determination < 0.5 μg/kg). A total of 17 samples were analysed.

In 1987, an environmental survey was conducted concerning DeBDE in fish. It was not detected in 75 fish samples in 1987 and was not detected in 138 fish samples collected at 46 locations in 1988-89 (limit of determination 5 μg/kg wet weight) (Environment Agency Japan, 1989, 1991).

5.2 Exposure of humans

5.2.1 Occurrence of DeBDE in human tissues

DeBDE was not found in 5 human adipose tissue samples obtained from a hospital in Osaka in 1985-86. The limit of determination was < 50 μg/kg fat (Watanabe, 1987; Watanabe et al., 1987a).

DeBDE was detected at concentrations of up to 5 μg/kg in 2 out of 40 samples of human hair obtained from barber shops in El Dorado and Magnolia, Arkansas (where the chemical is manufactured) in 1978 (DeCarlo, 1979).

In the USA, Cramer et al. (1990a,b) studied PBDD/PBDF levels in human fat tissue samples during 1987 (National Human Adipose Tissue Survey). The 865 specimens were combined to form 48 composites based on 9 census divisions and their age groups. The PBDD/PBDF analysis was carried out using HRGC/HRMS. No PBDD/PBDF were found (detection limit of 1-40 ng/kg, depending on congener). Identification of PBDE was based on comparison of full scan mass spectra of the samples with available standards, application of SIM techniques to compare theoretical ion ratios with observed ion ratios, and measurement of fragment losses from molecular ion clusters. Five samples were also monitored for DeBDE. No DeBDE was detected in 2 out of 5 samples; a weak DeBDE response was found in 1 out of 5 samples, and, in 2 out of 5 samples, DeBDE was estimated at 400 and 700 ng/kg, respectively.

5.2.2 Occupational exposure

Wipe samples collected during an industrial hygiene survey in a DeBDE manufacturing plant in the USA, indicated that workers in the reactor area were exposed to 3.6 mg DeBDE/cm^2. Personal

samples collected from workers in the mill area indicated that the airborne levels of DeBDE ranged from 0.08 to 0.21 mg/m^3, as a 8-h time-weighted average. Following a spill in the mill area, personal airborne levels ranged from 1.3 to 1.9 mg/m^3 (Bialik, 1982).

Human exposure to DeBDE occurs in the course of manufacture and use. Surveys have determined employee time-weighted average exposures of 1-4 mg/m^3 in air with excursions up to 42 mg/m^3 during short tasks. More than 90% of the particles in air were smaller than 10 μm in diameter. On the basis of its classification as a nuisance material by OSHA, the recommended workplace environmental exposure level in air is 5 mg/m^3 (8-h time-weighted average for a 40-h week) (NTP, 1986) (see also section 4.2).

Studies on worker exposure to PBDF/PBDD during the production of polymers containing PBDE are given in section 4.3.3.2.

6. KINETICS AND METABOLISM IN LABORATORY ANIMALS AND HUMANS

6.1 Absorption and elimination

Three male and 3 female Sprague-Dawley rats were administered orally ^{14}C-labelled DeBDE suspended in corn oil. The elimination in urine and expired air was measured at 24-h intervals over a 16-day period. Less than 1% was found in urine and expired air. The principal route of elimination was via the faeces. Within 24 h, 90.6% of the ^{14}C activity was excreted and all the ^{14}C was accounted for by day 2 of the study. The data indicate that there is minimal absorption of DeBDE by the gastrointestinal tract (Norris et al., 1973, 1974, 1975a,c; Dieter, 1979).

As a supplement to the carcinogenicity studies (sections 7.3 and 7.7), additional experiments were conducted to quantify DeBDE absorption from the gastrointestinal tract of male rats and to determine the effect of dose on absorption. Radiolabelled ^{14}C-DeBDE (97.9-99.2%) was diluted with unlabelled DeBDE to yield the desired concentrations. DeBDE was mixed in the diet at approximate concentrations of 250, 500, 5000, 25 000, or 50 000 mg/kg, or was administered by intravenous injection. Animals were preconditioned by being fed diets containing the respective dose of unlabelled DeBDE for 7 days before being fed diets containing ^{14}C-DeBDE for 1 day, then being returned to diets containing unlabelled material for the remainder of the holding period. Results indicated that, after exposure to all doses in the diet, more than 99% of the radioactivity recovered was eliminated in the faeces within 72 h. Excretion in the urine accounted for approximately 0.01% or less of the dose. The high ^{14}C-DeBDE content of the gastrointestinal tissues was attributed to intimate contact with the diet. Concentrations of DeBDE in other tissues were near the limits of determination.

After an intravenous dose of 1 mg/kg, 61% of the recovered radioactivity was eliminated in the faeces in 72 h and approximately 0.1% in the urine.

Estimates indicate that 0.33% $\pm$ 0.19% of the 50 000 mg/kg dose was absorbed. Data for the 25 000 mg/kg diet showed that

the percentage of the dose absorbed was not significantly different from that of the highest dose. Radioactivity present in the liver following exposure in the diet was confirmed as DeBDE. However, the minimal absorption of DeBDE from the gastrointestinal tract, and, presumably, from other potential routes of exposure may explain the low toxicity of DeBDE (NTP, 1986; El Dareer et al., 1987).

6.2 Distribution

The distribution of radioactivity was measured in various tissues by Norris et al. (1973, 1975a,c). On day 16, no ^{14}C-activity was found in the tissues, with the exception of 0.01% of the administered dose/g in the adrenal glands and 0.06% in the spleen.

In studies in which concentrations of ^{14}C-labelled DeBDE of 250-50 000 mg/kg diet were fed to male Fischer 344 rats, more than 99% of the radioactivity was recovered in the faeces and intestinal contents (see section 6.1). The liver contained approximately 0.5% of the consumed dose, 24 h after feeding, and this declined to 0.016% after 72 h. Labelled material was extracted from the liver and found to be mainly unchanged DeBDE. Trace amounts of label were found in the kidneys, spleen, lung, brain, muscle, fat, and skin. Seventy-two hours following an intravenous dose of ^{14}C-labelled DeBDE, the faeces and gut contents contained 74% of the dose, suggesting significant biliary excretion. Of the extracted faecal label, 63% were metabolites of DeBDE and 37% unchanged DeBDE. Labelled materials were found in the liver, kidneys, and lungs and in lower concentrations in muscle, skin, and fat (NTP, 1986; El Dareer et al., 1987).

Rats were administered DeBDE in the diet at 0, 25, or 50 g/kg to determine the concentrations of DeBDE in the liver. The mean concentrations in the livers were 0.21 ± 0.43 (9), 2.09 ± 0.89 (8), and 8.6 ± 2.83 mg/kg liver (20), respectively. The number of livers studied is given in brackets (Rogers & Hill, 1980) (no details available).

6.3 Retention and turnover

A 2-year tissue accumulation study on the rat was carried out. Groups of 3 male and 3 female Sprague-Dawley rats were maintained on diets providing 0, 0.01, 0.1, or 1.0 mg DeBDE (FR-300 BA)/kg body weight per day for designated periods of time. The tissues/organs analysed for total bromine content were serum, adipose tissue, liver, kidneys, skeletal muscle, and testes (see section 7.3.1.2). Interim results after 10, 30, 90, 180 days, and 12 and 18 months of exposure showed that the total bromine values in serum, liver, kidneys, skeletal muscle, and testes were comparable with the control values. The mean total bromine content of adipose tissue showed a time- and dose-related (significant) increase, especially in the groups receiving 0.1 and 1.0 mg DeBDE/kg per day. Although there was a continuing increase in total bromine content, the concentrations in adipose tissue of rats ingesting 0.01, and 0.1 mg DeBDE/kg per day for 23-24 months were 2.8 $\pm$ 0.9, and 7.5 $\pm$ 3.0 mg/kg, respectively, compared with 2.0 $\pm$ 0.2 mg/kg for the control rats. In the liver, the concentrations for the controls and the rats treated with 1.0 mg/kg were 2.9 $\pm$ 0.2 and 5.9 $\pm$ 1.1, respectively. In serum, after 23-24 months, the concentrations for the 4 groups were 8.0 $\pm$ 1.2 (control), 9.1 $\pm$ 1.1 (0.01 mg/kg), 7.9 $\pm$ 0.6 (0.1 mg/kg) and 8.1 $\pm$ 1.0 (1.0 mg/kg) (Norris et al., 1974, 1975a; Kociba et al., 1975,1975a).

The elimination of bromine from tissues was studied in male Sprague-Dawley rats maintained for 90 days on a diet providing a dose of 1.0 mg DeBDE/kg per day, and then on a control diet. Four rats out of each group were sacrificed on the last day of exposure or after a recovery period of 0, 10, 30, 60, or 90 days. Serum, kidneys, adipose tissue, and liver were analysed. The low level of total bromine accumulated in adipose tissue remained unaffected during 90 days of recovery. Bromine was cleared from the liver within 10 days of recovery (Norris et al., 1974, 1975a,c).

The half-life for the disappearance of ^{14}C-activity from the body of DeBDE-treated rats was less than 24 h. The principal route of elimination was the faeces. No sex-related differences were found. ^{14}C-activity was rapidly cleared in DeBDE-treated rats.

7. EFFECTS ON LABORATORY MAMMALS AND *IN VITRO* TEST SYSTEMS

The toxicological information on DeBDE has been summarized in several publications including: Norris et al. (1973, 1974, 1975a,b,c), AIHA (1981), and NTP (1986).

7.1 Single exposure

7.1.1 Oral: Rat

Intragastric intubation of single doses of 126-2000 mg commercial DeBDE/kg body weight, as a 10% corn oil suspension, to female Sprague-Dawley rats (Spartan strain), did not produce any indications of toxicity or gross pathological changes during a 14-day period (Norris et al., 1973, 1974, 1975a,c).

Groups of 5 male Spartan rats received single oral doses of up to 5 g/kg body weight, by gavage, as suspensions in corn oil. No deaths occurred and the animals showed normal weight gain during a 14-day observation time. The acute oral LD_{50} in rats was > 5 g/kg body weight (Great Lakes Chemical Corporation, undated b).

7.1.2 Dermal: Rabbit

Commercial DeBDE was applied and to the occluded, clipped, intact skin of 2 male and 2 female New Zealand white rabbits, each at a dosage of 200 or 2000 mg/kg body weight, for 24 h. Observation time was 14 days. No mortality occurred. The acute dermal LD_{50} in rabbits was > 2 g/kg body weight (Great Lakes Chem. Corp., undated b).

7.1.3 Inhalation: Rat

Groups of 10 male and 10 female Spartan rats were exposed for 1 h to concentrations of commercial DeBDE of 2 or 48.2 mg/litre air and subsequently observed for 14 days. All rats survived. At 2 mg/litre, salivation was noted in 2 rats on the first

day, but, from there on, all the rats in this group appeared normal, except one with respiratory difficulties and another with ocular discharge during the observation period. At 48.1 mg/litre, eye squint and increased motor activity were noted in the animals up to day 4. Respiratory difficulties were noted in 2 rats on days 3-6 and in one rat on day 8 and one on day 7. A few rats showed eye squint and ocular discharge on days 7-12. All rats were normal on day 14. The acute inhalation LD_{50} in rats was > 48.2 mg/litre (Great Lakes Chemical Corporation, undated b).

7.2 Short-term exposure

7.2.1 Oral

7.2.1.1 Mouse

In a 14-day study, groups of 5 B6C3F1 mice, of each sex, were exposed to DeBDE (99%) in the diet at concentrations of 0, 20, 50, or 100 g/kg. No effects on health, survival, or body weights were observed and no compound-related clinical signs or gross pathological effects were reported (NTP, 1986).

In a 13-week study, groups of 10 male and 10 female B6C3F1 mice were administered DeBDE (two lots of DeBDE were used; one of 99% and the other > 97%) in the diet at 0, 31, 62, 12.5, 25, or 50 g/kg, for 13 weeks. No evidence was found for compound-related effects on physical appearance, behaviour, food consumption, body weight gain, survival, and gross and microscopic pathology. This study was used to establish the dose levels for the long-term study (Rutter & Machotka, 1979; NTP, 1986).

7.2.1.2 Rat

In 3 separate, 28-day feeding studies, each with groups of 10 male and 10 female Charles River CD rats, commercial DeBDE was administered at 0, 100, or 1000 mg/kg diet. The rats were observed for appearance, mortality, food consumption, body weight gain, and organ weights. After sacrifice, gross pathological and microscopic examinations of the liver, kidneys, and thyroid were carried out. Adverse effects or lesions associated with

DeBDE administration were not found in these 3 rat studies. The total bromine contents of the liver, and adipose tissue were determined and a slight increase in bromine concentration was found at the highest dose level (Great Lakes Chemical Corporation, undated b) (no details available).

Groups of 5 male Sprague-Dawley rats were administered a diet containing 0, 0.01, 0.1, or 1.0% [equivalent to 0, 8, 80, or 800 mg DeBDE (77.4% DeBDE, 21.8% NBDE, and 0.8% OBDE)/kg body weight per day], for 30 days. No influence on food intake or body weight gain was found. No haematological changes were observed in the 8 and 80 mg/kg dose groups, but, at 800 mg/kg, there were decreases in packed cell volume and red blood cell count. Urinalysis parameters were not affected at any dose level. No differences in heart, testes, brain, and kidney weights were observed. Enlarged livers were found in rats exposed to 80 and 800 mg DeBDE/kg. The liver lesions consisted of centrolobular cytoplasmic vacuolization. Furthermore, in the rats receiving 80 and 800 mg/kg, hyaline degenerative cytoplasmic changes in the kidneys and thyroid hyperplasia were found. At a dietary level of 0.1 g/kg (equivalent to 8 mg/kg body weight), no treatment-related changes in the liver or thyroid, or other changes were found. (Remark: limited histopathology was carried out) (Sparschu et al., 1971; Norris et al., 1973, 1974, 1975a; Kociba et al., 1975a).

In a 14-day study with DeBDE (99%) administered in the diet to Fischer 344/N rats at concentrations of 0, 5, 20, 50, or 100 g/kg, no effects were seen on health, survival, and body weight, and no compound-related clinical signs or gross pathological effects were observed. Similarly, no toxic effects were seen in a 90-day study in which doses of DeBDE (> 97%) of 0, 3.1, 6.2, 12.5, 25, or 50 g/kg were administered in the diet. No effects on survival, body weight, or feed consumption were observed. No gross or microscopic effects were reported. Liver weights were not recorded in these studies, but, in subsequent studies, liver weights were significantly increased in Fischer 344/N rats at dose levels of 25 and 50g DeBDE (92%)/kg diet, for 14 days (NTP, 1986).

7.2.2 Inhalation

7.2.2.1 Rat

Pulmonary tissue response and pulmonary clearance of commercial DeBDE were evaluated following intratracheal administration of the dust to rats. The study was conducted to evaluate the possible health hazards for man from inhalation of the dust generated during the production and handling of DeBDE. Fifty male, Sprague-Dawley rats were given an intratracheal injection of 20 mg DeBDE (77.4%) dust (length mean diameter 2.65 μm, surface mean diameter 2.91 μm, and volume mean diameter 3.17 μm) suspended in 1 ml of rat serum. A control group of 35 rats received only the serum vehicle. The rats were observed for appearance, demeanour, and body weights. Groups of 5 treated and 2 control rats were killed on days 3, 10, 30, 91, and 365 for determination of total bromine content in the lungs. The calculated DeBDE equivalent values were used to determine the half-life of DeBDE in lungs, which was determined to be 150 days. To assess the respiratory tissue response, gross and histopathological examinations were conducted on rats killed on days 10, 30, 416, and 556 and on rats that died. 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 out of 5 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).

7.3 Long-term exposure

7.3.1 Oral

7.3.1.1 Mouse

A two-year study was carried out on B6C3F1 mice. The animals were administered DeBDE in the diet at concentrations of

0, 25, or 50 g/kg, for 113 weeks (NTP, 1986) (for details of the study see section 7.7.1.1).

7.3.1.2 Rat

A long-term/carcinogenicity study was carried out on Sprague-Dawley rats administered daily doses of 0, 0.01, 0.1, or 1.0 mg DeBDE/kg body weight in the diet for 2 years (Kociba et al., 1975, 1975a; Norris et al., 1975a,b). In another 2-year study, Fischer 344 rats were administered DeBDE at 0, 25, or 50 g/kg diet (NTP, 1986) (for details of these 2 studies see section 7.7.1.2).

7.4 Skin and eye irritation; sensitization

7.4.1 Skin irritation

Skin irritation studies conducted with commercial DeBDE, applied as a dry solid (500 mg) on the shaved skin (under occlusion) of 2 groups of 3 New Zealand white rabbits caused no irritation on intact skin and no, or only slight, erythematous and oedematous responses on abraded skin, after a single exposure for 24 h and an observation period of 72 h. A comparable study on 3 male and 3 female New Zealand white rabbits in which 500 mg DeBDE was applied on intact or abraded skin showed no skin irritation. Repeating the exposures of intact skin for 5 days/week for 2 weeks or to abraded skin for 3 days did not alter the response (Norris et al., 1973, 1974, 1975a,c; Great Lakes Chemical Corporation, undated c).

7.4.2 Eye irritation

Eye irritation studies on 3 male and 3 female New Zealand White rabbits showed that 100 mg Saytex 102/eye, applied as a dry solid, caused only transient irritation (redness and chemosis) of the conjunctival membranes. The cornea, iris, and lens were unaffected (sodium fluorescein and UVR were used). After 24 h, the eyes had recovered. The observations were made at 1, 24, 48, 72 h, and 7 days after treatment (Norris et al., 1973, 1974, 1975a,c; Ethyl Corp., 1986; Mallory et al., 1986; Great Lakes Chemical Corporation, undated c).

7.4.3 Sensitization

Repeated application of a suspension of 5% DeBDE (77.4% DeBDE, 21.8% NBDE, 0.8% OBDE) in petrolatum, 3 times a week for 3 weeks, to the skin of 50 human volunteers did not result in skin sensitization reactions during the sensitizing period or, on challenge 2 weeks following the last application. Skin irritation was observed in 14 out of the total 450 applications (11 of the reactions were classified as very slight and 3 as mild erythema). These reactions were seen in 9 out of the 50 persons (Norris et al., 1974, 1975a,c; Dow Chemical Comp. USA, 1978).

7.4.4 Chloracnegenic activity

Chloracnegenic activity was studied on the ear of each of 4 New Zealand White male and female rabbits. The test material (Saytex 102) was administered once daily at 0.1 ml/day, 5 times per week, for 4 weeks, at concentrations of 1, 10, 100, or 1000 g/kg, in chloroform. Observations were recorded prior to the initial dose and at 7, 14, 21, and 28 days of dosing. Saytex 102 as a 10% chloroform solution caused a slight erythematous response and slight exfoliation, but no chloracne was observed during the study (Naismith & Matthews 1981).

In the period 1971-74, approximately 40 samples of DeBDE (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 DeBDE did not induce any responses, but responses to the mother liquor and still bottom samples were positive, except in a few cases where the result was equivocal (Rampy, 1971-74).

7.5 Reproductive toxicity, embryotoxicity, and teratogenicity

7.5.1 Reproductive toxicity

A one-generation reproduction study was performed in which 10 male, and 20 female, Sprague-Dawley rats at the two lower

dose levels (3 and 30 mg/kg body weight) and 15 male and 30 female rats at the higher dose level (100 mg/kg body weight) were given commercial DeBDE with the diet (weekly adjustment), for 60 days prior to mating, 15 days during mating, and subsequently throughout gestation and lactation. Twenty male and 40 female rats served as controls. No signs of toxicity were observed in the adult rats or the neonates during the study or at necropsy. Unaffected parameters included body weight gain and food consumption by adults, reproductive parameters (the percentage pregnant and neonatal growth, survival, and development), preterminal urinalysis and clinical chemistry in adult rats, gross examination of all adult and weanling rats, and microscopic examination of tissues from both age groups. No cytogenetic changes were observed in the bone-marrow of parents and weanling rats. Thus, no toxicological manifestations were associated with the ingestion of 100 mg DeBDE/kg in this reproduction study (Norris et al., 1975c; Schwetz et al., 1975).

7.5.2 Teratogenicity

Pregnant female rats were given 0, 10, 100, or 1000 mg commercial DeBDE/kg body weight, suspended in corn oil, by intragastric gavage, on days 6-15 of gestation.

Maternal food consumption and body weight did not differ from those of the controls. Liver weights of the mothers were comparable with those of the control animals. The position and number of fetuses *in utero*, the number of *corpora lutea*, individual pup weight, crown-rump length, and sex ratio, were similar to those of the controls. A significant increase in resorptions was found at low dose levels, but not at the high dose level. No gross external abnormalities were seen in the fetuses of dams treated at any dose level. Soft tissue and skeletal examinations revealed an increased number of litters with subcutaneous oedema and delayed ossification of bones of the skull of fetuses of dams treated with 1000 mg/kg, but not with 100 mg/kg body weight. Analysis of maternal and fetal livers for total bromine revealed a significantly increased concentration in maternal livers of rats treated with 1000 mg/kg. Treatment with 100 mg/kg or less did not produce any increase in total bromine contents. No increase in total bromine contents was observed in

the livers of fetuses from dams receiving any of the dose levels of DeBDE (Norris et al., 1973, 1974, 1975a; Hanley, 1985; US EPA, 1989).

7.6 Mutagenicity and related end-points

7.6.1 Mutation

A technical product, HFO 102, was tested in a *Salmonella typhimurium* assay with the strains TA 98, TA 100, TA 1535, and TA 1537 with, or without, metabolic activation. The HFO 102 was not completely soluble in DMSO at a concentration of 10 mg/litre. However, the suspension was used for the test and for preparation of the solutions. The dose levels that were tested were 0.4, 4.0, 40, and 1000 μg/plate. No evidence for mutagenic activity was found (Shoichet & Ehrlich, 1977).

Results of studies with *Saccharomyces cerevisiae* with, or without, liver microsomal enzyme preparations, were also negative (no details) (Great Lakes Chemical Corporation, undated b).

Commercial DeBDE in concentrations of 100-10 000 μg/plate was not mutagenic in *Salmonella typhimurium*, TA 100, TA 1535, TA 1537, and TA 98 strains, in the presence, or absence, of an exogenous metabolic system from Aroclor 1254-induced male rat liver S9 and male Syrian hamster liver S9 (NTP, 1986).

7.6.2 Chromosomal effects

Cytogenetic examination of bone marrow cells, taken at necropsy from the femur of the parent animals from a reproduction study (see section 7.5.1) as well as from the neonates at weaning, showed no increase in cytogenetic aberrations compared with the controls (Norris et al., 1975c) (no details).

Commercial DeBDE was not mutagenic in the mouse lymphoma L5178Y/TK+/- assay in the presence, or absence, of Aroclor 1254-induced male F344 rat liver S9. Tests for cytogenic effects in Chinese hamster ovary cells indicated that commercial DeBDE does not cause chromosomal aberrations or sister-chromatid exchanges in either the presence or absence of S9,

prepared from livers of Aroclor 1254-induced male Sprague-Dawley rats (NTP, 1986).

7.7 Carcinogenicity

7.7.1 Oral

7.7.1.1 Mouse

Groups of 50 male and 50 female B6C3F1 mice (nine weeks old) were fed 0, 25, or 50 g DeBDE (purity 94-99%; no brominated dioxins or furans were found)/kg diet for 103 weeks; all survivors were killed in weeks 112-113. The average daily consumption of DeBDE was estimated to be 3200 mg/kg for low-dose and 6650 mg/kg for high-dose male mice and 3760 mg/kg for low-dose and 7780 mg/kg for high-dose female mice. Body weights and survival of treated animals were comparable with those of the controls. Non-neoplastic lesions observed in treated mice were granulomas in the liver of low-dose males and hypertrophy in the liver of low- and high-dose males. The combined incidence of hepatocellular adenomas and carcinomas was significantly increased in males: control 8/50, low-dose 22/50, and high-dose 18/50 (but not increased in comparison with historical control groups); the combined incidence of thyroid gland follicular-cell adenomas and carcinomas was increased, but not significantly, in treated males: control 0/50, low-dose 4/50, high-dose 3/50; females: control 1/50, low-dose 3/50, high-dose 3/50. Follicular-cell hyperplasia of the thyroid gland was increased in both groups of treated male and female mice (NTP, 1986; Huff et al., 1989).

7.7.1.2 Rat

Groups of 25 male, and 25 female, Sprague-Dawley rats, 6-7 weeks of age, were fed 0, 0.01, 0.1, or 1.0 mg DeBDE/kg body weight (purity DeBDE 77.4%, nonabromodiphenyl ether 21.8%, octabromodiphenyl ether 0.8%) in the diet for 100-105 weeks. Additional groups of 10-34 rats/sex per dose level were killed at various times during the study to investigate the accumulation of total bromine in the tissues. Ingestion of up to 1.0 mg DeBDE/kg did not influence survival rates; appearance, mean body weights,

feed consumption, haematology, urinalysis, clinical chemistry, and organ weights of treated groups were similar to those of controls. No discernible toxicological effects were produced by DeBDE and no significant differences in the number of rats developing tumours, the total number of tumours, or the specific type of tumours were observed between treated and control groups, when evaluated by the Fisher's exact probability test. Adrenal phaeochromocytomas were the most frequent tumours in the male rats in all groups. During the study, there was a slight build up of the total bromine content in the tissues of rats ingesting the 2 highest dose levels, as measured by neutron activation analysis. However, the source of bromine may, or may not, have been DeBDE, because NBDE and OBDE were also present in the product. Serum, muscle, and kidneys did not show any increase in total bromine content. In the liver, low-level, steady-state conditions were attained by 12 months. Adipose tissue showed a time- and dose-related increase in total bromine content, subsequent to ingestion of 0.1 or 1.0 mg/kg. The total bromine content of adipose tissue of rats ingesting 0.01 mg/kg for 2 years was 2.8 $\pm$ 0.9 mg/kg compared with a control value of 2.0 $\pm$ 0.2 mg/kg (section 6.3) (Kociba et al., 1975, 1975a; Norris et al., 1975a,b). [The IARC Working Group (1990) noted the very low dose levels used].

Groups of 50 male, and 50 female, Fischer 344/N rats, 7-8 weeks of age, were fed DeBDE (purity 94-99%; no brominated dioxins or furans were found) at 0, 25 or 50 g/kg diet, for 103 weeks; all survivors were killed in weeks 111-112. The average daily consumption of DeBDE was estimated to be 1120 and 2240 mg/kg for low-dose and high-dose male rats, respectively, and 1200 and 2550 mg/kg for low-dose and high-dose female rats, respectively. Body weights of treated rats were not significantly different from those of the controls. Thrombosis and degeneration of the liver, fibrosis of the spleen, and lymphoid hyperplasia were observed in high-dose male rats. Significant increases were observed in the incidence of neoplastic nodules of the liver (adenomas) in treated males: control 1/50; low-dose 7/50; high-dose 15/49 and females: control 1/50; low-dose 3/49; high-dose 9/50. No differences in the incidence of hepatocellular carcinomas were seen among the groups. The incidence of acinar-cell adenomas of the pancreas in males was: control 0/49; low-dose

0/50; high-dose 4/49. The difference between the controls and the high-dose group was not significant. A high incidence of mononuclear-cell leukaemia was observed in treated and control rats of both sexes (NTP, 1986; Huff et al., 1989).

7.8 Other special studies

7.8.1 Liver

Carlson (1980a) administered commercial DeBDE (in corn oil), by gavage, at a dose of 0.1 mmol/kg body weight to male Sprague-Dawley rats (200-250 g) for 14 days. Twenty-four hours after the last (seventh) dose, the liver/body weight ratio increased. Koster et al. (1980) found no evidence of a porphyrinogenic action after exposure of cultures of chick embryo liver cells to a concentration of 5 μg DeBDE (in DMSO)/ml medium with, or without, pretreatment with naphthoflavone, an inducer of P450, P448, and of delta-levulinic acid synthethase.

A sample of DeBDE, obtained from the NTP repository, was administered by gavage (vehicle not clear) at 1500 mg/kg body weight to 9, three-month-old, female Sprague-Dawley (CD) rats, 21 h and 4 h before they were killed. No changes were observed in hepatic cytochrome P450 content, hepatic DNA damage, as determined by alkaline elution, hepatic ornithine decarboxylase activity, or serum alanine aminotransferase activity (Kitchin et al., 1992).

7.8.2 Miscellaneous

Hefner (1973) studied, in an *in vitro* model, the rupture of erythrocyte membranes (haemolysis) induced by dust particles. The test approximates the *in vivo* rupture of the secondary lysosomal membranes. Fibrogenic dusts are capable of rupturing the erythrocyte membrane, while non-fibrogenic dusts are not. On the basis of the *in vitro* model, DeBDE of the particle size studied (shown by optical microscopy to have a 2.65 μm number length mean diameter with 94.5% of the particles being 3.77 μm and below) appears to be non-fibrogenic (only 0.1% haemolysis) at 1-15 mg dust/ml suspension and time from 15 to 120 min.

7.8.3 Toxicity of soot, char, and other waste products from combustion of DeBDE-containing polymers

7.8.3.1 Acute oral toxicity

Groups of 5 male, and 5 female, Sprague-Dawley rats were administered a mixture of soot and char (61/39%), generated from the combustion of high-impact polystyrene, as a single dose, by gavage at 0(vehicle), 0.5, 5.0, 50, 500, or 2000 mg/kg body weight. These amounts were given in 10 ml 1% methyl cellulose/kg body weight. Observation time was 28 days. Body weight gain, mortality, and weights of 10 organs were studied, and these organs in the control and 2000 mg groups were also examined microscopically. No overt signs of toxicity were observed. The acute oral LD_{50} was > 2 g/kg body weight (Fulfs & Dahlgren, 1987a).

The acute toxicity of the combustion products of a matrix composed of high-impact polystyrene, DeBDE, and antimony trioxide was investigated. Six dose groups of 5 male and 5 female rats were treated, by gavage, with 0, 0.5, 5, 50, 500, or 2000 mg/kg of combined soot and char, generated from the combustion of the flame retarded high-impact polystyrene (HIPS) suspended in 1% methyl cellulose and observed for 28 days. No animals died during the course of the study and no clinical signs of toxicity were observed. No histological lesions were detected in the following organs examined: thyroid, parathyroid, and adrenal glands, spleen, gonads, heart, liver, lung, brain, kidneys, and thymus. The LD_{50} was > 2000 mg/kg body weight (Fulfs & Dahlgren, 1987b; Pinkerton et al., 1989).

Undiluted solids from mother liquor (waste tars) were tested for acute oral toxicity in rats. No acute oral lethality was seen with 0.126 g/kg body weight in corn oil, but 100% mortality was found, with 0.5 g in water. The animals displayed tremors (Norris, 1971).

7.8.3.2 Skin irritation and comedogenicity

Soot and char generated from the combustion of high-impact polystyrene retarded with, or without, DeBDE and Sb_2O_3 were tested for their comedogenicity using a New Zealand albino rabbit

ear bioassay (Draize, 1979). The soot and char samples were mixed in different ratios. The dose levels were; 0.001, 0.003, 0.005, 0.008, 0.01, 0.03, 0.05, 0.08, and 0.1 g. The highest dose level (0.1 g) of the mixture was actually in excess of the amount that remained on the ear. The materials were applied in 0.1 ml of water. Five male rabbits, with 2 healthy ears each, were randomly selected for these studies and the original design required 10 exposure levels, 1 per ear. Dosing was continued for 5 consecutive days. Ears were checked to grade the erythema on day -1 and day 0, and then daily, and the final grading was done on the day following the last dosing. The results showed that, without flame retardants, very slight to well defined erythema occurred with doses of 0.005 g and higher. In cases where the polymer was flame retarded, the effect was stronger, very slight to moderate/severe erythema occurred with doses of 0.001-0.003 g or more (see Table 24) (Fulfs 1987a,b).

Table 24. Skin irritation by soot or char generated from the combination of HIPS with, or without, DeBDE

Soot/char	Mixture soot/char	Dose	Erythema score
High impact polystyrene	61/39%	0.005 g and higher	score 1-2 (increasing with dose level from day 2 onwards)
High impact polystyrene with DeBDE and antimony trioxide	47/53%	0.003 g and higher	score 1-3 (increasing with dose level, from day 1)
		0.001 g and higher	same result, increasing from day 3

Two groups of four (mainly 2 male and 2 female) New Zealand white rabbits were used to test a mixture of soot and char (61/39%), generated from the combustion of high-impact polystyrene treated without flame retardants, in a rabbit ear comedogenicity bioassay. Daily dose levels of 2, 5, 8, 20, or 50 mg of the mixture were administered. Each daily dose was rubbed with 0.1 ml of water on the inner surface of the pinna of

one ear of the respective rabbit. The animals were dosed 5 days per week for a total of 4 weeks. The total cumulative dose levels were 40, 100, 160, 400, and 1000 mg. The ears were graded for irritation (Draize test) and for hyperkeratosis (Adams test). During the study, dermal irritation was found in all treated groups with a score of 1-2. No comedogenic (score 0) responses were observed on any of the ears. A slight increase in hyperkeratosis of the sebaceous follicles was seen during histopathological examination of the skin in the animals treated with the 2 highest dose levels. No evidence of overt toxicity was seen among any of the animals tested (Fulfs & Dahlgren, 1987c; Pinkerton et al., 1989).

A similar study was carried out with a combined soot and char (47/53%) mixture, generated from the combustion of HIPS flame retarded with DeBDE and antimony trioxide. The results were comparable with those of the combustion products of HIPS without flame retardants. There was no microscopic evidence of any significant hyperkeratotic response (Fulfs & Dahlgren, 1987d).

Undiluted solids from mother liquor (waste tars) were tested for skin irritation in rabbits. Slight skin irritation was observed at a dose of 1.1 g/day for 3 days (Norris, 1971).

7.8.3.3 Eye irritation

Solids from mother liquor (waste tars) were tested for eye irritation. The material is a mixture of brominated DeBDE (Br = 7-10). A dose of 0.1 g of the mixture caused severe eye irritation and slight corneal injury (Norris, 1971).

8. EFFECTS ON HUMANS

8.1 General population exposure

No data are available.

8.2 Occupational exposure

8.2.1 Skin sensitization

Human volunteers (80 males and 120 females) were treated with 9 induction patches of 2 batches of DeBDE, identified as DBDO-1 and XD 8186.02. The first sample was evaluated as such, and the second as a 2% (W/V) aqueous solution. The upper arm was used in the males and the upper back in the females. The patches were applied once every 2 days and the substance left in contact with the skin for 24 h, after which it was removed. After the application of 9 patches, there followed a non-patching period of 12 days, after which the challenge patch was applied to detect sensitization. A new skin site was used for this 24-h patch. After removal of the patch, reactions were observed after 24 and 48 h. This study did not reveal any evidence of skin sensitization with either test material in any of the subjects (Industrial Bio-test Laboratories, 1975).

8.2.2 Neurotoxicity

A health assessment of workers exposed to polybrominated biphenyls and polybromodiphenyl ethers, e.g., DeBDE, during manufacture revealed a higher than normal prevalence of primary hypothyroidism and a significant reduction in sensory and fibula motor velocities; no other dermatological or neurological effects were seen. The authors could not conclude whether these effects were caused by DeBDE or by PBB, which was also produced (earlier) in the plant. DeBDE was not detected in the serum of the workers (Bahn et al., 1980).

8.2.3 Epidemiological studies

The health of workers in facilities where flame retarded polymers were extruded has been evaluated in 3 studies, 2 at Celanese and 1 at General Electric (BFRIP, 1990).

A study was conducted by Celanese Corporation in the late 1970s at their Bishop, Texas, facility. The primary purpose of this study, conducted by Tabershaw Associates, was to investigate the possible effects of employee exposure to formaldehyde. However, brominated flame retardants have been used at the facility since 1970, and, therefore, significant effects resulting from the use of these materials might also have been revealed by the study. No effects that might be attributable to the use of the brominated flame retardants were observed (EBFRIP, 1990).

A more complete study was conducted by General Electric Plastics at their Mt. Vernon, Indiana, facility early in 1988. In the conclusions of the study, it is stated that "there appears to be no evidence that the workers in the study zone display any symptoms associated with exposure to dioxins or related substances. More critically, as a statistical group, the general medical examinations for these workers compare very favorably with the examination for the workers in the control zone or with published values for the general population". It is finally concluded that "the study gives reasons to continue to be observant but no reason to be alarmed" (EBFRIP, 1990).

A comprehensive medical evaluation of workers involved in the processing of polymers containing brominated flame retardants was undertaken at the BASF facility in Ludwigshafen, Germany. In this study, some 40 potentially exposed workers and an equivalent number of workers from a control group were subjected to complete medical and psychological examination. The health of the workers compared favourably with workers in the control zones. None of the workers displayed symptoms associated with exposure to dioxin or related substances, therefore, it was concluded that the workers did not show any symptoms that could be associated with PBDD or PBDF emitted during the polymer processing. It should be kept in mind that there might also be exposure during the formulation of PBDE- containing polymers

and from products made of these polymers. Furthermore, exposure to dusts may also occur (EBFRIP, 1990).

Zober et al. (1992) carried out a morbidity study of extruder personnel with potential exposure to brominated dioxins and brominated furans. The presence of PBDF/PBDD in air was established through air-monitoring during the extrusion blending of polybutyleneterephthalate with DeBDE. Biomonitoring results of 42 workers (exposed during the period 1975-88) and immunological tests for exposed and 42 control employees were presented. Among potentially exposed men, 2,3,7,8-TeBDF/TeBDD concentrations in blood lipid ranged from nd to 112 and from nd to 478 ng/kg, respectively. The control workers had concentrations of 7 and 7-48 ng/kg respectively. Results of the immunological studies showed that the immune system of exposed workers was not adversely affected at these burdens of TeBDF/TeBDD for up to 13 years.

9. EFFECTS ON OTHER ORGANISMS IN THE LABORATORY AND FIELD

Marine unicellular algae, *Skeletonema costatum, Thalassiosira pseudonana*, and *Chlorella* sp. were exposed to commercial DeBDE in 6 algal growth media. The duration of the exposure was 72 h for *S. costatum* and *T. pseudonana* and 96 h for *Chlorella* sp. The population density was estimated by cell counts using a haemocytometer. Inhibition by 1 mg DeBDE/litre acetone was less than 50% in all species (Walsh et al., 1987).

10. PREVIOUS EVALUATIONS BY INTERNATIONAL BODIES

An evaluation by IARC (1990) concluded that there is limited evidence for the carcinogenicity of DeBDE in experimental animals. No data were available from studies on the carcinogenicity of DeBDE in humans. Overall evaluation: DeBDE is not classifiable as to its carcinogenicity for humans (Group 3).

NONABROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

Nonabromodiphenyl ether is not manufactured or used. No data are available on the following topics:

- Environmental transport, distribution, and transformation
- Environmental levels and human exposure
- Kinetics and metabolism in laboratory animals and humans
- Effects on laboratory mammals and *in vitro* test systems
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

1.1 Summary and evaluation

There is no database on which to make an evaluation.

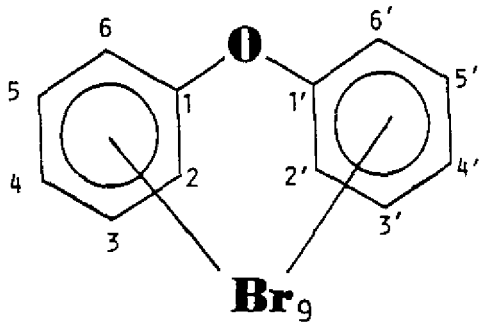
1.2 Recommendations

Levels of contamination of commercial brominated flame retardants with nonabromodiphenyl ether should be minimized to avoid contamination of the environment and exposure of humans.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Chemical structure:



Chemical formula:	C_{12} H Br_9 O
CAS registry number:	63936-56-1
Chemical name:	pentabromo(2,3,4,5-tetrabromophenoxy)-benzene
Common name:	nonabromodiphenyl ether (NBDE); nonabromodiphenyloxide
Relative molecular mass:	880.37

Based on the chemical structure, there are three possible isomers of nonabromodiphenyl ether.

From: US EPA (1984, 1986).

2.2 Physical and chemical properties

No data are available.

2.3 Analytical methods

No specific data are available (see General Introduction section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

NBDE has not been reported to occur naturally (see General Introduction section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

Nonabromodiphenyl ether has been prepared from decabromodiphenyl ether by heating with NaSH in xylene at 130 °C for 2 h. The removal of the reactive Br in the *ortho*-position of decabromodiphenyl ether led to the photostability of the product (Noguchi et al., 1977).

3.2.2 Uses

Nonabromodiphenyl ether is not used commercially as a flame retardant. It is present as an impurity in OBDE at a concentration of 10%.

OCTABROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

Pure octabromodiphenyl ether is not manufactured or used. No data are available on the following topics:

- Kinetics and metabolism in laboratory animals and humans
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

1.1 Summary and evaluation

1.1.1 Identity, physical and chemical properties

Commercial OBDE is a mixture of approximately 11% PeBDE/HxBDE, 44% HpBDE, 31-35% OBDE, 10% NBDE, and 0.5% DeBDE. On the basis of the chemical structure, there are 12 possible isomers of OBDE and 24 possible isomers of HpBDE.

The melting point varies from about 80 °C to > 200 °C. The vapour pressure is $< 10^{-7}$ mmHg. The solubility in water is low and the *n*-octanol/water partition coefficient (log P_{ow}) > 5.5. The above variations in physical data may be explained by the differences in composition of the mixtures tested.

1.1.2 Production and uses

The worldwide consumption of commercial OBDE per year is 6000 tonnes, 70% of which is used as a flame retardant in ABS for the production of computers and business cabinets. OBDE is the second most widely used PBDE flame retardant.

1.1.3 Environmental transport, distribution, and transformation

Components of commercial OBDE have been found in aquatic sediment and human fat. Some lower brominated components (HxBDE and PeBDE) of commercial OBDE have been found in

biota. OBDE has not been detected, but HpBDE and NBDE have generally not been looked for. Commercial OBDE components are likely to be persistent but, as bromination levels rise beyond HxBDE, they are increasingly unlikely to bioaccumulate. A bioaccumulation factor of less than 2 has been found in carp for a commercial OBDE product.

Pyrolysis of commercial OBDE, as such, or of polymers with OBDE as a flame retardant (with, or without, Sb_2O_3) at 600 °C has been shown to produce PBDF and, in much lower concentrations, PBDD. Processing of ABS with OBDE/Sb_2O_3 under different conditions, showed that under normal processing conditions, only low levels of PBDF were formed. Under abusive conditions, the concentrations were much higher. PBDD concentrations were low in both cases.

1.1.4 Environmental levels and human exposure

OBDE and the lower brominated components of commercial OBDE were not detected in water samples collected in Japan in 1987 and 1988. Sediment samples were also analysed and, in approximately 2-6% of the samples, OBDE was detected in concentrations ranging from 8 to 22 μg/kg dry weight. Lower brominated components were also found in the sediment.

OBDE was not detected in fish samples collected in Japan in 1987 and 1988.

In the USA, samples of human fat were investigated for the presence of PBDF and PBDD in 1987. The samples were derived from 865 specimens combined to form 48 composite analogues. The composite design was based on 9 census divisions and 3 age groups. In these samples, PBDE were also identified and preliminary evidence showed the presence of OBDE at a frequency of 60% and an estimated concentration of up to 8000 ng/kg.

1.1.5 Kinetics and metabolism in laboratory animals and humans

No data are available.

1.1.6 Effects on laboratory mammals and in vitro *test systems*

The acute toxicity of commercial OBDE for laboratory mammals is low. The substance is not irritant to the skin and gives only slight eye irritation in rabbits. In short-term toxicity studies (4-week and 13-week), rats administered dietary levels of 100 mg/kg had increased liver weights and microscopic changes characterized by enlarged centrolobular and midzonal liver parenchymal cells containing granular structures. These liver changes were more severe at higher dose levels, i.e., 1000 and 10 000 mg/kg diet. In addition, hyperplasia of the thyroid was seen. Total bromine content in the tissues increased during the study and decreased slowly during a recovery period. The liver changes were reversible. In an inhalation study with micronized dust of OBDE (8 h/day for 14 consecutive days), no effects were observed with exposure to 1.2 mg/m^3, but a level of 12 mg/m^3 caused the liver changes described in the oral studies.

In rats, commercial OBDE at relatively low doses increased cytochrome P450 and induced hepatic microsomal enzymes, such as UDP-glucuronyl transferase and benz[*a*]pyrene hydroxylase. Commercial OBDE induced a porphyrinogenic effect in cultures of chick embryo liver cells.

OBDE was tested for teratogenic potential in rats; at high dose levels (25.0 and 50.0 mg/kg body weight), resorptions, or delayed ossification of different bones and fetal malformations were observed. The malformations observed with doses of 25 mg/kg body weight and higher were most likely associated with maternal toxicity. These changes were not seen at dose levels of 15.0 mg/kg body weight or less. In rabbits, there was no evidence for teratogenic activity, but fetotoxicity was seen at a maternally toxic dose level of 15 mg/kg body weight. Teratogenicity studies showed a no-effect level of 2.5 mg/kg body weight.

In 28-day and 90-day rat studies, 100 mg OBDE per kg diet (equivalent to 5 mg/kg body weight) induced minimal effects in the liver. No no-effect level was established.

Results of the mutagenicity tests including an unscheduled DNA assay, *in vitro* microbial assays, and an assay for sister chromatid exchange with Chinese hamster ovary cells were all negative.

No long-term/carcinogenicity test results are available.

1.1.7 Effects on humans

No data are available.

1.1.8 Effects on other organisms in the laboratory and field

Minimal data are available.

1.2 Conclusions

1.2.1 OBDE

Commercial OBDE is a mixture of hexa-, hepta-, octa-, and nonabromodiphenyl ether, all of which persist in the environment, largely bound to sediment.

OBDE is widely incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure by extraction from polymers is unlikely.

The acute toxicity of OBDE is low. There is no information on uptake and loss in mammals. OBDE is not teratogenic or mutagenic. Long-term toxicity and carcinogenicity studies are not available.

Several components of commercial OBDE have been identified in human adipose tissue. The acute risk for the general population is likely to be low. Risk assessment of long-term exposure is not possible, because of the lack of relevant toxicity studies.

No information is available to draw conclusions on occupational exposure to, or effects of, OBDE.

Limited information is available on the toxicity of OBDE for organisms in the environment. Components of the commercial OBDE mixture with lower levels of bromination may bioaccumulate in organisms.

1.2.2 Breakdown products

Formation of PBDF, and to some extent PBDD, may occur when OBDE, or products containing it, are heated to 400-800 °C. The possible hazards associated with this have to be addressed.

Exposure of the general population to PBDF impurities in flame-retarded polymers is unlikely to be significant. Properly controlled incineration should not lead to the emission of significant quantities of brominated dioxins and -furans. Any uncontrolled combustion of products containing commercial OBDE can lead to the generation of unquantified amounts of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future EHC on PBDF/PBDD.

1.3 Recommendations

1.3.1 General

- Best available techniques should be used in the manufacture of commercial OBDE, to minimize levels of hexa- and lower brominated congeners, because of their bioaccumulation potential in the environment.
- Workers involved in the manufacture of OBDE, and products containing the compound, should be protected from exposure using appropriate industrial hygiene measures, monitoring of occupational exposure, and engineering controls.
- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled to minimize environmental contamination with this persistent material and its breakdown products.
- Incineration of materials, flame retarded with OBDE, should only be in properly constituted incinerators running under consistently optimal conditions. Burning by any other means may lead to production of PBDF and/or PBDD.

1.3.2 Further studies

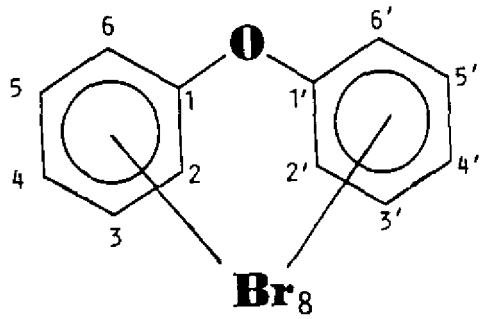
Because the present toxicological database is inadequate to evaluate the hazards of commercial OBDE for humans and the environment, and, to support its use, the following studies should be carried out:

- Investigations on the bioavailability and ecotoxicity of sediment-bound components of commercial OBDE using the relevant organisms
- Extended monitoring of environmental levels of components of commercial OBDE
- Long-term toxicity and carcinogenicity studies of commercial OBDE
- Monitoring of occupational exposure to commercial OBDE
- Further investigations on the generation of PBDF under real fire conditions
- Further studies on environmental biodegradation and photodegradation in compartments other than water
- Investigation of possible methods and consequences of recycling of OBDE-containing polymers
- Validation of analytical methods for OBDE in various matrices
- Investigations on the possibility of migration from different types of polymers.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Chemical structure:



Chemical formula:	$C_{12}H_2Br_8O$
Relative molecular mass:	801.47
Common names:	octabromodiphenyl ether (OBDE) octabromodiphenyl oxide
CAS registry number:	32536-52-0
EINECS number:	2510879
MITI number:	3-3716
CAS name:	1,1'-oxy(bis)- octabromo-benzene
Synonyms:	octabromodiphenyl ether; benzene, 1,1'-oxy-bis-,octabromo-phenyl ether

Based on the chemical structure, there are 12 possible isomers of octabromodiphenyl ether.

From: IRPTC (1988); US EPA (1984); Ethyl Corp. (1992b).

2.1.1 Technical product

Trade names: Bromkal 79-8 DE; DE-79™; FR 143; Tardex 80; FR 1208; Adine 404; Saytex 111

The commercial product is a mixture of polybrominated diphenyl ethers with the following typical composition (see Table 1):

0-0.7%	decabromodiphenyl ether
9.5-11.3%	nonabromodiphenyl ether
31.3-35.3%	octabromodiphenyl ether
43.7-44.5%	heptabromodiphenyl ether
10.5-12.0%	hexabromo- and pentabromodiphenyl ether.

Commercial OBDE has also been reported to be a mixture of 4% hexabromo-, 62% hepta-, and 34% octabromodiphenyl ether (De Kok et al., 1979).

2.2 Physical and chemical properties

Commercial products based on OBDE are off-white powders with a faint odour, and a bromine content of 79-81%. In case of fire, and, in the presence of fuels, hydrogen bromide and/or bromine may be liberated (Kopp, 1990).

Melting point: 200 (167-257) °C, Ethyl Corp. (1992b); 79-87 °C; 75-125 °C, Kopp (1990); and 170-220 °C, De Kok et al. (1979)

Vapour pressure: $< 10^{-7}$ mmHg at 25 °C

Solubility at 25 °C in g/litre:

water	< 1
methanol	2 (7)
methylene chloride	110
toluene	190 (353)
benzene	200
styrene	250
methyl ethyl ketone	40
acetone	20 (122)

(From: Great Lakes Chemical Corporation, 1987, 1990a)

Specific gravity: 2.76 (2.63)

(From: US EPA, 1989, 1986)

n-Octanol/water partition coefficient (log Pow): 5.5; 8.35-8.90

(From: Watanabe & Tatsukawa, 1990; Ethyl Corporation, 1992b).

2.3 Analytical methods

No specific data are available (see General Introduction section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

Octabromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

Octabromodiphenyl ether is synthesized by treating diphenyl ether with 8 equivalents of Br_2 in the presence of Al_2Cl_6/Al_2Br_6, first at 35 °C and then at 120 °C (US EPA, 1986). No data are available on production levels.

The annual consumption of OBDE in Japan was 150 tonnes in 1983, and 1000 tonnes in 1987, mainly used in the preparation of ABS (Watanabe, 1987; Watanabe et al., 1987b). Consumption in Germany was 600-800 tonnes/year in plastics in 1988 (CEM, 1989). Estimation of total use of octabromodiphenyl ether in the Netherlands in 1988 was 600-800 tonnes.

The actual worldwide consumption of OBDE per year is 6000 tonnes (Arias, 1992).

3.2.2 Uses

The high bromine content and its broad melting range make OBDE the material of choice for a large variety of thermoplastics. Its use is recommended for injection mouldings, especially when high surface quality is desirable. Applications: ABS, nylon, high impact polystyrene, low density polyethylene, polypropylene random copolymer (Flick, 1986). It is also used in adhesives and coatings.

The major use of OBDE is in computer and business equipment cabinets (Personal communication, McAllister).

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

4.1 Biotransformation

No data are available.

4.2 Abiotic degradation

4.2.1 Pyrolysis of octabromodiphenyl ether

Pyrolysis of octabromodiphenyl ether (OBDE) at 630 °C, in air, resulted in approximately 96% decomposition leading to the formation of polybrominated benzenes (PBBz) and about 5% of PBDF and PBDD, mainly two pentabromodibenzodioxins and a hexabromodibenzofuran. Small amounts of tri- to heptabromodibenzodioxins and tetra- to heptabromodibenzofurans were present (Buser, 1986).

4.2.2 Pyrolysis studies with polymers containing octabromodiphenyl ether

Pyrolysis studies were conducted on ABS containing OBDE (15%) and antimony trioxide (6%) at 600 °C (Neupert et al., 1989). Brominated dibenzofurans and brominated dibenzodioxins were identified in the pyrolysis residues, however, the brominated dibenzodioxins and 2,3,7,8-TeBDF were present in very low quantities.

The pyrolysis of Cycolac, flame retarded with OBDE in combination with antimony trioxide, gave high levels of brominated dibenzodioxins and dibenzofurans and significant levels (9.3 mg/kg) of 2,3,7,8-isomers at 600 °C. Pyrolysis temperatures were 200, 250, and 600 °C during 30 min. The total PBDF were 110.8, 666, and 1631 mg/kg, respectively. The values for PBDD were 1.75, 0.75, and 31.5 mg/kg, respectively (Fresenius Institute, 1990).

4.2.3 Behaviour of octabromodiphenyl ether during processing

BFRIP designed an experiment to investigate the behaviour of OBDE in ABS under controlled moulding or extrusion conditions. The polymer system ABS/OBDE was operated under different conditions (Table 25). After moulding, all the samples were analysed for brominated dibenzodioxins and dibenzofurans. With the exception of a single sample, brominated dibenzodioxins were not identified in any of the samples. In this sample, the 2,3,7,8-brominated dibenzofurans were seen only at very low concentrations (Table 26). The data show that processing of the resin systems under normal conditions (225 °C; 1-min cycle) resulted in no change in composition from that of the base resin formulation (BFRIP, 1990; McAllister et al., 1990).

Table 25. Moulding study with ABS/OBDE system at different processing temperatures[a]

Polymer/FR	Severity	Conditions
ABS/OBDE	normal	225 °C, 1 min cycle
	abusive	245 °C, 10 min cycle
ABS/OBDE	acrylonitrile-butadiene-styrene/	79.8%
	OBDE +	16.0%
	antimony trioxide	4.2%

[a]From: McAllister et al. (1990).

Craig et al. (1989) measured the PBDF and PBDD contents of pre- and post-extruded Cycolac resin treated with OBDE and antimony trioxide. Two samples were tested at extrusion temperatures around 220 °C. PBDF levels varied from one another by a factor of 4 in the pre-extrusion samples and by a factor of 2 in the post-extrusion samples. The higher levels of total PBDF were 38 300 μg/kg in the pre-extruded and 84 500 μg/kg in the post-extruded resins. PBDD was not detected in the pre-extruded resin, but, in one post-extruded sample, it was found at a level of 112 μg/kg. The fumes emitted during extrusion were also analysed and a level of 1850 μg/kg was found. PBDD was found in a concentration of 0.54 μg/kg. (Fume data expressed as μg/kg of extruded resin).

Table 26. Comparison of Triangle Laboratories Inc. (TLI) (Research Triangle Park) and US EPA Laboratory (Las Vegas) results on moulded polymer samples containing various flame retardants. (All concentrations are in mg/kg)[a]

ABS with octabromodiphenyl ether

	Normal 1222-16-4		Abusive 1222-16-5	
Compound	TLI	US EPA[c]	TLI	US EPA
1,2,3,7,8-PeBDD	< 0.002		0.02	
2,3,7,8-TeBDF	< 0.002		0.004	
Total TeBDD	< 0.001		0.01	
Total PeBDD	0.03		< 0.13	
Total TeBDF	0.003	0.003	0.17	0.16
Total PeBDF	1.1	1.3	< 14.0	31.5
Total HxBDF	< 135.0	2.2	< 118.0	9.1
Total HpBDF[b]	< 6.6	0.6	< 2.9	0.7
Total OBDF[b]	< 34.5	0.04	< 13.9	0.02

[a]From: BFRIP (1990). Values preceded by < are maximum possible. Analytical signals met identification criteria, but may include contribution from interferences. US EPA and TLI used different identification criteria resulting in differences in reported values.
[b]Concentration of HpBDF and OBDF from TLI are not validated because of lack of standards. Concentrations are reported for comparison only.
[c]Average of two analysis of same sample.

4.3 Bioaccumulation

A single study on a mixture of PBDE including HxBDE to DeBDE indicated little bioaccumulation in carp with a bio-concentration factor of < 4 after 8 weeks of exposure (CBC, 1982).

4.4 Ultimate fate following use

For the ultimate fate of OBDE in the environment see General Introduction, section 6.1.

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 Environmental levels

5.1.1 Water

In Japan, OBDE was not detected in 75 water samples (limit of determination 0.1 μg/litre) in 1987 and was not detected in 147 water samples collected at 49 areas (limit of determination, 0.07 μg/litre) in 1988-89 (Environment Agency Japan, 1989, 1991).

5.1.2 Aquatic sediments

In 1987, environmental surveys were conducted concerning OBDE in bottom sediment. OBDE was detected in 3 out of 51 samples at concentrations ranging from 8 to 21 μg/kg in 1987 (limit of determination 7 μg/kg dry weight) and was detected in 3 out of 135 samples, collected at 45 areas, at concentrations ranging from 15 to 22 μg/kg dry weight (limit of determination 5 μg/kg) in 1988-89 (Environment Agency Japan, 1989, 1991).

5.1.3 Aquatic and terrestrial organisms

In Japan, OBDE was not detected in 75 fish samples in 1987 and was not found in 144 fish samples collected in 48 areas in 1988-89 (limit of determination 5 μg/kg wet weight) (Environment Agency Japan, 1989, 1991).

5.2 Exposure of the general population

In the USA, Cramer et al. (1990a,b) studied the presence of PBDD/PBDF in human adipose tissue samples of the fiscal year 1987 (National Human Adipose Tissue Survey). The samples were derived from 865 specimen combined to form 48 composite analogues. The composite design was based on 9 census divisions and 3 age groups. The analysis was carried out using HRGC/HRMS to determine PBDD/PBDF. No PBDF/PBDD was

found (limits of determination, 10-40 ng/kg, depending on congeners). Identification of the PBDE was based on comparison of full scan mass spectra of the samples with the available standards, application of SIM techniques to compare theoretical ion ratios with observed ion ratios for characteristic ions, and measurement of fragment losses from the molecular ion clusters. Preliminary evidence for the presence of OBDE was found (frequency, 60%) with an estimated concentration range of ND-8000 ng OBDE/kg (Cramer et al., 1990a,b; Stanley et al., 1991).

5.3 Occupational exposure during manufacture, formulation, or use

No data are available.

6. EFFECTS ON LABORATORY MAMMALS AND *IN VITRO* TEST SYSTEMS

6.1 Single exposure

6.1.1 Oral: Rat

The acute oral LD_{50} in the rat is > 28 g/kg body weight (Kalk, 1982); > 5 g/kg body weight (Kopp, 1990; Great Lakes Chemical Corporation, 1990a).

Male Charles River CD rats were administered commercial OBDE, suspended in corn oil, by intubation, at doses of 50, 500, or 5000 mg/kg body weight. The observation period was 14 days. The rats showed normal weight gain and no animals died (Great Lakes Chem Corp., 1987; 1990a).

6.1.2 Dermal: Rabbit

Commercial OBDE was applied to the clipped, abraded, or intact skin of male and female albino rabbits at concentrations of 200 or 2000 mg/kg body weight for 24 h. During the observation period of 14 days, none of the rabbits died and all had normal weight gain. The dermal LD_{50} for rabbits is > 2 g/kg body weight (Great Lakes Chemical Corporation, 1987, 1990a).

6.1.3 Inhalation: Rat

The inhalation LC_{50} of Saytex 111 in rats was > 50 mg/litre (US EPA, 1986).

Male and female Charles River CD rats were exposed for 1 h to concentrations of commercial OBDE in air of 2 or 60 mg/litre. The physical nature of the substance precluded administration at higher levels than 60 mg/litre. Rats exposed to 2 and 60 mg/litre had decreased motor activity, erythema, and eye squint, during exposure. The animals exposed to 60 mg/litre also had tachypnea. During the 14-day observation period, the animals appeared normal, and exhibited normal body weight gain, except for one rat at the highest dose level, which showed salivation on days 5 and 7

of the observation period (Great Lakes Chemical Corporation, 1987) (no further details).

6.2 Short-term exposure

5.2.1 Oral: Rat

Charles River CD rats were fed commercial OBDE at daily, dietary dose levels of 0, 100, or 1000 mg/kg for 28 days. There were 10 male and 10 female rats in each dose group. No changes in appearance, behaviour, mortality, feed consumption, or body weight gain were observed. Results of haematology, blood chemistry, and urinalysis were similar to those in the controls. Absolute and relative liver weights were significantly increased in female rats given 100 mg/kg and in rats of both sexes given 1000 mg/kg diet. Other increases in organ weights were not considered compound-related. No gross pathological lesions were noted in rats in any of the groups. Compound-related histopathological liver lesions were observed in both treated groups of rats. They consisted of enlarged centrolobular and midzonal liver parenchymal cells in which the cytoplasm had large areas of finely granular structures containing eosinophilic "round bodies". These changes occurred more frequently and with greater severity in the male animals. Their incidence and severity were dose-related. Rats given 1000 mg/kg had a slight to moderate hyperplasia of the thyroid, but it was not clear whether this was compound-related. Dose-related increases in total bromine levels of the liver were noted in both males and females and ranged from about 6 to 137 times the levels found in controls (Great Lakes Chemical Corporation, 1987).

Another 28-day feeding study was carried out on 10 male and 10 female Charles River CD rats per group, which were administered a diet containing 100, 1000, or 10 000 mg commercial OBDE/kg. The control group consisted of 35 male and 35 female rats from the 90-day feeding study, described below. At the end of the study, 5 rats of each sex/group were sacrificed and the remaining 5 animals/sex per group were maintained on normal diets for 4 weeks (recovery period). No changes in appearance, behaviour, or mortality were observed. Food consumption and body weight gain were slightly higher in

the control group. Haematology values were normal, but serum urea nitrogen levels were slightly elevated in some of the rats given 10 000 mg/kg diet. An increase in absolute and relative liver weights was observed in some of the rats given 1000 and 10 000 mg/kg. At necropsy, the livers of some animals in the 10 000 mg/kg group showed accentuated lobulization and discoloration. The livers of rats from all 3 dose levels showed enlargement of the centrolobular and midzonal hepatocytes, the cytoplasm of which had large areas of finely granular appearance and frequently contained eosinophilic "round bodies". In the 10 000 mg/kg group, vacuolization of hepatocytes and necrosis of scattered individual hepatocytes were seen. In all 3 treated groups, the liver lesions were less severe after the 4-week recovery period than during the administration of the compound. A dose-related increase in liver total bromine content was seen in rats in all treated groups after 4 weeks of treatment, but these total bromine levels decreased rapidly in the recovery period. Only in the rats receiving the lowest dose level did the liver total bromine concentration approach control levels after a 4-week withdrawal period (Great Lakes Chemical Corporation, 1987).

Charles River CD rats were fed commercial OBDE at dietary levels of 0, 100, 1000, or 10 000 mg/kg for up to 13 weeks. There were 35 male and 35 female rats in each dose group. Behaviour, appearance, body weight, food consumption, haematology, blood chemistry, and urinalysis were studied after 1 and 2 months, and, at the end of the study, in groups of 5 rats/sex per group. The remaining 20 rats per group were used to study the recovery and 5 rats/sex per group were sacrificed after 13 and 21 weeks and 6 months after withdrawal. During the study, a few rats out of each group died, but without any dose-relationship, the majority of these deaths occurring after the collection of blood.

In the 100 mg/kg diet group, the only effect that was seen was an increase in absolute and relative liver weights. Microscopic changes were seen in 4 out of 10 rats, and were typified by granular cytoplasmic changes. Liver total bromine contents increased during the 13-week treatment, but decreased during the recovery period.

In the 1000 mg/kg group, a decrease in body weight gain was observed, but haematology, blood chemistry, and urinalysis results

were comparable with the controls. Increases in absolute and relative liver and thyroid weights were observed, but these effects were not seen in the animals sacrificed during the recovery period. Microscopic lesions were seen in the cytoplasm of the centrolobular and midzonal hepatocytes and included vacuolization, and hyaline intracytoplasmic inclusions. A hyperplastic nodule was found, after 6 months withdrawal, in one rat each from the 1000 and 10 000 mg/kg groups.

In the 10 000 mg/kg group, a decrease in body weight gain was observed, even during the withdrawal period. Decreases in haemoglobin, haematocrit, and erythrocyte counts were also observed. One female animal had hypochromia, polychromia, and anisocytosis of the erythrocytes. Glucose levels in the blood were slightly lower than in the controls. Orange colouration of the urine was observed during weeks 13-39. A significant increase in absolute and relative liver, kidney, and thyroid weights was observed. At autopsy, there was accentuated lobulation and yellowish mottling of the livers and brownish discoloration of the liver and kidneys. After one year of recovery, no such gross changes were observed. Histopathologically, the liver changes consisted of granular cytoplasmic changes, cytoplasmic vacuolization (possibly representing fatty degeneration), necrosis of scattered parenchymal cells or of centrolobular cells, centrolobular fibrosis, and pigmented Kupfer cells. In the kidneys, the changes were characterized by the occurrence of small to moderate numbers of cortical regenerative tubules. One rat had a severe tubular nephrosis. Cellular changes in the thyroid were probably compound-related. During the recovery period, the histological changes decreased in severity and frequency.

The total bromine content of the liver increased during the 13 weeks of treatment and decreased during the recovery period, but remained higher (not significantly) than the control values after one year (Great Lakes Chemical Corporation, 1987).

6.2.2 *Inhalation: Rat*

Charles River CD rats were exposed (whole-body) to a micronized dust of commercial OBDE, introduced into inhalation chambers at nominal concentrations of 1.2, 12, 120, and 1200 mg/m^3 for 8 h/day on 14 consecutive days. Actual airborne

dust concentrations were 15-45% of the nominal values. It was not possible to measure the extent of oral intake of the substance. There were 5 male and 5 female rats in each dose group and in the controls. No animals died during the test period nor were there any changes in appearance or general behaviour in the 1.2 and 12 mg/m^3 groups. By the end of the 8-h exposure period, all animals in the 1200 mg/m^3 group and part of the 120 mg/m^3 group exhibited a fast breathing pattern, which had disappeared by the morning following exposure. Food consumption, body weight gain, haematology, blood chemistry, and urinalysis in all of the dose groups were normal. The total bromine concentrations in the lung, liver, and fat were significantly higher than in the controls. At autopsy, the average total bromine concentrations in the lung and fat were about 1.5-12.5 times higher than in the liver. The relative liver weights of the animals in the 12, 120, and 1200 mg/m^3 dose groups were significantly increased in a dose-related manner. These changes were accompanied by histopathological lesions consisting of focal to multifocal cytoplasmic enlargement of the hepatocytes, and focal acidophilic degeneration of individual, and small groups of, liver cells. At the 2 highest dose levels, the enlargement of the hepatocytes was multifocal to diffuse in distribution and small to large areas had necrosis in the centrolobular regions of the affected liver lobules, especially in the 1200 mg/m^3 group. No other compound-related effects were observed (Great Lakes Chemical Corporation, 1987).

6.3 Long-term exposure

No data are available.

6.4 Skin and eye irritation; sensitization

6.4.1 Skin irritation

Commercial OBDE was applied to the clipped and occluded intact, or abraded, skin of male and female albino rabbits at a dose of 500 mg. After 24 h, the skin was washed and examined for irritation. The examination was repeated after 72 h. One rabbit had slight erythema at 72 h; the remaining rabbits did not have

skin changes. It was concluded that OBDE is not a primary skin irritant (Great Lakes Chemical Corporation, 1987).

6.4.2 Eye irritation

Single applications of 100 mg commercial OBDE were made into the conjunctival sac of the eye of 3 male and 3 female New Zealand white rabbits. Examinations were made at 24, 48, and 72 h, and 7 days. A slight discharge was noted from the eyes of 2 rabbits at 24 h and a slight redness was noted in the eye of one rabbit at 48 h. No ocular irritation or corneal damage (sodium fluorescein and UVR were used) was observed (Great Lakes Chemical Corporation, 1987).

6.5 Teratogenicity, reproductive toxicity, and embryotoxicity

6.5.1 Teratogenicity

6.5.1.1 Oral: Rat

In a range-finding study, female rats (number not specified) were dosed daily, by gavage, from days 6 to 15 of gestation with 2.5, 10.0, 15.0, 25.0, or 50.0 mg commercial OBDE (DE-79)/kg body weight. All animals survived until gestation day 20, when they were sacrificed. At 25.0 mg/kg, increased serum bromine levels were observed. Mean maternal body weight gain was reduced in the 50.0 mg/kg group during gestation. Increased numbers of late resorptions and significantly reduced mean fetal weights were observed at the highest dose level. The cholesterol level was slightly increased in the dams given 50.0 mg/kg. No compound-related microscopic findings were observed in the liver and kidneys of the mothers. No compound-related effects were observed at 15.0 mg/kg or lower. The malformations and developmental variations observed in the 50.0 mg/kg group were associated with maternal toxicity. Fetal anasarca and bent limb bones were observed at this dose level. Mean fetal body weight and increased post implantation loss due to late resorptions was also observed at this level, but the losses were not statistically significant, compared with the controls. Reduced ossification of the skull, various unossified bones, and two instances of bent ribs

were noted at this dose level, and were probably secondary to maternal toxicity (Great Lakes Chemical Corporation, 1987) (abstract).

Four groups of 25 pregnant Charles-River Crb:COBS CD (SD) BR rats were administered corn-oil suspensions of Saytex 111, by gavage, at doses of 0, 2.5, 10.0, or 25 mg/kg body weight per day on days 6-15 of gestation. The dams were sacrificed on day 20 of gestation and the fetuses were examined for gross visceral and skeletal abnormalities. The substance was more toxic to the conceptus than to the dam. At 25.0 mg/kg, dose-dependant effects on the conceptus were observed. These included reduced average fetal body weight, increased embryo/fetal deaths (resorptions), fetal malformations, such as enlarged heart, rear limb malformation, and delayed skeletal ossification. At 10 mg/kg, the only observed effect was a statistically insignificant reduction in average fetal body weight (US EPA, 1986).

6.5.1.2 *Oral: Rabbit*

Groups of 26 inseminated adult New Zealand White rabbits (weight 3.5-4.5 kg) were treated with 0 (corn oil), 2.0, 5.0, or 15 mg Saytex 111/kg body weight per day, by gavage, on days 7-19 of gestation. Saytex 111 was a mixture containing; 0.2% PeBDE, 8.6% HxBDE, 45.0% HpBDE, 33.5% OBDE, 11.2% NBDE, and 1.4% DeBDE. Body weight gain was recorded on gestation days 0, 7, 10, 13, 16, 20, and 28. In addition, maternal liver, kidneys, and gravid uterine weights were measured at the time of hysterectomy. The offspring were examined on day 28 of gestation. A statistically significant increase in liver weight and a decrease in body weight gain were observed in the 15 mg/kg group. There was no statistically significant deviation in maternal mortality, number of pregnancies, number of litters with viable pups, corpora lutea/dam, implantations/dam, live fetuses/litter, percentage of resorptions, and fetal body weight. Slight fetal toxicity was observed in the 15 mg/kg group, as evidenced by a significant increase in delayed ossification of the sternebrae. There was an increase in the incidence of retrocaval ureter in the 5 and 15 mg/kg group and fused sternebrae in the 5 mg/kg group. These increases were not dose related. It was concluded by the authors

that there was no evidence for teratogenic activity but that there was slight fetotoxicity at maternally toxic dose levels, e.g., 15 mg/kg body weight (Breslin et al., 1989).

6.6 Mutagenicity and related end-points

6.6.1 DNA damage

An unscheduled DNA synthesis (UDS) assay, a test to induce DNA damage followed by repair in mammalian cells, was carried out with monolayers of WI-38 human fibroblast cells, which were exposed to commercial OBDE in the presence of radiolabelled thymidine. OBDE was tested at 5 concentrations ranging from 60 to 300 μg/ml. UDS was not induced by OBDE either in the presence or in the absence of a metabolic activation system (Great Lakes Chemical Corporation, 1987).

6.6.2 Mutation

Commercial OBDE was examined for mutagenic activity at a number of concentrations in *in vitro* microbial assays using *Salmonella typhimurium* and *Saccharomyces cerevisiae* with, and without, liver microsomal enzyme preparations from Aroclor-induced rats. The results of these tests were all negative (Great Lakes Chemical Corporation, 1987) (no details).

6.6.3 Chromosomal effects

In an assay for sister chromatid exchanges, Chinese hamster ovary cells were exposed to concentrations of commercial OBDE of 7.5, 25, 75, 250, or 750 μg/ml (in DMSO), for 2 h, in the presence, or absence, of a metabolic activation system. The exposure period was followed by a 24-h expression period. No statistically significant increases in the number of exchanges per chromosome or the number of exchanges per cell were seen at any of the levels tested (Great Lakes Chemical Corporation, 1987).

6.7 Carcinogenicity

No data are available.

6.8 Other special studies

6.8.1 Liver

Commercial OBDE in corn oil was administered by gavage to six male Sprague-Dawley rats (200-250 g) for 90 days. When extensive induction was revealed at all the original doses of 6.25, 12.5, and 25 μmol/kg per day, the study was repeated at doses of 0.78, 1.56, and 3.13 μmol/kg per day. OBDE did not cause induction of NADPH cytochrome c reductase and cytochrome P450 at the lower doses. However, a dose of 0.78 μmol/kg per day caused increases in both *O*-ethyl-*O*-*p*-nitrophenyl phenylphosphonothioate (EPN) detoxification and *p*-nitroanisole demethylation; larger increases were seen with increasing dose levels. After a 30-day recovery period, evidence of the maintenance of an induced state was seen only in animals receiving 3.13 μmol/kg per day. These elevations were still observable 60 days after the last dose. No histological liver abnormalities were observed in rats treated with 3.13 μmol/kg body weight or less (Carlson, 1980b).

In another study on male rats (200-250 g) administered commercial OBDE, by gavage, at 0.1 mmol/kg per day in corn oil for 14 days, the above increase in enzyme activity was accompanied by an increase in activity of UDP-glucuronyl transferase and benzo[*a*]pyrene hydroxylase 24 h after the seventh dose (Carlson, 1980a). Measurements made on days 30 and 60 of recovery after 90 days exposure showed that the indicators of induced xenobiotic metabolism returned slowly to control values.

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

6.9 Appraisal

In 28-day and 90-day rat studies, 100 mg OBDE per kg diet (equivalent to 5 mg/kg body weight) induced minimal effects in the liver. No no-effect level was established. In a 14-day inhalation study with micronized dust of OBDE, no effects were found with exposure to 12 mg/m^3. Teratogenicity studies showed a no-effect level of 2.5 mg/kg body weight.

At the highest reported value of OBDE of 8000 ng/kg, from the Human Adipose Tissue Sample Study, assuming 15% adipose tissue in the adult male, a "stored" dose of 1.2 μg/kg can be calculated. Assuming 1% of the administered dose was absorbed, this would extrapolate to a total dose of 120 μg/kg. With the further assumption that the total exposure occurred over one year, a daily dose of 0.38 μg/kg per day can be calculated. This dose is approximately 4 orders of magnitude below the most sensitive end-point in mammalian toxicity testing on OBDE (NOEL = 2.5 mg/kg body weight in a teratology study).

HEPTABROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

Heptabromodiphenyl ether is not manufactured or used.

There is no database on pure HpBDE on which to make an evaluation.

No data are available on the following topics:

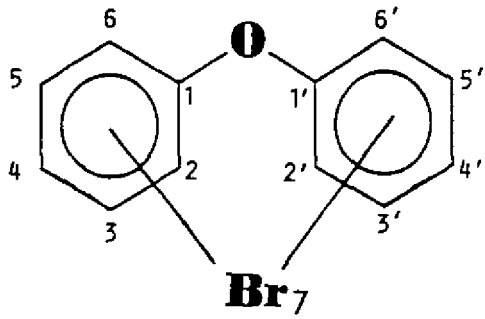
- Kinetics and metabolism in laboratory animals and humans
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

Because HpBDE is the major component of commercial octabromodiphenyl ether, the summary, evaluation, conclusions, and recommendations on commercial OBDE, are relevant to "commercial" HpBDE.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, AND ANALYTICAL METHODS

2.1 Identity

Chemical structure:



Chemical formula:	$C_{12} H_3 Br_7 O$
Relative molecular mass:	722.3
CAS registry number:	68928-80-3
CAS name:	1,1'-oxy-bis(heptabromobenzene)
Common name:	heptabromodiphenyl ether (HpBDE)

From: US EPA (1986).

On the basis of the chemical structure, there are 24 possible isomers of heptabromodiphenyl ether.

2.2 Physical and chemical properties

Melting point:	70-150 °C (decomposition > 232 °C)
Density:	2.6 at 20 °C

Vapour pressure:	< 13.3 Pa at 20 °C
n-Octanol/water partition coefficient (log P_{ow}):	not available

From: US EPA (1986).

2.3 Analytical methods

No specific data are available (See General Introduction, section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

Heptabromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

Heptabromodiphenyl ether is not produced commercially or used, but octabromodiphenyl ether contains approximately 44% HpBDE (see General Introduction, Table 1).

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

A single study on mixed PBDE ranging from HxBDE and DeBDE indicated little bioaccumulation in carp with a bioconcentration factor of < 4, after 8 weeks of exposure (CBC, 1982).

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

Cramer et al. (1990a,b) studied the presence of PBDD/PBDF in human adipose tissue samples in the USA in the fiscal year 1987 (National Human Adipose Tissue Survey). The samples were derived from 865 specimens combined to form 48 composite analogues. The composite design was based on 9 census divisions and 3 age groups. The analysis was carried out using HRGC/HRMS to determine PBDD/PBDF. No PBDF/PBDD were found, the limit of determination ranging from 10 to 40 ng/kg, depending on the congeners. Identification of the PBDE was based on comparison of full scan mass spectra of the samples with the available standards, the application of SIM techniques to compare theoretical ion ratios with observed ion ratios for characteristic ions, and the measurement of fragment losses from the molecular ion clusters. Preliminary evidence for the presence of heptabromodiphenyl ether was found at a frequency of 100%, with an estimated concentration range of 1-2000 ng HpBDE/kg (Cramer et al., 1990a,b; Stanley et al., 1991).

6. EFFECTS ON LABORATORY MAMMALS AND *IN VITRO* TEST SYSTEMS

No data are available on the following topics:

- Short-term exposure
- Long-term exposure
- Reproductive toxicity, embryotoxicity, and teratogenicity
- Mutagenicity
- Carcinogenicity.

6.1 Single exposure

The acute oral LD_{50} for the rat is > 5 g/kg and the dermal LD_{50} for the rabbit, > 2 g/kg body weight (Kopp, 1990).

6.2 Skin and eye irritation; sensitization

The substance is not irritant for either the skin or eyes (Kopp, 1990).

HEXABROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

Hexabromodiphenyl ether is not manufactured or used, but occurs as a contaminant of commercial brominated diphenyl ethers. Such levels of hexabromodiphenyl ether should be minimized to avoid contamination of the environment and exposure of humans.

There is no database on which to make an evaluation.

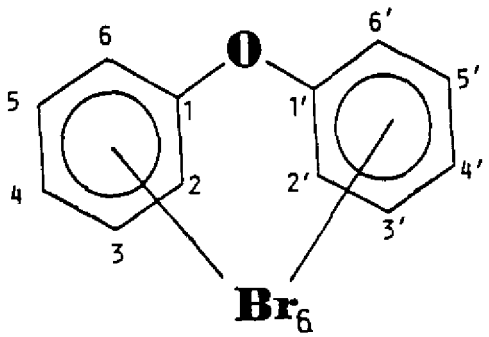
No data are available on the following topics:

- Effects on laboratory mammals and *in vitro* test systems
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Chemical structure:



Chemical formula:	$C_{12} H_4 Br_6 O$
Relative molecular mass:	643.62
CAS registry number:	36483-60-0
CAS name:	1.1'-oxy-bis-hexabromobenzene
Common names:	hexabromodiphenyl ether (HxBDE) hexabromodiphenyl oxide

From: (US EPA, 1984, 1986).

On the basis of the chemical structure, there are of 42 possible isomers of hexabromodiphenyl ether.

2.1.1 Technical product

Trade names:	BR 33N

2.2 Physical and chemical properties

Vapour pressure:	0.95-0.99 kPa at 25 °C
n-Octanol/water partition coefficient (log Pow):	6.86-7.92

From: Pijnenburg & Everts (1991).

2.3 Analytical methods

No specific data are available (see General Introduction, section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

Hexabromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

As far as is known, hexabromodiphenyl ether has not been produced commercially or used, but it is a component of TeBDE, PeBDE, and OBDE at concentrations ranging from 4 to 12% (see General Introduction, Table 1).

3.3 Uses

Total use of penta- and hexabromodiphenyl ethers in the Netherlands in 1988 was estimated to be 350 tonnes (Anon, 1989).

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

A single study on a mixture of PBDE, ranging between HxBDE and DeBDE, indicated little bioaccumulation in carp with a bioconcentration factor of < 4, after 8 weeks of exposure (CBC, 1982).

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 Levels in the environment

5.1.1 Water

In Japan, HxBDE was not detected in 75 samples of water in 1987 or in 150 samples collected in 50 areas in 1988-89 (in both cases the limit of determination was 0.04 μg/litre) (Environment Agency Japan, 1989, 1991).

5.1.2 Aquatic sediments

Marine, estuarine, and river sediment samples were collected at different places in Japan in 1981-83 and analysed for HxBDE. Five out of 15 samples contained 9-26 μg/kg (Watanabe, 1987; Watanabe et al., 1987b).

In 1987, environmental surveys were conducted on HxBDE levels in sediment in Japan. HxBDE was detected in 4 out of 69 samples at concentrations ranging from 7 to 77 μg/kg dry weight (limit of determination 5.1 μg/kg dry weight) in 1987, and, in 4 out of 141 samples collected in 47 areas in 1988-89, at concentrations ranging from 4.5 to 18 μg/kg dry weight (limit of determination 3.5 μg/kg dry weight) (Environment Agency Japan, 1989, 1991).

5.1.3 Aquatic and terrestrial organisms

Mussel and a few species of fish (mullet, goby, and Japanese sea bass) were collected from different seashores in Japan from 1981 to 1985. Other fish species were purchased at a wholesale commercial source in Osaka Prefecture in 1981. HxBDE could not be detected (< 0.2 μg/kg wet weight) in any of the 5 mussel samples or in the 12 fish samples (Watanabe, 1987; Watanabe et al., 1987b).

In 1987, environmental surveys were conducted on HxBDE levels in fish in Japan. HxBDE was detected in 5 out of 75 fish

samples at concentrations ranging from 3.8 to 14 μg/kg wet weight in 1987 and was detected in 5 out of 144 samples collected at 48 areas at concentrations ranging from 2 to 6 μg/kg wet weight in 1988-89 (limit of determination 2 μg/kg wet weight) (Environ. Agency Japan, 1989, 1991).

5.2 General population exposure

In the USA, Cramer et al. (1990a,b) studied the levels of PBDD/PBDF in human adipose tissue samples in 1987 (National Human Adipose Tissue Survey). The samples were derived from 865 specimens combined to form 48 composite analogues. The composite design was based on 9 census divisions and 3 age groups. The analysis was carried out using HRGC/HRMS to determine PBDD/PBDF. No PBDF/PBDD were found, the limit of determination ranging from 10 to 40 ng/kg, depending on the congeners. Identification of the PBDE was based on comparison of full scan mass spectra of the samples with the available standards, application of SIM techniques to compare theoretical ion ratios with observed ion ratios, for characteristic ions, and measurement of fragment losses from the molecular ion clusters. Preliminary evidence for the presence of HxBDE was found at a frequency of 72%, in an estimated concentration range of ND to 1000 ng HxBDE/kg (Cramer et al., 1990a,b; Stanley et al., 1991).

6. KINETICS AND METABOLISM IN LABORATORY ANIMALS AND HUMANS

The half-life of pentabromodiphenyl ether (Bromkal 70) was investigated in the perirenal fat of groups of 3 male and 3 female Wistar rats (weight 160-180 g), following a single oral dose of 300 mg/kg body weight in peanut oil. The groups were killed on days 1, 2, 3, 4, and 7 and then weekly for 10 weeks. Perirenal fat was collected and analysed. Half-lives in male and female rats of 2 hexabromodiphenyl ethers (HxBDE(1) and HxBDE(2)) were: for female rats, 44.6 (37.4-51.9) days and 90.0 (78.7-103.6) days, and, for male rats, 55.1 (48.4-61.7) and 119.1 (102.8-136.1) days, respectively (Von Meyerinck et al., 1990).

PENTABROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

Pentabromodiphenyl ether is not manufactured or used.

No data are available on the following topics:

- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by other international bodies.

1.1 Summary and evaluation

1.1.1 Identity, physical and chemical properties

Commercial pentabromodiphenyl ether (PeBDE) is a mixture of tetra-, penta-, and hexabromodiphenyl ethers. It contains approximately 50-60% PeBDE and 24-38% TeBDE. On the basis of the chemical structure, there are 46 possible isomers of PeBDE and 42 possible isomers of TeBDE. The commercial products seem to contain 3 main components, i.e., 2,2′,4,4′,5-PeBDE, 2,2′,4,4′-TeBDE, and an unidentified congener containing 5 bromines.

The melting point is -7 to -3 °C and the boiling point, above 200 °C. The vapour pressure is low: $< 10^{-7}$ mmHg and the solubility in water is negligible. The *n*-octanol/ water partition coefficient (log P_{ow}) > 6.

1.1.2 Production and uses

PeBDE is used as an additive in epoxy resins, phenol resins, polyesters and polyurethane, and textiles. Worldwide consumption is approximately 4000 tonnes per year. It is one of the major commercial brominated diphenyl ether flame retardants.

1.1.3 Environmental transport, distribution, and transformation

Components of commercial PeBDE have been found in biota, sediment, and sewage sludge samples. Commercial PeBDE

components are likely to be persistent and bioaccumulate. A bioconcentration factor of over 10 000 has been found in carp for PeBDE.

Pyrolysis studies with commercial PeBDE showed that PBDF and PBDD are formed. The optimal temperature for the formation of the PBDF and PBDD was between 700-800 °C. When PeBDE was pyrolysed in the absence of oxygen, polybromobenzenes, polybromophenols, and PBDF were formed.

1.1.4 Environmental levels and human exposure

Sediment samples taken from rivers and estuaries in Japan showed levels ranging from no PeBDE (< 2 μg/kg) up to 28 μg/kg dry weight. In Sweden, the concentrations in sediment samples of certain rivers were up to 1200 μg 2,2',4,4,'5-PeBDE/kg. Sewage sludge, analysed in Sweden also contained this PeBDE.

In mussel and fish collected from different seashores in Japan in the period 1981-85, concentrations of 0.4 and 2.8 μg PeBDE/kg wet weight were found in 2 out of 5 mussel samples. No PeBDE was detected in fish (limit of determination < 0.2 μg/kg). Concentrations of 1.9-22 μg/kg, on a fresh weight basis, were reported in liver samples from cod from the North Sea. In Sweden, concentrations of between 7.2 and 64 μg 2,2',4,4',5-PeBDE/kg fat were found in freshwater whitefish and herring collected at different places.

Pooled blubber of ringed seal and of grey seal collected in Sweden in 1979-85 contained average concentrations of 1.7 μg and 40 μg 2,2',4'4',5-PeBDE/kg fat, respectively.

Pooled samples of muscle of rabbits, moose, and suet samples of reindeer collected in 1985-86 in Sweden contained < 0.3 μg, 0.64 μg, and 0.26 μg 2,2',4,4',5-PeBDE/kg fat, respectively.

Muscle samples of osprey, collected in Sweden in 1982-86, contained an average concentration of 140 μg 2,2',4,4',5-PeBDE/kg fat.

The levels of 2 PeBDE isomers in guillemot eggs from the Baltic have increased by one order of magnitude during the last decades. The levels of these isomers in pike from a lake in Southern Sweden also showed an increase (by a factor of about 4).

Baltic sediments representing different sampling years also indicate a considerable increase during the last decade.

There is minimal information on human exposure, but a rough estimate of exposure of the Swedish population through fish consumption would suggest an intake of 0.1 μg PeBDE/person per day.

1.1.5 Kinetics and metabolism in laboratory animals and humans

The half-life of PeBDE has only been investigated in the perirenal fat in rats. The average half-life was between 25 and 47 days, depending on the sex of the animal and the type of isomer determined.

1.1.6 Effects on laboratory mammals and in vitro *test systems*

The acute oral toxicity of commercial PeBDE is low in rats; the dermal toxicity in rabbits is also low. Short-term inhalation exposure in rats and the application of PeBDE to the conjunctival sac in rabbits caused only mild, transient effects.

In short-term toxicity studies on rats (4-week and 13-week), dietary concentrations of 100 mg/kg increased liver weights and caused slight histological alterations. Changes consisted of the enlargement of hepatic parenchymal cells, which had a granular appearance and contained eosinophilic "round bodies". Dose-related increases in total bromine content in the liver occurred and levels remained elevated for as long as 24 weeks. A mild degree of thyroid hyperplasia, which was reversible, was observed.

Hepatic enzyme induction and increases in cytochrome P450 c occurred after oral administration of daily doses of PeBDE as low as 0.78 μmol/kg body weight. The results of tests for teratogenicity and mutagenicity were negative.

No long-term/carcinogenicity studies have been reported.

1.1.7 Effects on humans

No data are available.

1.1.8 Effects on other organisms in the laboratory and field

Minimal data are available.

1.2 Conclusions

1.2.1 PeBDE

Commercial PeBDE (a mixture of 24-38% tetra-, 50-60% penta-, and 4-8% hexabromodiphenyl ether) is persistent and accumulates in organisms in the environment.

Commercial PeBDE is widely used, incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure by extraction from polymers is unlikely. Human exposure to PeBDE via the food chain may occur, since the substance has been detected in organisms in the environment that are human food items, such as fish, shellfish, etc. In fish and birds from Sweden, increasing levels have been measured over the last 2 decades.

The acute toxicity of commercial PeBDE is low. There is no information on uptake and loss in mammals. Reproduction, long-term toxicity, and carcinogenicity studies are not available.

The risk to the general population cannot be determined from the available data.

No information is available to draw conclusions on occupational exposure levels or the effects of commercial PeBDE.

Limited information is available on the toxicity of commercial PeBDE for organisms in the environment.

1.2.2 Breakdown products

PBDF and, to some extent, PBDD are formed when PeBDE (or products containing it) are heated to 400-800 °C. The possible hazards associated with this have to be addressed.

Exposure of the general population to PBDF in polymers flame retarded with PeBDE is unlikely to be of significance. Properly controlled incineration does not lead to the emission of significant quantities of brominated dioxins and -furans. Any

uncontrolled combustion of products containing PeBDE can lead to the generation of unquantified amounts of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future EHC on PBDF/PBDD.

1.3 Recommendations

1.3.1 General

Persistence in the environment and accumulation in organisms suggest that commercial PeBDE should not be used. However, if use continues, the following points should be taken into account:

- Workers involved in the manufacture of PeBDE and products containing the compound should be protected from exposure using appropriate industrial hygiene measures, the monitoring of occupational exposure, and engineering controls.
- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled to minimize environmental contamination with this persistent and accumulating material and its breakdown products.
- Incineration of materials flame retarded with PeBDE should only be carried out in properly constituted incinerators running consistently under optimal conditions. Burning by any other means will lead to production of toxic breakdown products.

1.3.2 Further studies

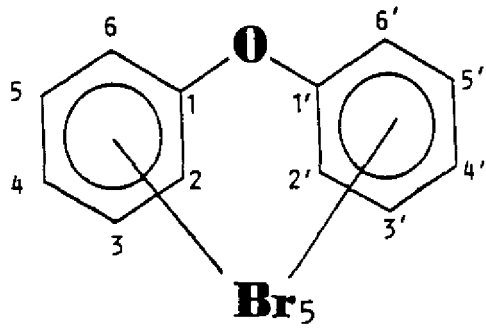
- Continued monitoring of environmental levels is required.
- Methods for the determination of PeBDE in various matrices should be validated.
- Because the present toxicological database is inadequate to evaluate the hazards of commercial PeBDE for humans and the environment, and to support its use, the following studies should be done:

- additional toxicological, carcinogenicity, and ecotoxicological studies;
- further investigations on the generation of PBDF under real fire conditions;
- investigations on possible methods and consequences of recycling of PeBDE-containing polymers;
- studies on the possibilities of migration from flame-retarded products.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES,ANALYTICAL METHODS

2.1 Identity

Chemical structure



Chemical formula:	$C_{12}H_5Br_5O$
Relative molecular mass:	564.75
Common name:	pentabromodiphenyl ether (PeBDE); pentabromodiphenyl oxide
CAS registry number:	32534-81-9
CAS name:	1,1'-oxybis-pentabromo-benzene, benzene, 1,1'-oxybis-, pentabromo

On the basis of the chemical structure, there are 46 possible isomers of pentabromodiphenyl ether.

From: IRPTC (1988).

2.1.1 Technical product

Trade names	DE 71; Bromkal 70-5 DE; FR 1205/1215; Bromkal 70; Bromkal G1; Pentabromprop; DE-60 F is a mixture of 85% PeBDE and 15% of an aromatic phosphate

Commercial pentabromodiphenyl ether is a mixture of polybrominated diphenyl ethers with the following typical composition (see Table 1): 0-1% tribromodiphenyl ether, 24-38% tetrabromodiphenyl ether, 50-62% pentabromodiphenyl ether, 4-8% hexabromodiphenyl ether (Arias, 1992).

DE-71 is primarily a mixture of tetra-, penta-, and hexabromodiphenyl ethers containing low levels of tribromodiphenyl ether (< 1%) and heptabromodiphenyl ether (< 2%) (McAllister & Ariano, 1982). Pentabromprop is a mixture of 39% tetra-, 61% penta-, and 9% hexabromodiphenyl ethers. Bromkal 70-5 DE is a mixture of 34.2% tetra-, 59.8% penta-, 5.8% hexa-, and 0.2% heptabromodiphenyl ethers, but 41.7% tetra- and 45% pentabromodiphenyl ethers, and 7% of a second pentabromodiphenyl ether have also been reported (Nylund et al., 1992). Another manufacturer produces a mixture of 35% tetra-, 58% penta-, and 4% higher brominated diphenyl ethers under the name of Pentabromodiphenyl ether. Bromkal 70 is a mixture containing 36% tetrabromo- and 74% pentabromodiphenyl ether. The bromine contents of the mixtures range from 67 to 71.8% (De Kok et al., 1979). Bromkal 70-5, a mixture of brominated diphenyl ethers containing 67-71% bromine, and an average of about 5 bromines per molecule, also contained various isomers of tri-, tetra-, penta-, and hexabromodiphenyl ethers. However, it is no longer produced commercially (McAllister, 1991).

Sundström & Hutzinger (1976) identified 2,2′,4,4′-tetra- and 2,2′,4,4′,5,-PeBDE as the major components of Bromkal 70-5 DE.

2.2 Physical and chemical properties

Pentabromodiphenyl ether (PeBDE) is a clear, amber to pale yellow, highly viscous liquid, with an organic smell. Under conditions of fire, hydrogen bromide and/or bromine occur.

Melting point	-7 to -3 °C[a]
Boiling point	> 300 °C (decomposition starts above 200°C)
Specific gravity	2.28 at 25 °C; 1.78 at 40 °C
Vapour pressure	9.3 mmHg at 22 °C[b] (6.26-6.66 Torr at 25 °C)
Solubility	Insoluble in water (9×10^{-7} mg/litre at 20 °C), methanol 10 g/litre at 25 °C, soluble in other organic solvents such as chloroform, benzene, toluene, acetone, carbon-tetrachloride, and methylene chloride
Viscosity at 50 °C	1-6 Pa (150 000 cp at 25 °C; 1500 cp at 60 °C)
n-Octanol/water partition coefficient (log Pow)	6.64-6.97

From: Great Lakes Chemical Corporation (undated a); Kalk (1982); Kopp (1990); US EPA (1989); Hallenbeck (1993); US Testing Comp. (1985).

2.3 Analytical methods

McAllister & Ariano (1982) developed a method for the determination of the arbitrarily defined "bromination level" of PeBDE (DE-71), both as the neat material and as a formulation in DE-60 F, and for the quantitative determination of aromatic phosphate ester in DE-60 F. The sample is dissolved in

dibromomethane containing an internal standard and the components separated by gas chromatography.

A multiresidue method has been developed for the determination of PBDE residues in environmental samples (see General Introduction, section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

Pentabromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

Pentabromodiphenyl ether is synthesized by treating diphenyl ether with 5 equivalents of Br_2 at 30-65 °C in the presence of powdered iron (US EPA, 1986).

The actual worldwide consumption of PeBDE per year is 4000 tonnes. In the Federal Republic of Germany, in 1988, the approximate level of use in plastics was 200-400 tonnes/year. The total use of penta- and hexabromodiphenyl ethers in the Netherlands in 1988 was estimated to be 350 tonnes (Anon., 1989b).

Production levels are not available.

3.2.2 Uses

PeBDE is used as an additive in epoxy resins, phenol resins, unsaturated polyesters, polyurethane flexible, and textiles.

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

4.1 Pyrolysis

PeBDE (Bromkal 70, 70-5 DE, G1) were heated in a quartz tube at 700, 800, or 900 °C and the concentrations of PBDD and PBDF determined. Monobromo- to pentabromodibenzofurans, as well as monobromo- to tetrabromodioxins, were found in yields of up to 90% in all 3 Bromkal samples. The optimal temperatures of formation were between 700 and 800 °C (Thoma et al., 1987a).

Bromkal 70-5-DE was pyrolysed at 600, 700, 800, and 900 °C, in the absence of oxygen, in a SGE pyrojector and the residues analysed by GC/MS in an on-line operation. The pyrolysis of Bromkal 70-5-DE yielded polybromobenzenes (PBBz), polybromophenols (PBP), and brominated dibenzofurans. Because this pyrolysis is performed in a pyrojector with a helium current, incorporation of oxygen is impossible, consequently dioxins do not form (Thoma & Hutzinger, 1987, 1989).

4.2 Workplace exposure studies

In the processing of PBT, finished with pentabromodiphenyl ether at 300 °C, PBDF were found in both the air at the workplace and the machine extractor. PBDF were also found in air samples taken from a vessel in which the granulate was stored. Since the bulk of the PBDF formed during processing remain in the product, it can be assumed that parts made from the polymers, such as computer casings, television sets, etc., are contaminated with PBDF (CEM, 1989).

4.3 Bioaccumulation

Carp exposed for 8 weeks to commercial pentabromodiphenyl ether at 10 or 100 μg/litre showed bioconcentration factors of more than 10 000 (CBC, 1982).

4.4 Ultimate fate following use

For the ultimate fate of PeBDE following use see section 6.1 of the General Introduction.

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 Levels in the environment

5.1.1 Sediment and sewage sludge

Sediment samples were taken from the rivers near the centre of Osaka City and marine sediments, from different estuaries in Japan and from Osaka Bay, during the period 1981-83. No PeBDE was found (< 2 μg/kg dry weight) in 9 estuarine or marine sediment samples. PeBDE was present in 5 out of 6 river sediment samples at concentrations of 9-28 μg/kg on a dry weight basis (Watanabe, 1987; Watanabe et al., 1987b).

Organic extracts, made from coastal sediments, collected off-shore from Barcelona, were analysed for the presence of organo-halogenated chemicals. A diversity of organohalogenated compounds were found, among them PeBDE (Fernandez et al., 1992).

Sellström et al. (1990a,b) analysed sediment samples, taken upstream and downstream from a factory, for the presence of tetrabromobisphenol-A and derivatives. Both tetrabromobisphenol A and 2,2',4,4',5-pentabromodiphenyl ether were found. The levels found in upstream and downstream sediments were 8.2 and 1200 μg/kg (ign loss), respectively.

A laminated sediment core collected in the southern part of the Baltic Proper (Bornholm Deep) was analysed for 2,2',4,4',5-PeBDE. The core was cut into 5 mm slices down to 50 mm depth and in 10 mm slices from 50 to 90 mm depth. The concentration of PeBDE at a depth of 5 mm was 0.98 μg/kg IG and decreased more or less gradually in the deeper layers to approximately 0.05 μg/kg at a depth of 40 mm. Below this depth, levels were mostly not detectable (Nylund et al., 1992).

Sellström et al. (1990a,b) analysed sewage sludge and found 19 μg 2,2',4,4',5-pentabromodiphenyl ether/kg ign loss.

Two sewage samples were collected from a Swedish treatment plant (Gothenburg) in September 1988 and analysed for PBDE.

One homogenate was composed of samples (40 g/day) taken over a 32-day period with little rain. Another homogenate was composed of samples (100 g/day) taken during a rainy period of 7 days. Both TeBDE and PeBDE were found. The concentration of 2,2',4,4',5-PeBDE was 19 μg/kg; concentrations of PeBDE of unknown structures were 3.4 and 3.7 μg/kg and total PeBDE, 37-38 μg/kg IG (Nylund et al., 1992).

5.1.2 Fish and shellfish

Mussels and some species of fish, e.g., mullet, goby, and Japanese sea bass, were collected from different seashores in Japan from 1981 to 1985. Other fish species were purchased from a commercial wholesale source in Osaka Prefecture in 1981. In 2 out of 5 mussel samples, levels of 0.4 and 2.8 μg PeBDE/kg wet weight were found. In 12 fish samples, no PeBDE (< 0.2 μg/kg wet weight) was found (Watanabe, 1987; Watanabe et al., 1987b).

2,2',4,4',5'-Pentabromodiphenyl ether (PeBDE) was found in cod liver (2 samples from each region) from the southern, central, and northern regions of the North Sea, in 1982-87. Levels were 3.6 and 22.0 μg/kg; 4.9 and 7.2 μg/kg; and 1.9 and 6.5 μg/kg, respectively, on a product basis (De Boer, 1989).

A multiresidue analytical method was applied to pooled muscle samples of 35 freshwater whitefish (*Coregonus sp.*), 15 samples of arctic char (*Salvelinus alpinus*), and a total of 260 samples of herring (*Clupea harengus*), collected at different places in Sweden during the period 1986-87. The average concentrations of 2,2',4,4',5-pentabromodiphenyl ether were 7.2, 64, and 9.8-46 μg/kg lipid, respectively (Jansson et al., 1993).

Samples of bream, pike, perch, and trout from Sweden were shown to contain 2,2',4,4',5-PeBDE in concentrations of 2.3-2.4 μg/kg, 60-1100 μg/kg, 380-9400 μg/kg, and 130-590 μg/kg lipid, respectively. Another PeBDE isomer of unknown structure was also found in all fish samples at concentrations of 11-37 μg/kg, 25-640 μg/kg, 230-3500 μg/kg, and 33-150 μg/kg lipid, respectively. The samples represent both background and industrialized areas (Sellström et al., 1993a).

A study of TeBDE and PeBDE in banked samples of pike from a lake in Southern Sweden revealed concentrations increasing

from 40 μg/kg lipid in 1974 to 180 μg/kg lipid in 1991 (Sellström et al., 1993b).

Krüger (1988) sampled 40 freshwater fish of various species from the waters of North-Rhine Westfalia in Germany and found PBDE in concentrations ranging from 18 to 983 μg/kg fat, measured as Bromkal 70-5DE. Concentrations in 6 sea fish from the Baltic Sea ranged from 12 to 57 μg PBDE/kg fat and those in 11 fish from the North Sea, from 1 to 120 μg/kg fat, measured as Bromkal 70-5DE.

5.1.3 Aquatic mammals

Pooled samples of blubber of 7 ringed seals (*Pusa hispida*), collected in 1981, and of 8 grey seals (*Halichoerus grypus*), collected in 1979-85, in Sweden were analysed using a multiresidue analytical method. The average concentrations of 2,2',4,4',5-pentabromodiphenyl ether were 1.7 and 40 μg/kg lipid, respectively (Jansson et al., 1993).

5.1.4 Terrestrial mammals

Pooled samples of muscle of 15 rabbits (*Orytolagus cuniculus*), 13 samples of moose (*Alces alces*), and 31 suet samples of reindeer, collected in the period 1985-86, in Sweden, were analysed using a multiresidue method. The average concentrations for rabbits, moose, and reindeer, were < 0.3, 0.64, and 0.26 μg 2,2',4,4',5-pentabromodiphenyl ether/kg lipid, respectively (Jansson et al., 1993).

Concentrations of 10 μg PBDE/kg fat, measured as Bromkal 70-DE, were detected in samples from 8 seals from Spitzbergen (Kruger, 1988).

PBDE, measured as Bromkal 70-DE, was detected in 4 samples of cow's milk at concentrations ranging from 2.5 to 4.5 μg/kg fat (Kruger, 1988).

5.1.5 Birds

Pooled samples of muscle of 35 osprey (*Pandion haliaetus*), collected in Sweden in the period 1982-86, were analysed using a

multiresidue method, for 2,2',4,4',5-pentabromodiphenyl ether. The average concentration was 140 μg/kg lipid (Jansson et al., 1993).

Newborn starlings from different places in Sweden have been shown to contain 2.3-4.2 μg 2,2',4,4',5-PeBDE/kg lipid and an unidentified PeBDE at 0.62-1.1 μg/kg lipid (Sellström et al., 1993a). The same authors reported concentrations of the same two PeBDE isomers in guillemot eggs from the Baltic Sea, caught during the period 1970-89 (see Table 27).

Table 27. Average PeBDE concentrations (μg/kg lipid) in guillemot eggs from the Baltic Sea[a]

Sampling year	2,2',4,4',5-PeBDE	PeBDE (unknown structure)
1970	24	4.2
1974	48	8.5
1975	33	4.6
1976	130	32
1979	130	37
1982	200	44
1983	210	49
1986	260	48
1987	160	40
1989	240	61

[a]From: Sellstrom et al. (1993a).

5.2 General population

Samples of human milk from 26 women in North Rhine Westfalia, Germany, were analysed for PBDE, measured as Bromkal 70-DE. Concentrations in the milk from 25 of the women

ranged from 0.62 to 11.1 μg/kg fat. In one Chinese woman, a level of 50 μg/kg fat was found (Kruger, 1988).

In Sweden, the major human exposure is via fish-related food and the levels of PeBDE in fish may be used to estimate this exposure route. Normal fish intake in Sweden is about 30 g/day, and, if herring is used as a model fish, this will give an estimate of intake of about 0.1 μg PeBDE/person per day (Personal Communication, Jansson).

6. KINETICS AND METABOLISM IN LABORATORY ANIMALS AND HUMANS

The half-life of pentabromodiphenyl ether (Bromkal 70) in perirenal fat was investigated in groups of 3 male and 3 female Wistar rats (weight 160-180 g) following a single oral dose of 300 mg/kg body weight in peanut oil. Animals from the groups were killed on days 1, 2, 3, 4, and 7 and then at weekly intervals for 10 weeks. The perirenal fat was collected and analysed. The half-lives of 2 PeBDE isomers, following extraction and separation with HPLC (containing also tetrabromo- and hexabromodiphenyl ethers), are summarized in Table 28 (Von Meyerinck et al., 1990).

Table 28. Half-lives of PeBDE in male and female rats[a]

PBDE	Half-lives in female rats in days	Half-lives in male rats in days
PeBDE(1)[b]	47.4 (42.5-52.4)	36.8 (33.7-40.0)
PeBDE(2)[b]	25.4 (22.6-28.4)	24.9 (22.6-27.1)

[a]From: von Meyerinck et al. (1990).
[b](1) and (2) means two different isomers. Confidence interval, P = 0.05.

7. EFFECTS ON LABORATORY MAMMALS AND *IN VITRO* TEST SYSTEMS

7.1 Single exposures

7.1.1 Oral

Groups of 5 male, albino Charles River CD rats were administered (by gavage) 50, 500, or 5000 mg commercial PeBDE (in corn oil)/kg body weight and observed for 14 days. The rats receiving 50 and 500 mg/kg survived and exhibited normal body weight gain. Four out of 5 rats dosed with 5000 mg/kg died within 5 days. The remaining rats survived and showed normal growth (Great Lakes Chemical Corporation, undated a).

Groups of 5 male and 5 female Wistar rats were administered 2400, 4800, 6048, 7621, or 9600 mg commercial PeBDE/kg body weight. The substance was given by gavage as an 80% w/v suspension in maize oil after which the rats were observed for 44 days. The acute oral LD_{50} was 7400 mg/kg for males and 5800 mg/kg body weight for females. The symptoms seen were decrease in growth, diarrhoea, piloerection, reduced activity, clonic persistent tremors of the fore limbs, and red staining around eyes and nose. A continual chewing movement of the jaws was also seen. Post-mortem examination revealed pale (mottled), enlarged, necrotic livers and multiple small ulcerations of the gastric mucosa (Great Lakes Chemical Corporation undated a).

7.1.2 Dermal

Commercial PeBDE was applied to the clipped intact or abraded skin of groups of 2 male and 2 female New Zealand white rabbits at doses of 200 or 2000 mg/kg body weight, for 24 h, under an occlusive dressing. The rabbits were observed for 14 days. No animals died during the observation period.
At 200 and 2000 mg/kg, normal body weight gain or only a slight decrease in growth was seen (Great Lakes Chemical Corporation, undated a).

7.1.3 Inhalation

The inhalation LC_{50} for the rat is > 200 mg/litre (Kopp, 1990). Groups of 10 male and 10 female Charles River CD rats were exposed for 1 h to an aerosol mist of commercial PeBDE mixed with corn oil at concentrations of 2 or 200 mg/litre of air and subsequently observed for 14 days. No rats died during the study. The rats exposed to 2 mg/litre exhibited increased and then decreased motor activity, erythema, and eye squint during the exposure and for the following 24 h. After 24 h, and up to the end of the study, the animals appeared normal. During exposure to 200 mg/litre, the same signs were observed but also lacrimation, salivation, and tachypnoea. At 24 h and 48 h, 2 rats exhibited nasal congestion and one rat showed respiratory congestion after 72 h. From day 4 to day 14, the animals appeared normal and showed normal body weight gain (Great Lakes Chemical Corporation, undated a).

7.2 Short-term exposure

Charles River CD rats were fed dietary levels of 0, 100, or 1000 mg commercial PeBDE (dissolved in corn oil)/kg daily for 28 days. There were 10 male and 10 female animals in each group. No changes were noted in behaviour, appearance, food con-sumption, or body weight gain. Absolute and relative liver weights were significantly increased in female rats fed with 100 mg/kg and in male and female rats fed with 1000 mg/kg. The liver lesions were more prevalent in male rats and increased with dose. A significant decrease in the relative weights of the pituitary and adrenal glands was found at the highest dose level. No compound-related, gross pathological lesions were noted. Microscopically, enlargement of the centrolobular and midzonal liver parenchyma cells was seen, and the cytoplasm included areas with a finely granular appearance; eosinophilic "round bodies" in enlarged hepatocytes were seen in the animals at both dose levels. Several rats from both the 100 mg and the 1000 mg/kg groups had slight to moderate hyperplasia of the thyroid, but control animals also had thyroid glands that could be considered hyperplastic. In thyroid glands designated as hyperplastic, most follicles were very small, devoid of colloid, and lined by basophilic columnar follicular epithelium. Whether these thyroid changes were compound-

related is not clear. Dose-related increases in total bromide levels in liver tissues from the (pooled) treated rats were 6-12 times higher than those in the controls (Great Lakes Chemical Corporation, undated a).

Commercial PeBDE (DE-71) was given in the diet to 3 groups of 30 male and 30 female CD Sprague-Dawley rats. Dosage levels of 0, 2, 10, or 100 mg/kg per day were administered for 90 days. Ten animals per sex were sacrificed after 4 weeks and after 90 days, 5 animals were sacrificed after a 6-week recovery period, and 5 animals, after a 24-week recovery period. No increased mortality or clinical effects were observed. Decrease in food consumption was seen in high-dose females and a decrease in body weight was observed in high-dose males and females. Haematology parameters and liver function were normal, but increased cholesterol values were observed for high-dose animals. Triiodothyronine (T3) levels were normal, but tetraiodothyronine (T4) levels were decreased (not dose-related) in the 10 mg and 100 mg/kg group; an increase in serum total bromide levels was observed in these 2 groups after 4 and 13 weeks. Compound-related increases in liver and urine porphyrins were observed in the high-dose animals after 13 weeks. Urine porphyrin levels were 13 times higher in females and up to 8 times higher in males and liver porphyrin levels were almost 400 times higher than those of the controls. Compound-related increases in tissue total bromine levels were noted in all tissues for males and females at both the low- and high-dose levels (mid-dose levels not determined). During the recovery period, a slow decrease in the total bromine levels was noted, but, even after 24 weeks, the levels did not reach the control values, especially in the highest dose group. Relative liver weights in the 10 and 100 mg/kg groups were increased, but, during the recovery period, liver weights that were still higher after 6 weeks were normal after 24 weeks. Microscopic examination revealed hepatocytomegaly and thyroid hyperplasia. The thyroid hyperplasia was reversible in 24 weeks recovery period, but the liver still showed slight hepatocytomegaly in the 10 and 100 mg/kg group. At the lowest dose level (2 mg/kg), the only effect observed after 24 weeks' recovery, i.e., liver cell degeneration and necrosis, was seen in females, but not in males (Great Lakes Chemical Corporation, undated a).

7.3 Long-term exposure

No data are available.

7.4 Skin and eye irritation; sensitization

7.4.1 Skin irritation

Commercial PeBDE was applied, under occlusion, to the clipped intact or abraded skin of groups of 3 male and 3 female New Zealand white rabbits at a dose of 0.5 ml (approximately 1135 mg). After 24 h, the wrappings were removed and the backs of the rabbits washed and examined for signs of irritation. The examinations were repeated at 72 h. At 24 and 72 h, no, or only very slight, erythema was noted. No oedema was seen (Great Lakes Chemical Corporation, undated a).

7.4.2 Eye irritation

A single application of 0.1 ml commercial PeBDE was instilled into the conjunctival sac of the eyes of 3 male, and 3 female, New Zealand white rabbits. Examinations were carried out at 24, 48, and 72 h, and at 7 days. At 24 h, all rabbits showed slight redness, slight chemosis, and slight discharge of the conjunctivae. These symptoms subsided during 7 days. At 7 days, slight alopecia around the eyelid was seen in 2 of the 6 animals. No irritation of the iris was observed. Examination at 72 h revealed slight evidence of corneal damage in one of the 6 animals (Great Lakes Chemical Corporation, undated a).

7.5 Reproductive toxicity, embryotoxicity, and teratogenicity

Pregnant female rats were given corn-oil suspensions of commercial PeBDE, by gavage, at dosages of 0, 10, 100, or 200 mg/kg body weight per day, on days 6-15 of gestation. The material was not teratogenic. The maternal no-effect level was 10 mg/kg and the embryo/fetal no-effect level was 100 mg/kg body weight. Inhibition of maternal body weight gain occurred at doses of 100 or 200 mg/kg. A slight, nonstatistically significant,

reduction in average fetal body weight per litter was found at the highest dose level (BFRIP, 1990) (no further details).

7.6 Mutagenicity and related endpoints

Commercial PeBDE was examined for mutagenic activity at a number of concentrations in a series of *in vitro* microbial assays using *Salmonella typhimurium* TA98, TA100, TA1535, and TA1537 and *Saccharomyces cerevisae* in the presence, and absence, of liver microsomal enzyme preparations from Aroclor-induced rats. A negative result was obtained with and without microsomal activation (Great Lakes Chemical Corporation, undated a).

7.7 Carcinogenicity

No data are available.

7.8 Other special studies

Commercial PeBDE in corn oil was administered, by gavage, to 6 male Sprague-Dawley rats (200-250 g) for 90 days. When the original doses of 6.25, 12.5, and 25 μmol/kg per day revealed extensive induction, the study was repeated at doses of 0.78, 1.56, and 3.13 μmol/kg per day. When the lower dose levels were tested, even the lowest dose of PeBDE (0.78 μmol/kg) caused increases in *O*-ethyl-*O*-*p*-nitrophenyl phenylphosphonothiate (EPN) detoxification, *p*-nitroanisole demethylation, and NADPH cytochrome c reductase and cytochrome P450 activity. A clear dose-response relationship was found for EPN detoxification and *p*-nitroanisole demethylation. When the animals were allowed a 30-day recovery period following the last (90th) dose, elevations in these two measurements were still observable at all doses, though increased NADPH cytochrome c reductase activity was found only at the highest dose. Within this period, the cytochrome P450 content had returned to normal. Even after 60 days recovery, elevations were noted in EPN detoxification and *p*-nitroanisole demethylation at the 1.56 and 3.13 μmol/kg levels. No histological liver abnormalities were observed in rats treated with doses of 3.13 μmol/kg or less (Carlson, 1980b).

In another study, rats (200-250 g) were administered commercial PeBDE at 0.1 mmol/kg per day, in corn oil, by gavage, for 14 days. In addition to the above described effects on the enzymes, increases in the activities of UDP-glucuronyl-transferase and benzo[*a*]pyrene-hydroxylase were found 24 h after the seventh dose (Carlson, 1980a).

Von Meyerinck et al. (1990) studied the hepatic microsomal enzyme inducing potential of Bromkal 70 in Wistar rats. A series of dosing regimes was used, which varied from single oral doses of up to 300 mg/kg body weight to 28 daily oral doses of 50 mg/kg body weight. In all cases, the vehicle was peanut oil (1 ml/kg), which was also administered to the vehicle control group. There were 3 male and 3 female rats per group, except in the 28-day study in which 4 male and 4 female rats were used. The treatments resulted in 31-53% increases in liver weight, 2.3-3.9-fold increases in cytochrome P450 c levels, up to 2-fold increases in benzphetamine *N*-demethylation activity, and 2.2-5.3-fold increases in benzo(*a*)pyrene oxidation. Increases in ethoxyresorufin *O*-deethylation activity ranged from not detectable to 0.35 nmol/min mg microsomal protein in control groups to between 4.1 and 16.6 nmol/min mg microsomal protein in treatment groups. These activities were sex and dose dependent. The most sensitive parameter was ethoxyresorufin *O*-deethylase induction, which showed no significant response in rats dosed once with 3 mg PeBDE/kg and killed 3 days later.

Commercial PeBDE (Bromkal 70-5 DE) showed the induction of ethoxyresorufin *O*-deethylase activity in H-4-II E cells (Hanberg et al., 1991).

TETRABROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

Tetrabromodiphenyl ether is not manufactured or used.

No data are available on the following topics:

- Effects on laboratory mammals and *in vitro* test systems
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

1.1 Summary and evaluation

1.1.1 Identity, physical and chemical properties

Commercial tetrabromodiphenyl ether, consisted of 41% tetra-, 45% penta-, and 7% hexabromodiphenyl ethers and about 7% PBDE of unknown structure. On the basis of the chemical structure, there are 42 possible isomers of tetrabromodiphenyl ether. Virtually no data are available on physical and chemical properties, except that the *n*-octanol/water partition coefficient (log P_{ow}) is 5.87-6.16.

1.1.2 Production and uses

There is a report of the production (use) of about 1000 tonnes of TeBDE in Japan in 1987. There is no known current production under the name of tetrabromodiphenyl ether, but TeBDE is present in quantities of from 24 to 38% in commercial pentabromodiphenyl ether.

1.1.3 Environmental transport, distribution, and transformation

Components of commercial TeBDE have been found in biota, sediment, and sewage sludge samples. Commercial TeBDE components (containing approximately equal quantities of PeBDE) are likely to be persistent and to bioaccumulate.

Pyrolysis studies with commercial TeBDE showed that PBDF and PBDD are formed at 800 °C. Higher PBDF and PBDD were not found.

1.1.4 Environmental levels and human exposure

TeBDE was found, in Japan, in river sediment at concentrations of 12-31 μg/kg dry weight and, in Sweden, at concentrations of up to 840 μg/kg ign. loss, respectively. TeBDE was also found in sewage sludge in Sweden, at a concentration of 15 μg/kg.

Mussels and fish, collected at different places in Japan, contained TeBDE in concentrations ranging from < 0.1 to 14.6 μg 2,2',4,4'-TeBDE/kg wet weight. In Sweden, different types of fish were collected from rivers and analysed for 2,2',4,4'-TeBDE. The mean concentrations ranged from ND (< 0.1mg/kg) to 110 mg/kg fat. The analysis indicated that there was at least one local source of pollution in a certain river. Whitefish, arctic char, and herring, collected at different places in Sweden in 1986-87, contained concentrations of 15, 400, and 59-450 μg 2,2',4,4'-TeBDE/kg fat, respectively. Fish collected from rivers in Germany contained up to 1 mg TeBDE/kg fat.

In herring and in the liver of cod, collected in the southern, central, and northern North Sea, in the period 1983-89, a decreasing trend in the concentrations of TeBDE was found from the southern region to the northern region. In the herring, concentrations of 8.4-100 μg 2,2',4,4'-TeBDE/kg, on a fat basis, were found.

The muscle tissue of birds nesting and wintering in the Baltic Sea, the North Sea, and Spitzbergen, contained from 80 to 370 μg 2,2',4,4'-TeBDE/kg, on a fat basis. Osprey collected in Sweden in the period 1982-86, contained average concentrations of 1800 μg/kg fat.

Increasing trends in the concentrations of 2,2',4,4'-TeBDE have been indicated for Baltic sediments, freshwater fish, and sea bird eggs from Sweden.

The blubber of seals collected in the Baltic Sea and Spitzbergen showed concentrations of 10-730 μg 2,2',4,4'-TeBDE/kg, on a fat basis. The chromatographic pattern of the PBDE was similar to that of Bromkal 70-5. Pooled samples of the blubber of ringed seals and grey seals, collected in Sweden in 1979-85 showed concentrations of 47 μg and 650 μg 2,2',4,4'-TeBDE/kg fat, respectively.

Pooled muscle samples of terrestrial mammals, e.g., rabbits, moose and reindeer, collected in 1985-86 in Sweden, showed average concentrations of < 2, 0.82, and 0.18 μg 2,2',4,4'-TeBDE/kg fat, respectively.

Levels of 2.5-4.5 μg PBDE/kg fat, measured as Bromkal 70DE, were found in 4 samples of cow's milk in Germany. PBDE, as Bromkal 70DE, was found in the milk of 25 women in Germany at concentrations ranging from 0.62 to 11.1 μg/kg fat.

A rough estimate of exposure via fish consumption among the Swedish population would suggest an intake of 0.3 μg TeBDE/ person per day.

1.1.5 *Effects on laboratory mammals and* in vitro *test systems*

There are no data on TeBDE itself, but acute and short-term data are available for commercial PeBDE containing 41% TeBDE.

1.1.6 *Kinetics and metabolism in laboratory animals and humans*

Minimal data are available.

1.1.7 *Effects on humans*

No data are available.

1.1.8 *Effects on other organisms in the laboratory and field*

No data are available.

1.2 Conclusions

1.2.1 TeBDE

Components of commercial TeBDE (a mixture of 41% 2,2′,4,4′-tetra-; 45% 2,2′,4,4′,5′-penta-; 7% hexa-, and 7-8% polybrominated diphenyl ethers with an unknown structure) are persistent and accumulate in organisms in the environment.

TeBDE as a component of pentabromodiphenyl ether is widely incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure by extraction from polymers is unlikely. Human exposure to TeBDE, via the food chain, may occur, because the substance has been detected in organisms in the environment that are human food items, such as fish, shellfish, etc. In fish and birds from Sweden, increasing levels have been measured over the last two decades.

There is a lack of information concerning short-, long-term toxicity/carcinogenicity, and reproduction studies. Furthermore, information on kinetics and metabolism in laboratory animals and humans is not available.

The risk for the general population cannot be determined on the basis of available data.

No information is available to draw conclusions on occupational exposure levels or the effects of TeBDE.

No data are available on the toxicity of commercial TeBDE for organisms in the environment.

1.2.2 Breakdown products

PBDF and PBDD are formed when TeBDE are heated to 800 °C. The possible hazards associated with this have to be addressed.

Exposure of the general population to PBDF in polymers, flame retarded with TeBDE, is unlikely to be of significance. Properly controlled incineration does not lead to the emission of significant quantities of brominated dioxins and furans. Any uncontrolled combustion of products containing TeBDE can lead to

the generation of of unquantified amounts of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future EHC on PBDF/PBDD.

1.3 Recommendations

1.3.1 General

Because of their persistence in the environment and accumulation in organisms, it is recommended that TeBDE should not be used. However, should use continue, the following points must be taken into account:

- Workers involved in the manufacture of TeBDE and products containing the compound should be protected from exposure using appropriate industrial hygiene measures, the monitoring of occupational exposure, and engineering controls.
- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled to minimize environmental contamination with this persistent and accumulating compound and its breakdown products.
- Incineration of materials, flame retarded with TeBDE, should only be carried out in properly constituted incinerators running under optimal conditions. Burning by any other means will lead to the production of furan breakdown products.

1.3.2 Further studies

- Continued monitoring of environmnental levels is required.
- Analytical methods for TeBDE in various matrices should be validated.
- Because the present toxicological data base is inadequate to evaluate the hazards of commercial TeBDE for humans

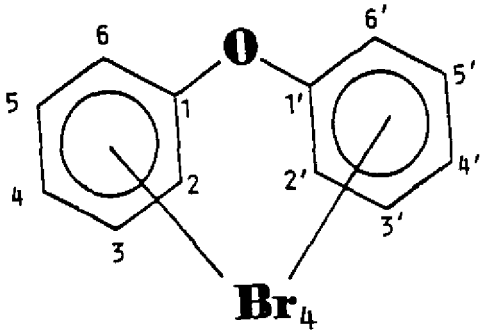
and the environment, if use is continued, the following studies should be done:

- additional toxicological, carcinogenicity, and eco-toxicological studies;
- further investigations on the generation of PBDF under real fire conditions;
- investigation into possible methods and consequences of recycling of TeBDE-containing polymers;
- investigations of the possibility of migration from flame-retarded products.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Chemical structure:



Chemical formula:	$C_{12}H_6Br_4O$
Relative molecular mass:	485.82
Common names:	tetrabromodiphenyl ether (TeBDE) tetrabromodiphenyl oxide
CAS registry number:	40088-47-9
CAS name:	1.1'-oxybis-tetrabromo-benzene

On the basis of the chemical structure, there are 42 possible isomers of tetrabromodiphenyl ether.

2.2 Physical and chemical properties

The technical product consist of 41.7% (41%) of 2,2',4,4'-tetrabromodiphenyl ether, 44.4% (45%) 2,4,5,2',4'-pentabromodiphenyl ether, 6% (7%) hexabromodiphenyl ether and 7.6% PBDE of an unknown structure (see also pentabromodiphenyl ether

and Table 1) (Sundström & Hutzinger, 1976; De Kok et al., 1979; US EPA, 1984; De Boer, 1989).

n-Octanol/water partition coefficient (log P_{ow}): 5.87-6.16

From: Pijnenburg & Everts (1991).

2.3 Analytical methods

A multiresidue method has been developed for the analysis of PBDE residues in environmental samples (see General Introduction, section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

Tetrabromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

See sections 2 and 3 of Pentabromodiphenyl ether.

3.2.2 Uses

A thousand tonnes of tetrabromodiphenyl ether (TeBDE) were used in Japan in 1987 (Watanabe, 1987c).

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

4.1 Pyrolysis

The pyrolysis of Bromkal 70-DE (a mixture of tetrabromodiphenyl ether and pentabromodiphenyl ether) resulted in the formation of high levels of PBDF and PBDD: approximately 60%. The substance was pyrolysed at 800 °C in a quartz tube for 10 min (Thoma et al., 1986). Bromkal 70-DE produced complex mixtures of mono- to pentabromodibenzofurans and of mono- to tetrabromodibenzodioxins. Higher PBDF and PBDD were not found (Zacharewski et al., 1988).

4.2 Ultimate fate following use

For the ultimate fate of TeBDE following use in the environment see section 6.1. of the General Introduction.

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 Environmental levels

5.1.1 Soil and sediment

Watanabe et al. (1987b) determined the residues of TeBDE in 9 marine and/or estuarine sediment samples and 6 fresh water river sediment samples collected at different sites in Osaka during 1981-83. The nine marine and/or estuarine samples did not contain TeBDE (limit of determination < 2 μg/kg). Five out of 6 river sediment samples contained 12-31 μg TeBDE/kg.

Sediment samples taken upstream and downstream from a factory were analysed for the presence of tetrabromobisphenol A (TBBP-A) and its dimethylated derivative. Besides TBBP-A, 2,2′,4,4′-tetrabromodiphenyl ether was also found. The levels found upstream and downstream were 3.5 and 840 μg/kg (IG), respectively (Sellström et al., 1990a,b).

A laminated sediment core collected in the southern part of the Baltic Proper (Bornholm deep) was analysed for 2,2′,4,4′-TeBDE. The core was cut into 5 mm slices down to 50 mm depth and in 10 mm slices from 50 to 90 mm depth. The concentration of TeBDE at 5 mm depth was 1.6 μg/kg IG and decreased gradually to 0.13 μg/kg at 40 mm depth. At a depth of 90 mm, the concentration was 0.06 μg/kg (Nylund et al., 1992).

Sellström et al. (1990b) analysed sewage sludge and found 15 μg 2,2′,4,4′-tetrabromodiphenyl ether/kg IG.

Two sewage samples were collected from a Swedish treatment plant (Gothenburg) in September 1988 and analysed for PBDE. One homogenate was composed of samples (40 g/day) taken during a 32-day period with little rain. Another homogenate was composed of samples (100 g/day) taken during a rainy period of 7 days. TeBDE and PeBDE were found. The concentration of 2,2′,4,4′-TeBDE was 15 μg/kg IG (Nylund et al., 1992).

5.1.2 Fish and shellfish

Watanabe et al. (1987b) determined the levels of TeBDE in fish and mussels collected from different places in Japan in 1981-85. In total, 42 samples of mussel, mullet, goby, sardine, Japanese sea bass, horse mackerel, and hairtail, were analysed. Seven out of 17 fish and shellfish samples collected in the Osaka area contained 0.1-14.6 μg TeBDE/kg and 3 samples of mussels from Osaka bay contained 1.6-14.6 μg/kg (wet weight). Single samples of sardine, Japanese sea bass, mackerel and hairtail contained levels ranging from 0.1 to 0.8 μg TeBDE/kg. The other species did not contain TeBDE (limit of determination < 0.1 μg/kg).

De Boer (1989, 1990) measured the concentration of 2,2',4,4'-tetrabromodiphenyl ether in the liver of cod (*Gadus morhua*), collected in the southern, central, and northern North Sea, in the period 1983-89. Each sample consisted of 25 fishes. The highest levels (up to 360 μg/kg) were found in the liver of cod from the southern part and the lowest levels (up to 68 μg/kg on a fat basis) in the northern part of the North Sea. The concentrations showed a decreasing trend from the southern region to the northern region. Herring (*Clupea harengus*) collected in the 3 areas and the Straits of Dover in 1985, contained average concentrations of 8.4-100 μg 2,2',4,4'-TeBDE/kg on a fat basis. Eels (*Anguilla anguilla*) collected in Dutch freshwater (rivers and lakes) at 10 places were analysed for the presence of 2,2',4,4'-TeBDE, during the period 1983-89. The concentrations ranged from < 20 to 1700 μg/kg, on a fat basis. In these marine and freshwater fish, 2,2',4,4'-TeBDE was always found as the main component, i.e., 70% of the total brominated diphenyl ethers.

Fish were collected from 5 different localities along the Viskan and Haggan river system and the Klosterfjorden bay in Sweden. Muscle and, in some cases, also the liver of bream (*Abramis brama*), eel (*Anguilla anguilla*), pike (*Esox lucius*), sea trout (*Salmo ocla*), and tench (*Tinca tinca*) were analysed. Expressed on a fat weight basis, the highest level found was 110 mg PBDE/kg in the liver of a pike. This pike specimen contained 27 mg PBDE/kg fat in the muscle tissue. In addition to the 3 main components (1 tetrabromo- and 2 pentabromo-isomers), another tetrabromo- as well as 1 tribromo- and 2 hexabromo-

isomers were identified by GC/MS. The maximum PBDE level obtained in the muscle of eel was 17 mg/kg fat. The analysis indicated that there was at least one local source of pollution along the River Haggan. 2,2',4,4'-TeBDE was the most abundant PBDE-component. In most samples, this compound accounted for 70-80% of total PBDE. The mean concentration of PBDE ranged from ND (0.1 mg/kg) to 88 mg/kg fat. Eel caught upstream, midstream, and in the Klosterfjorden bay contained mean concentrations of ND (0.1 mg/kg), 4.3-16, and 0.9-1.4 mg PBDE/kg fat, respectively (Andersson & Blomkvist, 1981).

Muscle tissue from bream, pike, and perch from the Viskan and Haggan rivers in Sweden contained levels of 2,2',4,4'-TeBDE of between 1 and 23 mg/kg (on a fat basis). Perch from the Viskan river had the highest levels (23 mg/kg) (Sellström et al., 1990b).

A method for the multiresidue analysis of organic pollutants was applied to pooled muscle samples of 35 fresh water whitefish (*Coregonus sp.*), 15 samples of arctic char (*Salvelinus alpinus*), and a total of 260 samples of herring (*Clupea harengus*), collected at different places in Sweden during the period 1986-87. The average concentrations of 2,2',4,4'-tetrabromodiphenyl ether for whitefish, arctic char, and herring were 15, 400, and 59-450 μg/kg lipid, respectively (Jansson et al., 1993).

Bream, pike, perch, and trout from Swedish waters contained 250-750, 2000-6500, 2200-24 000, and 120-460 μg 2,2',4,4'-TeBDE/kg lipid, respectively. These samples were from background and industrialized areas (Sellström et al., 1993a). Pike samples from a Swedish lake indicated a 4-fold increase in the same isomer from 1974 to 1991 (Sellström et al., 1993b).

5.1.3 *Birds*

Jansson et al. (1987) analysed pectoral muscle tissue of adult guillemot (*Uria aalge*) nestling and wintering in the Baltic Sea, adult birds of the same species nestling and wintering in the North Sea, and adult guillemot collected at Spitzbergen. The pectoral muscle of a single, adult, white tailed sea eagle (*Haliaetus*

albicilla) from the Baltic Sea was also analysed. The concentrations of polybrominated diphenyl ethers (PBDE), calculated as Bromkal 70-5D, in the muscle of the guillemots of the Baltic, North Sea, and Spitzbergen were 370, 80 and 130 μg/kg, respectively, and that for the Baltic eagle, 350 μg/kg on a fat basis. The chromatographic pattern of the PBDE was similar to that of the Bromkal 70-5 product used as a reference substance.

A method for multiresidue analysis was applied to pooled muscle samples of 35 osprey (*Pandion haliaetus*), collected in Sweden in the period 1982-86. The average concentration of 2,2′4,4′-tetrabromodiphenyl ether in osprey was 1800 μg/kg lipid (Jansson et al., 1993).

A 10-fold increase in 2,2′,4,4′-TeBDE has been indicated in guillemot eggs from the Baltic Sea (Sellström et al., 1993a) (Table 29).

5.1.4 Aquatic mammals

Blubber samples of harbour seals (Phoca vitulina), collected in the southern Baltic Sea and the Kattegat, and a ringed seal (*Pusa hispida*), collected at Spitzbergen, were analysed by Jansson et al. (1987). The concentrations of PBDE were 90, 10, and 40 μg/kg, on a fat basis, respectively. The chromatographic pattern of the PBDE was similar to that of the Bromkal 70-5 product used as a reference substance. Sellström et al. (1990b) reported a concentration of 730 μg PBDE/kg, on a fat basis, in a grey seal from the Baltic Sea.

Seven pooled samples of blubber of ringed seal (*Pusa hispida*), collected in 1981, and 8 pooled samples of blubber of grey seals (*Halichoerus grypus*), collected in Sweden in 1979-85, were analysed using a multiresidue analytical method. The average concentrations of 2,2′4,4′-tetrabromodiphenyl ether were 47 and 650 μg/kg lipid, respectively (Jansson et al., 1993).

Table 29. Average concentrations of 2,2',4,4'-TeBDE in guillemot eggs from the Baltic Sea (in μg/kg lipid)[a]

Sampling year	2,2',4,4'-TeBDE
1970	130
1974	170
1975	130
1976	600
1979	640
1982	820
1983	880
1986	1200
1987	650
1989	1500

[a]From: Sellström et al. (1993a).

5.1.5 *Terrestrial mammals*

Multiresidue analysis of organic pollutants was applied to pooled muscle samples of 15 rabbits (*Oryctolagus cuniculus*), 13 samples of moose (*Alces alces*), and 31 samples of suet of reindeer (*Rangifer tarandus*). The samples were collected in Sweden in the period 1985-86. The average concentrations of 2,2',4,4'-tetrabromodiphenyl ether were < 2, 0.82, 0.17 μg/kg lipid, for rabbit, moose, and reindeer, respectively (Jansson et al., 1993).

5.2 General population exposure

No measurements are available of human exposure to TeBDE. In Sweden, the major human exposure is via fish-related food, and the levels of TeBDE in fish may be used to estimate this route of exposure. Normal fish intake in Sweden is about 30 g/day, and, if herring is used as a model fish, this will give an estimated intake of approximately 0.3 μg TeBDE/person per day (Personal Communication, Jansson).

No data are available on occupational exposure during manufacture, formulation, or use.

6. KINETICS AND METABOLISM IN LABORATORY ANIMALS AND HUMANS

The half-life of pentabromodiphenyl ether (Bromkal 70) was investigated in the perirenal fat of groups of 3 male and 3 female Wistar rats (weight 160-180 g) following a single dose of 300 mg/kg body weight in peanut oil. Animals from the groups were killed on days 1, 2, 3, 4, and 7, and then once a week for 10 weeks. Perirenal fat was collected and analysed. The half-life of TeBDE was 19.1 days for male rats and 29.9 days for female rats (Meyerinck et al., 1990).

TRIBROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

Tribromodiphenyl ether is not manufactured or used.

No data are available on the following topics:

- Environmental transport, distribution, and transformation
- Kinetics and metabolism in laboratory animals and humans
- Effects on laboratory mammals and *in vitro* test systems
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

1.1 Summary and evaluation

There is no database on which to make an evaluation.

1.2 Recommendations

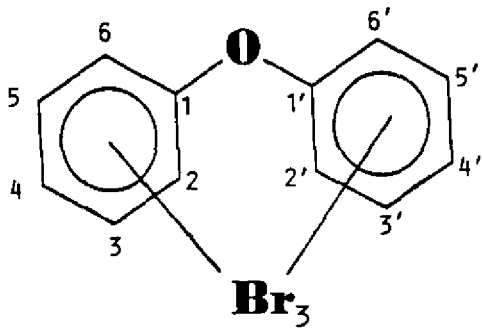
Levels of contamination of commercial products with tribromodiphenyl ether should be minimized to avoid contamination of the environment and the exposure of humans.

Use of such commercial products leading to environmental contamination should be avoided.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Chemical structure



Chemical formula:	$C_{12} H_7 Br_3 O$
Relative molecular mass	407.1
Common names	tribromodiphenyl ether (TrBDE); tribromodiphenyl oxide
CAS registry number	49690-94-0
CAS name	1,1'-oxybis-tribromo-benzene

On the basis of the chemical structure, there are 24 possible isomers of tribromodiphenyl ether.

2.2 Physical and chemical properties

Vapour pressure	4.70-4.95 Pa at 25 °C
n-Octanol/water partition coefficient (log P_{ow})	5.47-5.58

From: US EPA (1984, 1986); Watanabe (1987c); Pijnenburg & Everts (1991).

2.3 Analytical methods

No specific data are available (see General Introduction, section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

Tribromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

4. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

4.1 Environmental levels

4.1.1 Birds

Stafford (1983) found tribromodiphenyl ether (TrBDE) in the eggs of the fish-eating bird, the black skimmer (*Rynchos niger*), collected from various nesting sites in Texas and Louisiana in the period 1980-81. The residues were not quantified.

DIBROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS, AND RECOMMENDATIONS

Dibromodiphenyl ether is not manufactured or used.

No data are available on the following topics:

- Kinetics and metabolism in laboratory animals and humans
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

1.1 Summary and evaluation

There is no database on which to make an evaluation.

1.2 Recommendations

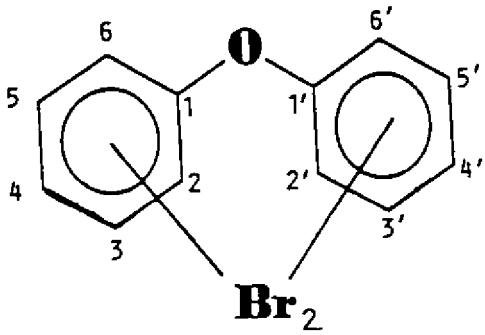
Contamination of commercial products with dibromodiphenyl ether should be minimized to avoid contamination of the environment and exposure of humans.

Use of such commercial products leading to environmental contamination should be avoided.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Chemical structure:



Chemical formula:	$C_{12} H_8 Br_2 O$
Relative molecular mass:	328.02
Common name:	dibromodiphenyl ether (DiBDE) dibromodiphenyl oxide
CAS registry number:	2050-47-7
Synonyms:	bis(bromophenyl) ether, 1.1'-oxybis (bromo), benzene

On the basis of the chemical structure, there are 12 possible isomers of dibromodiphenyl ether, and *p,p'*-dibromodiphenyl ether is one of them.

2.2 Physical and chemical properties

p,p'-Dibromodiphenyl ether (DiBDE) is a crystalline compound.

Melting point:	60.5 °C (58-60 °C)
Boiling point:	338-340 °C
Vapour pressure:	3.85-4.02 Pa at 25 °C
Specific gravity:	1.8 (solution)
Solubility:	very soluble in benzene, soluble in alcohol, and ethyl ether
n-Octanol/water partition coefficient (log P_{ow}):	5.03

From: US EPA (1984, 1986); Environment Agency Japan (1987); Pijnenburg & Everts (1991).

2.3 Analytical methods

No specific data are available (see General Introduction, section 2.1, and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

Dibromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

p,p'-Dibromodiphenyl ether is prepared from *p*-phenoxyaniline by sequential treatment with HBr + $NaNO_2$ and Br_2 + HBr followed by warming in acetic acid (US EPA, 1986).

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

The *in vitro* microbial degradation of dibromodiphenyl ether was studied with a soil isolate, strain S93B1, identified as *Pseudomonas cruciviae*. After enrichment and isolation, the bacteria was cultivated in an agar-slant at 30 °C for 12-17 days and growth was determined. Strain S93B1 did not grow on DiBDE as the sole source of carbon (Takase et al., 1986).

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 Environmental levels

5.1.1 Water

In Japan, *p,p'*-dibromodiphenyl ether was not detected in 27 water samples (limit of determination 0.01-0.03 μg/litre) in an environmental survey in 1984 (Environment Agency Japan, 1987).

5.1.2 Soil/sediment

In Japan, *p,p'*-dibromodiphenyl ether was not detected in 27 sediment samples (limit of determination 0.05-13 μg/kg dry weight) in an environmental survey in 1984 (Environment Agency Japan, 1987).

5.1.3 Birds

Stafford (1983) found *p,p'*-dibromodiphenyl ether in eggs of the fish-eating bird, the black-skimmer (*Rynchops niger*), collected from various nesting sites in Texas and Louisiana in the period 1980-81. The residues were not quantified.

5.2 General population exposure

No data are available.

6. EFFECTS ON LABORATORY MAMMALS AND *IN VITRO* TEST SYSTEMS

No data are available on the following topics:

- Short-and long-term toxicity
- Skin and eye irritation, sensitization
- Reproductive toxicity, embryotoxicity, teratogenicity, mutagenicity, and carcinogenicity.

6.1 Single exposure

The acute intraperitoneal LD_{50} in mice is 125 mg/kg body weight (US EPA, 1984).

6.2 Other special studies

6.2.1 Liver

Carlson (1980a) and Kociba (undated) tested *p,p'*-dibromodiphenyl ether in a dose of 0.1 mmol/kg body weight per day, by gavage, in corn oil, in male Sprague Dawley rats (200-250 g) for 14 days. Twenty-four hours after the last (seventh) dose, increases in liver/body weight ratio, NADPH cytochrome c-reductase, and cytochrome P-450 were found.

MONOBROMODIPHENYL ETHER

1. SUMMARY, EVALUATION, CONCLUSIONS AND RECOMMENDATIONS

No data are available on the following topics:

- Kinetics and metabolism in laboratory animals and humans
- Effects on humans
- Previous evaluations by international bodies.

1.1 Summary and evaluation

1.1.1 Physical and chemical properties

There are 3 possible isomers of monobromodiphenyl ether.

p-Bromodiphenyl ether is a liquid at ambient temperature with a boiling point of 305-310 °C. Its solubility in water is calculated to be 48 mg/litre. The log *n*-octanol water partition coefficient is between 4 and 5. Vapour pressure at 20 °C is 0.0015 mmHg.

1.1.2 Production and uses

MBDE is not used as a flame retardant. A report of production appeared in 1977, but the use is unknown.

1.1.3 Environmental transport, distribution, and transformation

The half-life of volatilization from water is in the range of hundreds of days.

MBDE did not significantly biodegrade in a 7-day culture with microorganisms from domestic waste water, but it has been reported to degrade by 95% in activated sewage sludge. A single study showed a strain of soil bacteria incapable of degrading MBDE as a sole carbon source.

1.1.4 Environmental levels and human exposure

MBDE has been detected in surface water samples taken near industrial sites in the USA but was not found in a similar survey in Japan. It was also detected in soil water close to an industrial plant in the USA. MBDE has been detected in aquatic sediment and aquatic biota in the USA.

1.1.5 Kinetics and metabolism in laboratory animals and humans

No data are available.

1.1.6 Effects on laboratory mammals and in vitro test systems

MBDE is not teratogenic, but there are no data on the acute, short-term, or long-term toxicity of MBDE and therefore no evaluation can be made.

1.1.7 Effects on humans

No data are available.

1.1.8 Effects on other organisms in the laboratory and field

A 96-h LC_{50} for bluegill sunfish has been reported at 4.9 mg/litre with a no-observed-effect concentration at less than 2.8 mg/litre. The 48-h LC_{50} for waterflea was 0.36 mg/litre with a NOEC at less than 0.046 mg/litre.

1.2 Conclusions and recommendations

Monobromodiphenyl ether does not have any flame retardant properties. It can accumulate in organisms in the environment and has been detected in different environmental compartments. There is some evidence that it can be biodegraded.

The limited information means that conclusions concerning exposure levels and effects on the general population and organisms in the environment cannot be reached.

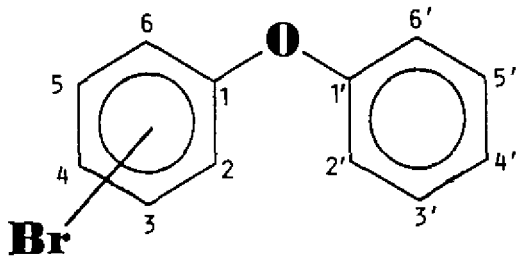
There is no toxicological data base to support its use.

Uses leading to environmental contamination should be avoided.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Chemical structure:



Chemical formula:	$C_{12}H_9BrO$
Relative molecular mass:	249.11
Common names:	monobromodiphenyl ether (MBDE) mono bromodiphenyl oxide
CAS registry number:	101-55-3
CAS name:	bromo-4-phenoxybenzene
Synonyms:	bromophenylphenyl ether, bromodiphenyl ether, bromophenyl ether, bromophenoxybenzene
Trade names:	HSDB 2747; NSC

On the basis of the chemical structure, there are 3 possible isomers of monobromodiphenyl ether. *p*-Monobromodiphenyl ether is one of them.

2.2 Physical and chemical properties

p-Bromodiphenyl ether is a liquid at common ambient temperatures.

Melting point:	18.72 °C
Boiling point:	310.14 °C (305 °C)
Vapour pressure at 20°C:	0.0015 mmHg
Specific gravity:	1.449 (1.4208 at 20 °C)
Refractive index, n 20/D:	1.607
Flash point:	> 230 °F
Solubility at 25 °C:	4.8 mg/litre water (calculated), soluble in ethyl ether
n-Octanol/water partition coefficient (log Pow):	4.28 (4.08-4.94)

From: US EPA (1984, 1986).

2.3 Analytical methods

p-Monobromodiphenyl ether (MBDE) can be determined by the standard US EPA method 611-Haloethers. Chromatographic conditions are described in US EPA (1986). The limit of determination in municipal and industrial waste waters is 2.3 µg/litre. Zogorski (1984) reported a limit of determination of 0.01 µg/litre using a gas chromatograph equipped with an electron capture detector. McMahon (1983) applied GC-MS (US EPA method 625) using a halide specific detector. Gurka et al. (1982) used GC/Fourier transform infrared spectroscopy to detect *p*-monobromodiphenyl ether (see also General Introduction, section 2.1 and Table 2).

3. SOURCES OF HUMAN AND ENVIRONMENTAL EXPOSURE

3.1 Natural occurrence

Monobromodiphenyl ether has not been reported to occur naturally (see General Introduction, section 1.1).

3.2 Anthropogenic sources

3.2.1 Production levels and processes

p-Monobromodiphenyl ether is prepared by brominating diphenyl ether with Br_2 at 95-100 °C in carbon tetrachloride (US EPA, 1986).

The production range (includes importation volumes) statistics from the 1977 TSCA Inventory were up to 450 kg of *p*-monobromodiphenyl ether (US EPA, 1986).

3.2.2 Uses

No data are available.

4. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

4.1 Transport and distribution between media

The half-life of *p*-monobromodiphenyl ether with respect to volatilization has been estimated to be within the range of hundreds of days (MacKay & Leinonen, 1975).

In contrast, by analogy to *p*-monochlorodiphenyl, Callahan et al. (1979) estimated the half-life of *p*-monobromodiphenyl ether to be 10 h. However, sorption of the agent by organic material in water will prolong its evaporative half-life in natural bodies of water. This value should be considered a minimum.

4.2 Biotransformation

4.2.1 Biodegradation

p-Monobromodiphenyl ether was not significantly biodegradable in a 7-day static-culture flask-screening procedure of Bunch and Chambers utilizing biochemical oxygen demand (BOD) dilution water containing 5 mg of yeast extract/litre, as the synthetic medium; 5 and 10 mg/litre concentrations of the test compound, a 7-day static incubation of 25 °C in the dark, followed by three weekly subcultures (totalling 28 days of incubation), and incorporating settled domestic waste water as microbial inoculum. At a test compound concentration of 5 mg/litre, only 2 out of 4 cultures showed any biodegradation in 7 days (19 and 36%), and, at a concentration of 10 mg/litre, only one out of 4 showed biodegradation (19%) (Tabak et al., 1981).

p-Monobromodiphenyl ether was not able to support the growth of Alcaligenes BM2, a strain of soil bacteria capable of using PCB (dichloro-) mixtures as the sole source of carbon (Yagi & Sudo, 1980). However, *p*-monobromodiphenyl ether was reported to be 95% biodegradable when introduced as a pollutant (360 µg/litre) in a full-scale activated sludge treatment system (US EPA, 1986).

The *in vitro* microbial degradation of *p*-monobromodiphenyl ether was studied with a soil isolate, strain S93B1, identified as *Pseudomonas crucivae*. After enrichment and isolation, the bacteria were cultivated in an agar-slant at 30 °C for 12-17 days and growth was determined. Strain S93B1 did not grow on the biphenyl ether as the sole source of carbon (Takase et al., 1986).

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

No data are available on general population exposure or on occupational exposure during manufacture, formulation, or use.

5.1 Environmental levels

5.1.1 Water

According to US EPA (1986), there are monitoring data for *p*-monobromodiphenyl ether in water in the USA. The mean concentration was 0.2 mg/litre (range 0-202.7 mg/litre, 2193 listings) in water. Most of these listings concerned river water samples taken near industrial sites. Only a few groundwater and community drinking-water samples were included (no further details were available). Plumb (1991) reported the presence of *p*-monobromodiphenyl ether in groundwater from only 1 out of 479 disposal sites that were analysed in the USA.

In Japan, *p*-monobromodiphenyl ether was not detected in 27 water samples (limit of determination 0.15-0.5 μg/litre) in an environmental survey in 1984 (Environment Agency Japan, 1987).

5.1.2 Soil/sediment

According to US EPA (1986), there are numerous US monitoring data for *p*-monobromodiphenyl ether in sediments. The mean concentration was 3.5 mg/kg (range 0-380 mg/kg, 585 listings) (no further details are available).

In Japan, *p*-monobromodiphenyl ether was not detected in 27 sediment samples (limit of determination 2.5-120 μg/kg dry weight) in an environmental survey in 1984 (Environment Agency Japan, 1987).

5.1.3 Aquatic organisms

According to US EPA (1986) there are numerous US monitoring data for *p*-monobromodiphenyl ether in tissue from aquatic organisms. The concentrations were 2.0 mg/kg (range 0-70.0 mg/kg, 346 listings) (no further details are available).

6. EFFECTS ON LABORATORY MAMMALS AND *IN VITRO* TEST SYSTEMS

No data are available on the following topics:

- Single exposure
- Short-term exposure
- Long-term exposure
- Skin and eye irritation; sensitization
- Mutagenicity and related endpoints.

6.1 Reproductive toxicity, embryotoxicity, and teratogenicity

Outbred Swiss (CD-1) mice (age 60 days) were treated with *p*-monobromodiphenyl ether (95%). There were 20 and 21 mice respectively in these treatment groups and 51 and 55 mice in untreated and vehicle control (1 ml corn oil/kg) groups, respectively. Two females per group were mated per male, until a copulation plug was found, or for maximum 5 days. MBDE in corn oil was administered by gavage in dose levels of 0, 100 or 1.000 mg/kg body weight/day, from day 5 up to day 14 of gestation. Pups were counted and weighed (by litter) on postnatal days 1, 3, 5, 10 and 15; they were sexed and weaned on day 21 and autopsied on days 25 and 30 to determine gross abnormalities and the weights of Harderian glands, liver, and kidneys. No adverse effects on any of these parameters were observed (Francis, 1989).

6.2 Carcinogenicity

Theiss et al. (1977) tested *p*-monobromodiphenyl ether (MBDE) in a short-term screening assay: the strain A mouse pulmonary tumour assay. Four groups of 20 A/St male mice (6-8 weeks old) were given 24 intraperitoneal injections of tricaprylin (solvent-control), 23 i.p. injections of 40 mg (low-dose), 17

injections of 100 mg (mid-dose) and 18 injections of 200 mg MBDE/kg body weight (high-dose), three times per week. Total doses administered in the four groups were 0, 920, 1700, and 3600 mg/kg body weight, respectively. Twenty-four weeks after the first injection, the mice were sacrificed and the lungs examined. The number of lung tumours/mouse and survival rates of the treated animals were not significantly different from the control animals. The number of lung tumours/mouse were; control 0.39 $\pm$ 0.06; low-dose 0.18 $\pm$ 0.10, mid-dose 0.15 $\pm$ 0.10 and high-dose 0.31 $\pm$ 0.15. MBDE was negative in this pulmonary assay.

7. EFFECTS ON OTHER ORGANISMS IN THE LABORATORY AND FIELD

The effects of acute exposure to *p*-monobromodiphenyl ether have been studied in several species of aquatic invertebrates and fish. The results are summarized in Table 30. The water flea (*Daphnia magna*), is more sensitive than fish to *p*-monobromodiphenyl ether (US EPA, 1984).

In an early-life-stage (embryo-larval) test on fathead minnow, conducted with *p*-monobromodiphenyl ether, adverse effects on survival and growth were produced. The geometric mean of the highest no-effect level was 0.122 mg/litre (US EPA, 1984).

Table 30. Acute toxic effects of *p*-monobromodiphenyl ether on aquatic organisms[a]

Species	Exposure duration (h)	Method	Mean concentration (mg/litre)	Effect	Reference
Rainbow trout *(Oncorhynchus mykiss)*[b]	24	static-aerated	5.0	stress observed	Applegate et al. (1957)
Bluegill sunfish *(Lepomis macrochirus)*	24	static-aerated	5.0	stress observed	Applegate et al. (1957)
Bluegill sunfish *(Lepomis macrochirus)*	24	static	50.9[c]	LC_{50}	US EPA (1978); Buccafusco et al. (1981)
	48	static	9.62	LC_{50}	US EPA (1978)
	72	static	4.94	LC_{50}	US EPA (1978)
	96	static	4.94	LC_{50}	US EPA (1978)
	96	static	< 2.80	no effect	US EPA (1978)
Sea lamprey *(Petromyzon marinus)*	24	static-aerated	5.0	stress observed	Applegate et al. (1957)
Water flea *(Daphnia magna)*	24	static	0.46	LC_{50}	US EPA (1978); LeBlanc (1980)
	48	static	0.36	LC_{50}	US EPA (1978); LeBlanc (1980)
	48	static	< 0.046	no effect	US EPA (1978)

[a]From: US EPA (1984).
[b]Old name = *Salmo gairdneri*.
[c]This dose exceeds the solubility of the test compound in water at 25 °C (4.8 mg/litre).

REFERENCES

AIHA (1981) Decabromo-diphenyloxide. Workplace environmental exposure level guide. Am Ind Hyg Assoc J, **42**: A76-A77.

Andersson O & Blomkvist G (1981) Polybrominated aromatic pollutants found in fish in Sweden. Chemosphere, **10(9)**: 1051-1060.

Anon (1989) Draft evalnation report on flame retardants; PBB's and PBBO's (in Dutch).

Applegate VC, Howell JH, Hall AE, & Smith MA (1957) Toxicity of 4,346 chemicals to larval lampreys and fish. Washington, DC, US Department of the Interior, Fish and Wildlife Service (Special Scientific Report, Fish No. 207).

Arias (1992) Brominated diphenyloxides as flame retardants; Bromine based chemicals. Consultant report to the OECD, Paris.

Bahn A, Bialik O, Oler J, Houten L, & Landau E (1980) Health assessment of occupational exposure to polybrominated biphenyl (PBB) and polybrominated biphenyl-oxide (PBBO). Washington, DC, US Environmental Protection Agency, Office of Pesticides and Toxic Substances, 72 pp (ISS EPA 560/6-80-001; NTIS No. PB81-159675).

Ball M, Päpke O, & Lis A (1991) [Further investigation on the formation of polybrominated dioxins and furans during thermal stress of flameproof plastics and textiles. Sub-project 1.] Berlin, Federal Office for the Environment (Research report No. 10403364/01; UBA-FB 91-082) (in German).

Ball M, Päpke O, & Lis A (1992) [Further investigation on the formation of polybrominated dioxins and furans during thermal stress of flameproof plastics and textiles. Sub-projects 1 and 2.] Berlin, Federal Office for the Environment (Research report Nos. 10403364/01 & /02; UBA-FB 91-082 & 92-097) (in German).

BFRIP (1990) Brominated flame retardants. A review of recent research (Compiled by The Brominated Flame Retardant Industry Panel and The European Brominated Flame Retardant Industry Panel). West Lafayette, Indiana, USA, BFRIP (Unpublished report No. III/4143/90, submitted to WHO by BFRIP).

Bialik O (1982) Endocrine function of workers exposed to PBB and PBBO: Terminal progress report. Cincinnati, Ohio, National Institute for Occupational Safety and Health.

Bieniek D, Bahadir M, & Korte F (1989) Formation of heterocyclic hazardous compounds by thermal degradation of organic compounds. Heterocycles, **28**: 719-722.

Breslin WJ, Kirk HD, & Zimmer MA (1989) Teratogenic evaluation of a polybromodiphenyl oxide mixture in New Zealand White rabbits following oral exposure. Fundam Appl Toxicol, **12**: 151-157.

Bromine Compounds Ltd (1992) Material safety data sheet FR-1210. Beer Sheva, Israel, Bromine Compounds Ltd, pp 1-5.

Brosier JS, Blanchard FA, & Takahashi IT (1972) Concentrations of octabromodiphenyl and decabromodiphenyloxide in aquaria water and trout flesh. Midland, Michigan, Dow Chemical Company (Unpublished report No. AL 37448, submitted to WHO by BFRIP).

Bruckmann P, Hackhe K, Ball M, Lis A, & Papke O (1990) Degassing of PBDD/PBDFs from a television set - PBDD/PBDF levels after a fire in a stock house - two case studies. In: Freij L ed. Proceedings of the Workshop on Brominated Aromatic Flame Retardants, Skokloster, Sweden, 24-26 October 1989. Solna, National Chemicals Inspectorate (KEMI), pp 99-104.

Buccafusco RJ, Ells SJ, & Leblanc GA (1981) Acute toxicity of priority pollutants to bluegill (*Lepomis macrochirus*). Bull Environ Contam Toxicol, **26**(4): 446-452.

Buser HR (1986) Polybrominated dibenzofurans and dibenzo-*p*-dioxins: Thermal reaction products of polybrominated diphenylether flame retardants. Environ Sci Technol, **20**(4): 404-408.

Carlson GP (1980a) Induction of xenobiotic metabolism in rats by short-term administration of brominated diphenylethers. Toxicol Lett, **5**: 19-25.

Carlson GP (1980b) Induction of xenobiotic metabolism in rats by brominated diphenylethers administered for 90 days. Toxicol Lett, **6**: 207-212.

Carte B & Faulkner DJ (1981) Polybrominated diphenyl ethers from *Dysidea herbacea*, *Dysidea chlorea* and *Phyllospongia foliascens*. Tetrahedron, **37**: 2335-2339.

CBC (1982) The bioaccumulation of compound S-511 by carp. Tokyo, Chemicals Inspection and Testing Institute, Chemical Biotesting Center (Unpublished report).

CEM (1989) Polybrominated dibenzodioxins and dibenzofurans (PBDDs/PBDFs) from flame retardants containing bromine. Assessment of risk and proposed measures. Report by the Brominated flame retardants CEM Working Group to the Conference of Environment Ministers, Bonn, September 1989. (Report III/4299/89. Appendix).

Chemag (1988) Information sheet on Chemflam 011. Frankfurt am Main, Chemag Aktiengesellschaft, p 1.

Clausen E, Lahaniatis ES, Bahadir M, & Bieniek D (1987) [Determination of brominated dibenzofurans formed during the thermolysis of polymers with

decabromodiphenylether as flame-proofing agent.] Fresenius Z Anal Chem, **327**: 297-300 (in German).

Craig DK, Mitchum RK, Bauer MR, Yancey MF, Peters AC, & Joiner RL (1989) Determination of polybrominated dibenzo-*p*-dioxins and polybrominated dibenzofurans in CYCOLAC plastic resins and the fumes evolved during normal thermal processing. Final report. Columbus. Ohio, Battelle (Report to General Electric Company, Mt. Vernon, Indiana, submitted to WHO by BFRIP).

Cramer PH, Stanley JS, & Thornburg KR (1990a) Mass spectral confirmation of chlorinated and brominated diphenyl ether in human adipose tissues. Kansas City, Missouri, Midwest Research Institute (Prepared for the US Environmental Protection Agency, Washington) (US NTIS report PB91-159699).

Cramer PH, Ayling RE, Thornburg KR, Stanley JS, Remmers JC, Breen JJ, & Schwemberger J (1990b) Evaluation of an analytical method for the determination of polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/PBDF) in human adipose. Chemosphere, **20**(7-9): 821-827.

Davidson JS & Ariano JM (1986) Decabromodiphenylether (DE-83): Determination of area percent assay. Analytical method No. QC-86-02. West Lafayette, Indiana, Great Lakes Chemical Corporation (Report submitted to WHO by BFRIP).

De Boer J (1989) Organochlorine compounds and bromodiphenylethers in livers of Atlantic cod (*Gadus morhua*) from the North Sea, 1977-1987. Chemosphere, **18**(11/12): 2131-2140.

De Boer J (1990) Brominated diphenylethers in Dutch freshwater and marine fish. In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar. Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (Short papers). Bayreuth, Germany, Ecoinforma Press, pp 315-318.

DeCarlo VJ (1979) Studies on brominated chemicals in the environment. Ann NY Acad Sci, **320**: 678-681.

Dieter MP (1979) Special studies protocol. Washington, Memorandum of the Department of Health, Education and Welfare. Public Health Service, National Institute of Health, National Cancer Institute.

Dow Chemical Company (1978) Compound: Decabromodiphenyl oxide (Analytical method). Midland, Michigan, Dow Chemical Company, pp 609-620 (Report prepared by Tracor Jitco, Inc., Rockville, Maryland) (Report No. 3250, submitted to WHO by BFRIP).

Dumler R, Lenoir D, & Hutzinger O (1990) Formation of brominated dibenzofurans and -dioxins from the combustion of the flame retardant decabromodiphenyl ether under

different conditions. In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar, Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (short papers). Bayreuth, Germany, Ecoinforma Press, pp 325-328.

Dumler R, Thoma H, Lenoir D, & Hutzinger O (1989a) Thermal formation of polybrominated dibenzodioxins (PBDD) and dibenzofurans (PBDF) from bromine containing flame retardants. Chemosphere, **19**(1-6): 305-308.

Dumler R, Lenoir D, Thoma H, & Hutzinger O (1989b) Thermal formation of polybrominated dibenzofurans from decabromodiphenyl ether in a polybutylene-terephthalate polymer matrix. J Anal Appl Pyrolysis, **16**: 153-158.

EBFRIP (1990) Information on polybrominated diphenylethers (PBDE's). Economic, technical and regulatory assessment of the European Brominated Flame Retardant Industry Panel - Responses to questions submitted by EEC, Brussels. Rijswijk (NL), The European Brominated Flame Retardant Industry Panel.

El Dareer SM, Kalin JR, Tillery KF, & Hill DL (1987) Disposition of decabromodiphenyl ether in rats dosed intravenously or by feeding. J Toxicol Environ Health, **22**: 405-415.

Environment Agency Japan (1983) Environmental monitoring of chemicals. Environmental survey report of F.Y. 1980 and 1981. Tokyo, Environment Agency Japan, Department of Environmental Health, Office of Health Studies.

Environment Agency Japan (1987) Chemicals in the environment. Report on environmental survey and wildlife monitoring of chemicals in F.Y. 1984 and 1985. Tokyo, Environment Agency Japan, Department of Environmental Health, Office of Health Studies.

Environment Agency Japan (1989) Chemicals in the environment. Report on environmental survey and wildlife monitoring of chemicals in F.Y. 1986 and 1987. Tokyo, Environment Agency Japan, Department of Environmental Health, Office of Health Studies.

Environment Agency Japan (1991) Chemicals in the environment. Report on environmental survey and wildlife monitoring of chemicals in F.Y. 1988 and 1989. Tokyo, Environment Agency Japan, Department of Environmental Health, Office of Health Studies.

Ethyl Corporation (1986) Laboratory report: Primary eye irritation. Saytex 102. Baton Rouge, Louisiana, Ethyl Corporation (Report No. PH 421-ET-010-86) (Report submitted to WHO by BFRIP).

Ethyl Corporation (1992a) Information sheet from Ethyl Corporation on Saytex 102E. Baton Rouge, Louisiana, Ethyl Corporation (Report submitted to WHO by BFRIP).

Ethyl Corporation (1992b) Information sheet from Ethyl Corporation on Saytex 111. Baton Rouge, Louisiana, Ethyl Corporation (Report submitted to WHO by BFRIP).

Faulkner DJ (1988) Brominated marine natural products. In: Price D, Iddon B, & Wakefield BJ ed. Bromine Compound: Chem. Appl., (Proceedings, International Conference on Chemical Applications of Bromine and its Compounds.) Amsterdam, Oxford, New York, Elsevier Science Publishers, Chapter 2, pp 121-144.

Faulkner DJ (1990) Naturally-occurring brominated compounds. In: Freij L ed. Proceedings of the Workshop on Brominated Aromatic Flame Retardants, Skokloster, Sweden, 24-26 October 1989. Solna, National Chemicals Inspectorate, pp 121-144.

Fernandez P, Grifoll M, Solanas AM, Bayona JM, & Albaiges J (1992) Bioasssay-directed chemical analysis of genotoxic components in coastal sediments. Environ Sci Technol, **26**: 817-829.

Flick EW (1986) Plastics additives: An industrial guide. Section IX - Fire and flame retardants. Park Ridge, New Jersey, Noyes Publications, pp 213-248.

Francis BM (1989) Relative developmental toxicities of nine diphenyl ethers related to nitrofen. Environ Toxicol Chem, **8**: 681-688.

Fresenius Institute (1990) Summary results on pyrolysis of different types of ABS. Battelle report on contents and vapour-emission of PBDD resp. PBDF's. Memorandum from Leeuwenburgh W.F., General Electric Plastics ABS, BV. Amsterdam. 12 March 1990 (Report submitted to WHO by BFRIP).

Fulfs JC (1987a) Rabbit ear bioassay for comedogenicity, dose-range finding study for soot and char generated from the combustion of high impact polystyrene. Fort Collins, CO, USA, Inhausen Research Institute, Inc. (Report to Ethyl Corporation, Baton Rouge, Florida, submitted to WHO by BFRIP).

Fulfs JC (1987b) Rabbit ear bioassay for comedogenicity, dose-range finding study for soot and char generated from the combustion of high impact polystyrene flame retarded with decabromodiphenyloxide and antimony oxide. Fort Collins, CO, USA, Inhausen Research Institute, Inc. (Report to Ethyl Corporation, Baton Rouge, Florida, submitted to WHO by BFRIP).

Fulfs JC & Dahlgren RR (1987a) Acute oral toxicity in the rat of soot and char generated from the combustion of high impact polystyrene (HIPS). Fort Collins, CO, USA, Inhausen Research Institute, Inc. (Report to Ethyl Corporation, Baton Rouge, Florida, submitted to WHO by BFRIP).

Fulfs JC & Dahlgren RR (1987b) Acute oral toxicity in the rat of soot and char generated from the combustion of high impact polystyrene flame retarded with decabromodiphenyloxide and antimony trioxide (HIPS FR). Fort Collins, CO, USA, Inhausen Research Institute, Inc. (Report to Ethyl Corporation, Baton Rouge, Florida, submitted to WHO by BFRIP).

Fulfs JC & Dahlgren RR (1987c) Rabbit ear bioassay for comedogenicity: Multiple-dose-level definitive study for soot and char generated from the combustion of high impact polystyrene. Fort Collins, CO, USA, Inhausen Research Institute, Inc. (Report to Ethyl Corporation, Baton Rouge, Florida, submitted to WHO by BFRIP).

Fulfs JC & Dahlgren RR (1987d) Rabbit ear bioassay for comedogenicity, multiple-dose-level definitive study for soot and char generated from the combustion of high impact polystyrene flame retarded with decabromo-diphenyloxide and antimony trioxide. Fort Collins, CO, USA, Inhausen Research Institute, Inc. (Report to Ethyl Corporation, Baton Rouge, Florida, submitted to WHO by BFRIP).

Great Lakes Chemical Corporation (1987) Toxicity data of octabromo-diphenyloxide (DE-79). West Lafayette, Indiana, Great Lakes Chemical Corporation (Unpublished data submitted to WHO by BFRIP).

Great Lakes Chemical Corporation (1990a) Great Lakes DE-79tm: Product information. West Lafayette, Indiana, Great Lakes Chemical Corporation (Report submitted to WHO by BFRIP).

Great Lakes Chemical Corporation (1990b) Great Lakes DE-83Rtm: Product information. West Lafayette, Indiana, Great Lakes Chemical Corporation (Report submitted to WHO by BFRIP).

Great Lakes Chemical Corporation (Undated a) Toxicity data of pentabromo-diphenyloxide. West Lafayette, Indiana, Great Lakes Chemical Corporation (Unpublished report submitted to WHO by BFRIP).

Great Lakes Chemical Corporation (Undated b) Toxicity data of decabromo-diphenyloxide. West Lafayette, Indiana, Great Lakes Chemical Corporation (Unpublished report submitted to WHO by BFRIP).

Gurka DF, Laska PR, & Titus R (1982) The capability of GC/FT-IR to identify toxic substances in environmental sample extracts. J Chromatogr Sci, 20: 145-154.

Hagenmaier H, She J, Dawidowsky N, Thomas B, & Dusterhoft L (1991) Analysis of sewage sludges for polyhalogenated dibenzo-*p*-dioxins, dibenzofurans and diphenylethers. In: Dioxin'91. Abstract from the 11th International Symposium on Chlorinated Dioxins and Related Compounds, Research Triangle Park, North Carolina, 23-27 September 1991, p 112.

Hallenbeck D (1993) Freezing point of DE-71. Inter-Office memorandum, Great Lakes Chemical Corporation. June 29, 1993 (Report submitted to WHO by BFRIP).

Hamm S & Theisen J (1992) Formation of polybrominated dibenzofurans and polybrominated dibenzo(*p*)dioxins at fires of electrical appliances. Poster presented at Dioxin'92. 12th International Symposium on Dioxins and Related Compounds, Tampere, Finland, 24-28 August 1992. Münster, Society for Workplace and Environmental Analysis GmbH.

Hanberg A, Stahlberg M, Georgellis A, De Wit C, & Ahlborg UG (1991) Swedish dioxin survey: Evaluation of the H-4-II E bioassy for screening environmental samples for dioxin-like enzyme induction. Pharmacol Toxicol, **69**: 442-449.

Hanley TR Jr (1985) Decabromodiphenyloxide: A summary of an oral teratology study in Sprague-Dawley rats. Midland, Michigan, Dow Chemical Company (Unpublished report submitted to WHO by BFRIP).

Hefner RE Jr (1973) A study of the rate of hemolysis induced by decabromodiphenoxide (DBDPO) particles with washed rat erythrocytes *in vitro*. Midland, Michigan, Dow Chemical Company (Unpublished report submitted to WHO by BFRIP).

Hoechst Celanese Corporation (1988) Report of air sampling for the presence of polybrominated dibenzodioxins and dibenzofurans during the production of polybutylene terephthalate resin with decabromodiphenyl oxide (Unpublished report submitted to WHO by BFRIP).

Huff JE, Eustis SL, & Haseman JK (1989) Occurrence and relevance of chemically induced benign neoplasms in long-term carcinogenicity studies. Cancer Metastasis, **8**: 1-21.

Hutzinger O & Thoma H (1987) Polybrominated dibenzo-*p*-dioxins and dibenzofurans: The flame retardant issue. Chemosphere, **16**(8/9): 1877-1880.

Hutzinger O, Sundstrom G, & Safe S (1976) Environmental chemistry of flame retardants. Part. I. Introduction and principles. Chemosphere, 1: 3-10.

IARC (1990) Some flame retardants and textile chemicals, and exposures in the textile manufacturing industry. Lyon, International Agency for Research on Cancer, 345 pp (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 48).

Industrial Bio-Test Laboratories (1975) Human repeated insult patch test with DBDO-1 and XD 8186.02. Northbrook, Illinois, USA. (Report to Dow Chemical Company, Midland, Michigan) (Report No. IBT 636-0654, submitted to WHO by BFRIP).

IRPTC (1988) Data profiles on flame retardants; Deca-, octa- and pentabromodiphenyloxide. Geneva, International Register of Potentially Toxic Chemicals, United Nations Environment Programme.

Jansson B, Asplund L, & olsson M (1987) Brominated flame retardants - Ubiquitous environmental pollutants? Chemosphere, **16**(10-12): 2343-2349.

Jansson B, Andersson R, Asplund L, Bergman A, Litzen K, Nylund K, Reutergardh L, Sellström U, Uvemo U-B, Wahlberg C, & Wideqvist U (1991) Multiresidue method for the gas-chromatographic analysis of some polychlorinated and polybrominated pollutants in biological samples. Fresenius J Anal Chem, **340**: 439-445.

Jansson B, Andersson R, Asplund L, Litzen K, Nylund K, Sellström U, Uvemo U-B, Wahlberg C, Wideqvist U, Odsjo T, & Olsson M (1993) Chlorinated and brominated persistent organic compounds in biological samples from the environment. Accepted for publication in Environ. Toxicol. Chem., **12**(7): 1163-1174.

Jersey GC, Frauson LE, & Schuetz DJ (1976) Pulmonary clearance and tissue response following a single intratracheal injection of decabromo-diphenyloxide (DBDPO) dust in male rats. Midland, Michigan, Dow Chemical Company (Unpublished report No. HET K-47298-(21), submitted to WHO by BFRIP).

Kaart KS & Kokk KY (1987) Spectrometric determination of decabromodiphenyl oxide in industrial sewage. Ind Lab, **53**: 289-290.

Kalk (1982) [CFK Bromkal(R) - fire protection equipment]. Cologne, Kalk Chemical Factory (Information sheet 3000-7/82) (in German).

Kitchin KT, Brown JL, & Kulkarni P (1992) Predictive assay for rodent carcinogenicity using *in vivo* biochemical parameters: operational characteristics and complementarity. Mutat Res, **266**: 253-272.

Klusmeier W, Voegler P, Ohrbach KH, Weber H, & Kettrup A (1988) Thermal decomposition of decabromodiphenyl ether. J Anal Appl Pyrolysis, **13**: 277-285.

Kociba RJ (undated) Comparative biologic activity and toxicity of brominated derivatives of diphenylether (oxide). (Unpublished report submitted to WHO by BFRIP).

Kociba RJ, Frauson LO, Humiston CG, Norris JM, Wade CE, Lisowe RW, Quast JF, Jersey GC, & Jewett GL (1975a) Results of a two-year dietary feeding study with decabromodiphenyl oxide (DBDPO) in rats. Midland, Michigan, Dow Chemical Company (Unpublished report submitted to WHO by BFRIP).

Kociba RJ, Frauson LO, Humiston CG, Norris JM, Wade CE, Lisowe RW, Quast JF, Jersey GC, & Jewett GL (1975b) Results of a two-year dietary feeding study with decabromodiphenyl oxide (DBDPO) in rats. Combust Toxicol, **2**: 267-285.

De Kok JJ, De Kok A, Brinkman UATh, & Kok RM (1977) Analysis of polybrominated biphenyls. J Chromatogr, **142**: 367-383.

De Kok JJ, De Kok A, & Brinkman UATh (1979) Analysis of polybrominated aromatic ethers. J Chromatogr, **171**: 269-278.

Kopp A (1990) [Documentation on fire-proofing agents containing bromine.] Bonn, Ministry of Environment, Nature Conservation and Nuclear Safety (Report to the European Economic Community, Brussels) (in German).

Koster P, Debets FMH, & Strik JJTWA (1980) Porphyrinogenic action of fire retardants. Bull Environ Contam Toxicol, **25**: 313-315.

Kraus HW (1990) Polybrominated dibenzodioxines and dibenzofurans (PBDDs/PBDFs) from flame retardants containing bromine. Bonn, Ministry for Environment, Nature Conservation and Nuclear Safety (Report to the Organisation for Economic Co-operation and Development, Paris).

Krüger C (1988) [Polybrominated biphenyls and polybrominated diphenyl ethers - detection and quantitation in selected foods.] Münster, University of Münster (Thesis) (in German).

Kuehl DW, Haebler R, & Potter C (1991) Chemical residues in dolphins from the U.S. Atlantic coast including Atlantic bottlenose obtained during the 1987/88 mass mortality. Chemosphere, **22**(11): 1071-1084.

Lahaniatis ES, Bergheim W, & Rainer C (1989) Hazardous halogenated substances formed during combustion processes. Toxicol Environ Chem, **20-21**: 501-506.

Lahaniatis ES, Bergheim W, & Bieniek D (1991) Formation of 2,3,7,8-tetrabromodibenzodioxin and -furan by thermolysis of polymers containing brominated flame retardants. Toxicol Environ Chem, **31/32**: 521-526.

Lahl U, Wilken M, & Wiebe A (1991) [Polybrominated diphenyl ethers in waste incineration.] Mull Abfall, **23**: 83-87 (in German).

Larsen ER (1978) Flame retardants. Halogenated fire retardants. In: Mark HF, Othmer DF, Overberger CG, Seaborg GT, & Grayson M ed. Kirk-Othmer encyclopedia of chemical technology, 3rd ed. New York, Chichester, Brisbane, Toronto, John Wiley and Sons, vol 10, pp 373-395.

Leblanc RB (1979) What's available for FR textiles. Text Ind, **143**: 78-83.

Leblanc GA (1980) Acute toxicity of priority pollutants to water flea (*Daphnia magna*). Bull Environ Contam Toxicol, **24**(5): 684-691.

Leung HW, Murray FJ, & Paustenbach DJ (1988) A proposed occupational exposure limit for 2,3,7,8-tetrachlorodibenzo-p-dioxin. Am Ind Hyg Assoc J, **49**(9): 466-474.

Luijk R & Govers HAJ (1992) The formation of polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs) during pyrolysis of polymer blends containing brominated flame retardants. Chemosphere, **25**(3): 361-374.

McAllister DL & Ariano JM (1982) DE-71/DE-60F. Determination of bromination level and aromatic phosphate ester concentration. Analytical method No. QCS-82-25. West Lafayette, Indiana, Great Lakes Chemical Corporation (Report submitted to WHO by BFRIP).

McAllister DL, Mazac CJ, Gorsich R, Freiberg M, & Tondeur Y (1990) Analysis of polymers containing brominated diphenyl ethers as flame retardants after molding under various conditions. Chemosphere, **20**(10-12): 1537-1541.

McAllister DL (1991) Letter of Great Lakes Chemical Corporation, West Lafayette to the IPCS/WHO, dated November 25, 1991.

MacKay D & Leinonen PJ (1975) Rate of evaporation of low-solubility contaminants from water bodies to the atmosphere. Environ Sci Technol, **9**(13): 1178-1180.

McMahon LW (1983) Organic priority pollutants in wastewater. In: Proceedings of the 1982 UCC-ND/GATT Environmental Protection Seminar, April, 5-7, 1982. Oak Ridge, TN. Oak Ridge National Laboratory/Union Carbide Corp. US (DOE Contract No. W-7405-eng-26) (US EPA, 1986).

Mallory VT, Naismith RW, & Matthews RJ (1986) Primary eye irritation (PH 421-ET-010-86) Saytex 102. Baton Rouge, Louisiana, Ethyl Corporation (Unpublished report submitted to WHO by BFRIP).

Naismith RW & Matthews RJ (1981) Assay of comedogenicity in the rabbit ear (PH 425-ET-001-81) Saytex 102. Baton Rouge, Louisiana, Ethyl Corporation (Unpublished report submitted to WHO by BFRIP).

Neupert M, Weis H, Thies J, & Stock B (1989) Analytical procedures in connection with acute animal toxicity studies. II. Pyrolysis products obtained from an ABS copolymer containing octabromodiphenylether as a flame retardant. Chemosphere, **19**(1-6): 219-224.

Noguchi Y, Noda E, Toyoshima K, & Mitsui Toatsu Chemicals Inc. (1977) Photostabilized polybromobiphenyl ethers. Japan Kokai 77 07,932, January 21, 1977. (as reported in Chem. Abstr. 87: 134511x) (US EPA, 1986).

Norris JM (1971) Decabromodiphenyloxide solids from mother liquor (waste tars). Midland, Michigan, Dow Chemical Company (Unpublished report TOX-No. T2.TX-1767-1, submitted to WHO by BFRIP).

Norris JM, Ehrmantraut JW, Gibbons CL, Kociba RJ, Schwetz BA, Rose JQ, Humiston

CG, Jewett GL, Crummett WB, Gehring PJ, Tirsell JB, & Brosier JS (1973) Toxicological and environmental factors involved in the selection of decabromodiphenyl oxide as a fire retardant chemical. Appl Polymer Symp, **22**: 195-219.

Norris JM, Ehrmantraut JW, Gibbons CL, Kociba RJ, Schwetz BA, Rose JQ, Humiston CG, Jewett GL, Crummett WB, Gehring PJ, Tirsell JB, & Brosier JS (1974) Toxicological and environmental factors involved in the selection of decabromodiphenyloxide as a fire retardant chemical. J Fire Flamm Combust Toxicol, **1**, 52-77.

Norris JM, Ehrmantraut JW, Kociba RJ, Schwetz BA, Rose JQ, Humiston CG, Jewett GL, Crummet WB, Gehring PJ, Tirsell JB, & Brosier JS (1975a) Evaluation of decabromodiphenyloxide as a flame-retardant chemical. Chem Hum Health Environ, **1**: 100-116.

Norris JM, Kociba RJ, Humiston CG, & Gehring PJ (1975b) The toxicity of decabromodiphenyloxide and octabromodiphenyl as determined by subacute and chronic dietary feeding studies in rats. Toxicol Appl Pharmacol, **33**(1): 170 (abstract).

Norris JM, Kociba RJ, Schwetz BA, Rose JQ, Humiston CG, Jewett GL, Gehring PJ, & Mailhes JB (1975c) Toxicology of octabromodiphenyl and decahromodiphenyloxide. Environ Health Perspect, **11**: 153-161.

NTP (1986) Toxicology and carcinogenesis studies of decahromodiphenyl oxide (CAS No. 1163-19-5) in F344/N rats and B6C3F1 mice (feed studies). Research Triangle Park, North Carolina, US Department of Health and Human Services, National Toxicology Program (NTP Technical Report Series No. 309).

Nylund K, Asplund L, Jansson B, Jonsson P, Litzen K, & Sellström U (1992) Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. Chemosphere, **24**(12): 1721-1730.

Oberg T & Bergström J (1990) Bromine and waste incineration - An environmental risk? In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar. Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (short papers). Bayreuth, Germany, Ecoinforma Press, pp 339-342.

Oberg T, Warman K, & Bergström J (1987) Brominated aromatics from combustion. Chemosphere, **16**(10-12): 2451-2465.

OECD (1991) Co-operation on existing chemicals: Risk reductions. Lead country report on brominated flame retardants. Sixteenth Joint Meeting of the Chemicals Group and Management Committee, 28-30 May 1991. Paris, Organisation for Economic Co-operation and Development (Report ENV/MC/CHEM (91)7).

Pijnenburg AMCM & Everts JW (1991) [Flame retardants: Occurrence and toxicity.]

The Hague, Ministry of Transport and Public Works (Note No. GWAO-91.001) (in Dutch).

Pijnenburg AMCM, Everts JW, De Boer J, & Boon JP (1992) Polybrominated biphenyl (PBB) and diphenylether (PBDE) flame retardants: Analysis, toxicity and occurrence in aquatic environments. Manuscript for discussion in 1992 Annual Meeting of the ICES Marine Chemistry Working Group (MCWG) and the Working Group on Biological Effects of Contaminants (WGBEC). The Hague, Ministry of Transport and Public Works (Unpublished report).

Pinkerton MN, Kociba RJ, Petrella RV, McAllister DL, Willis ML, Fulfs JC, Thoma H, & Hutzinger O (1989) A preliminary report on the investigation of the comparative toxicity of combustion products of high impact polystyrene with and without decabromodiphenyloxide/antimony trioxide as a flame retardant using 2,3,7,8-tetrabromodibenzo-*p*-dioxin and 2,3,7,8-tetrabromodibenzofuran as positive controls. Chemosphere, **18**(1-6): 1243-1249.

Plumb RH Jr (1991) The occurrence of Appendix IX organic constituents in disposal site ground water. Groundw Monit Rev, **11**(2): 157-164.

Rampy LW (1971-1974) Chloracne studies on DBDPO and DBDPO mother liquor. A series of working protocols with results from the Chemical Biology Research Department of Dow Chemical USA, Midland, Michigan (The work was carried out mainly by Rampy alone or with co-workers in the period 1971-1974) (Report submitted to WHO by BFRIP).

Ranken PF, Ricks GM, Lynam DR, & Ariano JM (1990) Is watching television toxic? BFRIP-sponsored study on the emission of PBDDs/PBDFs from operating television sets. In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar. Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (short papers). Bayreuth, Germany, Ecoinforma Press, pp 343-346.

Remmers JC, Breen JJ, Schwemberger J, Stanley JS, Cramer PH, & Thornburg KR (1990) Mass spectral confirmation of chlorinated and brominated diphenyl ethers in human adipose tissues. In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar. Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (short papers). Bayreuth, Germany, Ecoinforma Press, pp 347-350.

Riggs KB, Pitts GE, White JS, Mitchum RK, Reuther JJ, & Glatz JA (1990) Polybrominated dibenzo-*p*-dioxin and polybrominated dibenzofuran emissions from incineration of flame-retarded resins in a simulated municipal waste incinerator. In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar. Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (short papers). Bayreuth, Germany, Ecoinforma Press, pp 351-356.

Rogers J & Hill JT (1980) Final report. Determination of decabromodiphenyl oxide (DBDPO) in rat livers. Vienna, Virginia, Hazleton Laboratories America, Inc. (Unpublished report to Tracor Jitco, Rockville, Maryland, submitted to WHO by BFRIP).

Rutter HA & Machotka S (1979) Final Report. Decabromodiphenyloxide: 13-week subchronic feeding study - mice. Vienna, Virginia, Hazleton Laboratories America, Inc. (Unpublished report to Tracor Jitco, Rockville, Maryland, submitted to WHO by BFRIP).

Schwetz BA, Smith FA, Nitschke KD, Humiston CG, Jersey GC, & Kociba RJ (1975) Results of a reproduction study in rats maintained on diets containing decabromodiphenyloxide. Midland, Michigan, Dow Chemical Company (Unpublished report No. HET K-47298-(14), submitted to WHO by BFRIP).

Sellström U, Andersson R, Asplund L, Janssou B, Jonsson P, Litzen K, Nylund K, Uvemo U-B, & Wideqvist U (1990b) Anthropogenic brominated aromatics in the Swedish environment. In: Freij L ed. Proceedings of the Workshop on Brominated Aromatic Flame Retardants, Skokloster, Sweden, 24-26 October 1989. Solna, National Chemicals Inspectorate (KEMI), pp 73-78.

Sellström U, Jansson B, Jonsson P, Nylund K, Odsjö T, & Olsson M (1990a) Anthropogenic brominated aromatics in the Swedish environment. In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar. Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (short papers). Bayreuth, Germany, Ecoinforma Press, pp 357-360.

Sellström U, Jansson B, Kierkegaard A, & De Wit C (1993a) Polybrominated diphenyl ethers (PBDE) in biological samples from the Swedish environment. Chemosphere, 26(9): 1703-1718.

Sellström U, Kierkegaard A, De Wit C, Jansson B, & Olsson M (1993b) Time trend studies of polybrominated diphenyl ethers (PBDE) in biological material from the Swedish environment. Paper presented at Dioxin'93, Vienna, 1 September 1993.

Shoichet A & Ehrlich K (1977) Mutagenicity testing of HFO 102. (Unpublished proprietary report from Gulf South Research Institute, New Orleans, Louisiana to Hexel Fine Organics (Report submitted to WHO by BFRIP).

Sovocool GW, Donnelly JR, Grange AH, Simmons RD, & Munslow WD (1990) Brominated dioxins and other bromoaromatics in plastic pyrolysates. In: Hutzinger O & Fiedler H ed. Dioxin'90. EPRI-Seminar. Tenth International Symposium on Chlorinated Dioxins and Related Compounds. Volume 2: Organohalogenated compounds (short papers). Bayreuth, Germany, Ecoinforma Press, pp 365-368.

Sparschu GL, Kociba RJ, & Clashman A (1971) Results of 30 day rat dietary feeding

studies on octabromobiphenyl SA-1902 and decabromodiphenyl oxide SA-1892.1. Midland, Michigan, Dow Chemical Company (Unpublished report submitted to WHO by BFRIP).

Stafford CJ (1983) Halogenated diphenylethers identified in avian tissues and eggs by GC/MS. Chemosphere, **12**(11/12): 1487-1495.

Stanley JS, Cramer PH, Thornburg KR, Remmers JC, Breen JJ, & Schwemberger J (1991) Mass spectral confirmation of chlorinated and brominated diphenylethers in human adipose tissues. Chemosphere, **23**(8-10): 1185-1195.

Striebich RC, Rubey WA, Tirey DA, & Dellinger B (1991) High temperature degradation of polybrominated flame retardant materials. Chemosphere, **23**(8-10): 1197-1204.

Sundström G & Hutzinger O (1976) Environmental chemistry of flame retardants. V. The composition of Bromkal (R) 70-5 DE - A pentabromo-diphenyl ether preparation. Chemosphere, **3**: 187-190.

Tabak HH, Quave SA, Mashni CI, & Barth EF (1981) Biodegradability studies with organic priority pollutant compounds. J Water Pollut Control Fed, **53**: 1503-1518.

Tabor TE & Bergman S (1975) Decabromodiphenyl oxide. A new fire retardant additive for plastics. In: Fire retardants. Proceedings of 1974 International Symposium on Flammability and Fire Retardants, Cornvall, Ontario, 1-2 May 1974. Westport, Connecticut, Technomic Publishing, pp 162-179.

Takase I, Ōmori T, & Midona Y (1986) Microbial degradation products from biphenyl-related compounds. Agric Biol Chem, **50**(3): 681-686.

Theiss JC, Stoner GD, Shimkin MB, & Weisburger EK (1977) Test for carcinogenicity of organic contaminants of United States drinking waters by pulmonary tumor response in strain A mice. Cancer Res, **37**: 2717-2720.

Thoma H & Hutzinger O (1987) Pyrolysis and GC/MS-analysis of brominated flame retardants in on-line operation. Chemopshere, **16**(6): 1353-1360.

Thoma H & Hutzinger O (1989) Pyrolysis and GC/MS-analysis of brominated flame retardants in on-line operation. Chemosphere, **18**(5): 1047-1050.

Thoma H, Hauschulz G, Knorr E, & Hutzinger O (1987a) Polybrominated dibenzofurans (PBDF) and dibenzodioxins (PBDD) from the pyrolysis of neat brominated diphenylethers, biphenyls and plastic mixtures of these compounds. Chemosphere, **16**(1): 277-285.

Thoma H, Hauschulz G, & Hutzinger O (1987b) PVC-induced chlorine-bromine

exchange in the pyrolysis of polybrominated diphenyl ethers, -biphenyls, dibenzodioxins and dibenzofurans. Chemosphere, **16**(1): 297-307.

Timmons LL & Brown RD (1988) Analysis of the brominated fire retardant decabromdiphenyloxide for low and trace levels impurities. Chemosphere, **17**: 217-234.

UK DOE (1992) Risk benefit analysis of hazardous chemicals. London, UK Department of Environment.

Ulsamer AG, Osterberg RE, & McLaughlin J Jr (1980) Flame retardant chemicals in textiles. Clin Toxicol, **17**(1): 101-131.

UMWELTBUNDESAMT (1989) Status report: Polybrominated dibenzodioxins and polybrominated dibenzofurans. Berlin.

US EPA (1978) Chemical screening. Initial evaluations of substantial risk notices: section 8(e), January 1, 1977 to June 39, 1979. Washington, DC, US Environmental Protection Agency, Office of Pesticides and Toxic Substances, Office of Testing and Evaluation, vol I, pp 39-40 (EPA 560/11-80-008).

US EPA (1984) Health and environmental effects profile for brominated diphenyl ethers. Cincinnati, Ohio, US Environmental Protection Agency, Environmental Criteria and Assessment Office (EPA/600/X-84/133).

US EPA (1986) Brominated diphenylethers. Chemical hazard information profile. Washington, DC, US Environmental Protection Agency.

US EPA (1988) Information review: Brominated diphenyl ethers. Washington, DC, US Environmental Protection Agency, TSCA, Interagency Testing Committee (Report No. IR-516).

US EPA (1989) Letter from Director Office of Toxic Substances, Washington, to Great Lakes Chemical Corporation, dated July 27, 1989.

US Testing Company (1985) Determination of vapour pressure and melting point. Chemical Services Division. Hoboken, New Jersey. Letter to Great Lakes Chemical Corporation. 7 October 1985 (Report submitted to WHO by BFRIP).

Vinci TM & Craig DK (1988) Characterization of fume components generated during the extrusion of flame-retarded polyester resins. Columbus, Ohio, Battelle (Unpublished report to GE Plastics, Mt. Vernon, Indiana, submitted to WHO by BFRIP).

Von Meyerinck L, Hufnagel B, Schmoldt A, & Benthe HF (1990) Induction of rat liver microsomal cytochrome P-450 by the pentabromodiphenyl ether Bromkal 70 and half lives of its components in the adipose tissue. Toxicology, **61**: 259-274.

Walsh GE, Yoder MJ, McClaughlin LL, & Lores EM (1987) Responses of marine unicellular algae to brominated organic compounds in six growth media. Ecotoxicol Environ Saf, **14**: 215-222.

Watanabe I (1987) Text from undated slide presentation.

Watanabe I & Tatsukawa R (1987) Formation of brominated dibenzofurans from the photolysis of flame retardant decabromodiphenyl ether in hexane solution by UV and sunlight. Bull Environ Contam Toxicol, **39**: 953-959.

Watanabe I & Tatsukawa R (1990) Anthropogenic brominated aromatics in the Japanese environment. In: Freij L ed. Proceedings of the Workshop on Brominated Aromatic Flame Retardants, Skokloster, Sweden, 24-26 October 1989. Solna, National Chemicals Inspectorate (KEMI), pp 63-71.

Watanabe I, Kashimoto T, & Tatsukawa R (1986) Confirmation of the presence of the flame retardant decabromodiphenyl ether in river sediment from Osaka, Japan. Bull Environ Contam Toxicol, **36**: 839-842.

Watanabe I, Kashimoto T, Kawano M, & Tatsukawa R (1987a) A study of organic bound halogens in human adipose tissue, marine organisms and sediment by neutro-activation and gas chromatographic analysis. Chemosphere, **16**(4): 849-857.

Watanabe I, Kashimoto T, & Tatsukawa R (1987b) Polybrominated biphenylethers in marine fish, shellfish and river and marine sediments in Japan. Chemopshere, **16**(10/12): 2389-2396.

Watanabe I, Kawano M, Wang Y, Chen Y, & Tatsukawa R (1992) Polybrominated dibenzo-p-dioxins (PBDDs) and -dibenzofurans (PBDFs) in atmospheric air in Taiwan and Japan. In: Dioxin'92. Twelfth International Symposium on Dioxins and Related Compounds, Tampere, Finland, 24-28 August 1992. Organohalogen Compounds - Volume 9: Sources of exposure.

Watanabe I, Kawano M, & Tatsukawa R (undated) Consumption trend and environmental research on brominated flame retardants in Japan and the formation of polyhalogenated dibenzofurans at the metal reclamation factory. Document distributed at the OECD Workshop on the Risk Reduction of Brominated Flame Retardants, Neuchatel, 1993.

WHO (1989) Environmental Health Criteria 88: Polychlorinated dibenzo-*p*-dioxins and bibenzofurans. Geneva, World Health Organization.

WHO (1994) Environmental Health Criteria 152: Polybrominated biphenyls. Geneva, World Health Organization.

Yagi O & Sudo R (1980) Degradation of polychlorinated biphenyls by microorganisms.

JWPCF 52(5), 1035-1043 and US EPA, 1986.

Yamamoto K, Mori Y, Uehira S, Tanaka T, Koyama T, Katuyama K, Taniguchi Y, & Sakamoto T (1991) Content of presence of the flame retardant decabromodiphenyl ether in Kino river Basin. Wakayama-ken Eisei Kogai Kenkyu Senta Nenpo, **37**: 116-122.

Zacharewski T, Harris M, Safe S, Thoma H, & Hutzinger O (1988) Applications of the *in vitro* aryl hydrocarbon hydroxylase induction assay for determining "2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents": pyrolyzed brominated flame retardants. Toxicology, **51**: 177-189.

Zier B, Lenoir D, Lahaniatis ES, & Kettrup A (1991) Surface catalyzed halogenation-dehalogenation reactions of aromatic bromine compounds adsorbed on fly ash. Chemosphere, **22**(12): 1121-1129.

Zober MA, Ott MG, Päpke O, Senft K, & Germann C (1992) Morbidity study of extruder personnel with potential exposure to brominated dioxins and furans. I. Results of blood monitoring and immunological tests. Br J Ind Med, **49**: 532-544.

Zogorski JS (1984) Experience in monitoring domestic water sources and process waters for trace organics. J Environ Sci Health, **A19**(2): 233-249.

Van Zorge JA, Bruijnes C, Van den Berg EV, & Sprong W (1992) Brominated flame retardants: Polybrominated biphenyls (PBBs) and polybrominated diphenyloxides (PBDOs). OECD Cooperative risk reduction activities for certain dangerous chemicals, Paris. Fifth draft, May 26th, 1992.

Zweidinger RA, Cooper SD, Erickson MD, Michael LC, & Pellizzari ED (1977) Sampling and analysis for semivolatile brominated organics in ambient air. In: Schuetzle D ed. Monitoring toxic substances. Washington, DC, American Chemical Society, pp 217-231 (ACS Symposium Series No. 94).

Zweidinger RA, Cooper SD, & Pellizzari ED (1978) Identification and quantitation of brominated fire retardants. In: Measurement of organic pollutants in water and waste water. Symposium of the American Society for Testing and Materials, Denver, Colorado, 19-20 June 1978. Philadelphia, Pennsylvania, American Society for Testing and Materials, pp 234-250 (ASTM Technical Publication No. 686).

RESUME ET EVALUATION, CONCLUSIONS ET RECOMMANDATIONS

DECABROMODIPHENYLETHER

1 Résumé et évaluation

1.1 Identité, propriétés physiques et chimiques

Le DeBDE du commerce se caractérise par une pureté de 97 à 98%, et une teneur en nona- et/ou octabromodiphényléthers de 0,3 à 3,0%. Le nonabromodiphényléther (NBDE) en est l'impureté principale. Contrairement aux autres polybromo-diphényléthers, le DeBDE n'a qu'un isomère.

Le point de fusion du DeBDE est d'environ 300 °C et il se décompose au dessus de 400 °C. Sa solubilité dans l'eau est de 20-30 μg/litre et le logarithme de son coefficient de partage *n*-octanol/eau est supérieur à 5. Sa tension de vapeur est $< 10^{-6}$ mmHg à 20°C.

1.2 Production et usages

De tous les bromodiphényléthers (mono- à déca-) le décabromodiphényléther est, de par sa production et son usage, le plus important du point de vue commercial.

On le produit depuis la fin des années 70 à un degré de plus en plus élevé de pureté. La production mondiale de DeBDE est d'environ 30 000 tonnes par an. On l'utilise comme retardateur de flamme dans de nombreuses matières plastiques, notamment dans le polystyrène choc, ainsi que pour le traitement des tissus d'ameublement, ou encore des textiles utilisés en sellerie automobile ou pour la confection de tentes.

1.3 Transport, distribution et transformation dans l'environnement

En solution dans des solvants organiques, le DeBDE subit une photodécomposition sous l'influence du rayonnement ultra-violet ou de la lumière solaire; cette réaction conduit à la formation de bromodiphényléthers moins substitués et de bromodibenzofuranes. Cette photodécomposition se produit également, quoique dans une moindre mesure, en solution aqueuse, sous l'action du rayonnement solaire; on ne retrouve plus alors d'homologues inférieurs du DeBDE ni de bromodibenzofuranes.

Les quantités de DeBDE que l'on peut extraire des polymères sont inférieures à la limite de détection ou très proches de cette limite, selon le type de polymère et le solvant d'extraction.

Du fait que sa solubilité dans l'eau et sa tension de vapeur sont très faibles, le DeBDE est vraisemblablement transporté essentiellement par adsorption sur des particules. Il est persistant et s'accumule probablement dans les sédiments et le sol.

On en dispose d'aucune donnée sur sa biodisponibilité à partir des sédiments et du sol. Une étude sur des truites arc-en-ciel n'a pas révélé de bioaccumulation dans la chair, la peau ou les viscères de ces poissons, sur une période de 48 heures. Il est improbable que le DeBDE subisse une bioaccumulation en raison de sa masse moléculaire relative élevée.

Les rebuts qui contiennent du DeBDE commercial finissent dans les décharges contrôlées ou les incinérateurs. Il se peut que du DeBDE s'échappe de ces décharges par lessivage. Le brûlage sur les décharges ou une incinération inefficace peuvent conduire à la formation de polybromodibenzofuranes (PBDF) et d'un mélange d'halogénodibenzofuranes et d'halogénodibenzodioxines. Les produits qui contiennent du DeBDE commercial peuvent contribuer à ces émissions.

La pyrolyse, en présence d'oxygène, de DeBDE commercial et de polymères contenant de ce produit (polystyrène choc, PBT, polypropylène industriel) produit des polybromodibenzofuranes et en moindre quantités, des polybromodibenzodioxines. C'est aux températures de 400 à 500°C que les PBDF sont produits en quantités maximales mais ils peuvent également se former à des températures allant jusqu'à 800°C et Sb_2O_3 en catalytise la formation.

La formation des PBDF et des PBDD ainsi que leurs proportions respectives, dépendent de la température, de la teneur en oxygène et de la durée de la pyrolyse. En l'absence d'oxygène, il se forme principalement des polybromobenzènes et des polybromonaphtalènes.

1.4 Concentrations dans l'environnement et exposition humaine

On a trouvé du DeBDE dans l'air à proximité d'unités de production, à des concentrations allant jusqu'à 25 $\mu g/m^3$. En revanche, on n'a pas décelé de DeBDE dans des échantillons d'eau prélevés au Japon entre 1977 et 1991. Cependant, on en a trouvé dans des sédiments de rivières, également prélevés au Japon au cours de la même période, à des déconcentrations allant jusqu'à environ 12 mg/kg de poids sec. On a également décelé la présence (jusqu'à 1 g/kg) de DeBDE dans des sédiments de cours d'eau aux Etats-Unis, à proximité d'une unité de production. On n'a pas décelé de DeBDE dans des échantillons de poissons recueillis au Japon, mais, dans un échantillon de moules on en a trouvé à des teneurs juste supérieures au seuil de détection. Le produit n'a pas été décelé dans des échantillons de tissus adipeux humains prélevés au Japon; en revanche, aux Etats-Unis, on en a trouvé dans trois échantillons sur cinq du même type de tissus.

Au cours de la production de DeBDE et de son adjonction aux polymères, il peut y avoir exposition humaine. En revanche, cette exposition est négligeable pour la population générale.

En cherchant à déterminer l'exposition professionnelle aux produits de décomposition du DeBDE lors de sa fabrication et de son incorporation par extrusion à des polymères, on a constaté la présence de fortes concentrations de PBDF dans des échantillons d'air prélevés au niveau de la filière de l'extrudeuse. Les concentrations étaient moindres dans l'air de l'atelier. Des PBDF ont été également retrouvés dans des échantillons obtenus lors de l'essuyage. Moyennant une bonne technique de travail, on peut réduire l'exposition professionnelle aux PBDF.

L'exposition de la population générale aux PBDF présents comme impuretés dans des polymères contenant des retardateurs de flamme, est vraisemblablement négligeable.

1.5 Cinétique et métabolisme chez les animaux de laboratoire et l'homme

Le DeBDE est faiblement résorbé dans les voies digestives et après injection, il est rapidement excrété.

D'après les résultats d'études de métabolisme chez le rat, au moyen de DeBDE marqué au ^{14}C, la demi-vie d'élimination de ce composé serait inférieure à 24 heures et la principale voie d'élimination après ingestion, serait la voie fécale. On n'a pas constaté la présence d'une activité appréciable de ^{14}C (moins de 1%) dans l'urine ou l'air expiré.

Des rats à qui l'on avait administré pendant des périodes allant jusqu'à deux ans, une dose quotidienne de 0,1 mg/kg de poids corporel de ce composé, n'ont présenté aucun accumulation de DeBDE dans leur sérum, leurs reins, leurs muscles ou leurs testicules, d'après le dosage du brome total. L'accumulation du brome dans le foie a atteint un palier au bout de 30 jours et l'élimination s'est effectuée dans les 10 jours suivants le traitement. Après 180 jours, la concentration de brome dans le foie n'était pas plus élevée chez les rats traités que chez les rats témoins. Dans les tissus adipeux, on a noté une faible accumulation de brome total, qui a subsisté après 90 jours de nourriture sans DeBDE; on ignore quelle est la nature du "brome" retenu. Etant donné que le DeBDE ne représentait que 77% du mélange commercial utilisé, ce "brome" pourrait provenir du NBDE ou de l'OBDE.

1.6 Effets sur les mammifères de laboratoire et les systèmes d'épreuve in vitro

Pour les animaux de laboratoire, la toxicité aiguë du DeBDE est faible. Le produit n'est pas irritant pour la peau ou les yeux des lapins. Il ne provoque pas de chloracné sur la peau des lapins et n'a pas d'effet sensibilisateur sur la peau humaine.

Les produits de combustion du polystyrène contenant un retardateur de flamme à base de DeBDE et de Sb_2O_3 ont été étudiés afin d'en déterminer la toxicité aiguë et la comédogénicité. Chez le rat, la DL_{50} par voie orale de la suie et du résidu de carbonisation était > 2000 mg/kg de poids corporel.

Lors d'études de toxicité à long terme effectuées sur des rats et des souris, du DeBDe (pureté > 97%) a été administré aux animaux mêlé à leur nourriture aux doses de 100 g/kg de nourriture (4 semaines) ou 50 g/kg (13 semaines, soit l'équivalent de 2500 mg/kg de poids corporel en ce qui concerne le rat) sans produire d'effets nocifs. Une étude de reproduction portant sur une génération de rats n'a pas révélé d'effets nocifs aux doses de 100 mg/kg de poids corporel. Le DeBDE n'a pas provoqué d'effets tératogènes chez des foetus de rats ayant reçu une dose de 100 mg/kg de poids corporel. A la dose de 1000 mg/kg de poids corporel, on a observé des malformations, par exemple un retard d'ossification. Soumis à un certain nombre d'épreuves, le DeBDE ne s'est pas révélé mutagène.

Lors d'une étude de cancérogénicité sur des rats et des souris, du DeBDE (pureté 94-99%) a été administré, mêlé à leur nourriture, à des doses allant jusqu'à 50 g/kg. On a observé une augmentation dans l'incidence des adénomes (mais pas des carcinomes) au niveau du foie chez les rats mâles qui en avaient reçu 25 g/kg et chez les femelles qui en avaient reçu 50 g/kg. Chez les souris mâles, on a observé une augmentation de l'incidence des adénomes et/ou des carcinomes hépatocellulaires (les deux ensemble) à la dose de 25 g/kg et une augmentation des adénomes et des cancers (les deux ensemble) médullaires de la thyroïde à ces deux doses. Chez les souris femelles, on n'a pas relevé d'augmentation dans l'incidence des tumeurs. C'est uniquement aux doses de 25 à 50 g de DeBDE/kg de nourriture que chez les rats mâles et femelles d'une part, et chez les souris mâles d'autre part, on a constaté l'existence de signes équivoques de cancérogénicité. Etant donné que les résultats de toutes les épreuves de mutagénicité sont restés négatifs, on peut en conclure que le DeBDE n'est pas un cancérogène génotoxique. Le CIRC (1990) est parvenu à la conclusion que les preuves d'une cancérogénicité du DeBDE chez les animaux de laboratoire sont limitées. Du fait des très fortes doses utilisées dans ces études, de l'absence de génotoxicité et des éléments de preuve très minimes en faveur d'une cancérogénicité de ce composé, on peut conclure que le DeBDE, aux taux d'exposition actuels, ne présente pas de risque cancérogène pour l'homme.

1.7 Effets sur l'homme

Chez des sujets humains exposés à du DeBDE lors d'une épreuve de sensibilisation, on n'a noté aucun signe de sensibilisation cutanée.

Une étude de morbidité sur des ouvriers qui procédaient à l'extrusion de polybutylène-téréphtalate contenant du DeBDE (avec par conséquent un risque potentiel d'exposition aux PBDD et aux PBDF pendant 13 ans) n'a pas révélé le moindre effet délétère, malgré la présence dans leur sang de 2,3,7,8-TeBDF et de 2,3,7,8-TeBDD. Les études immunologiques effectuées ont montré que le système immunitaire des personnes exposées n'avait pas souffert au cours de ces 13 années.

1.8 Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel

La CE_{50} relative à la croissance de trois algues marines unicellulaires s'est révélée supérieure à 1 mg de DeBDE par litre. On ne dispose d'aucune autre information concernant les effets du DeBDE sur les autres êtres vivants au laboratoire ou dans leur milieu naturel.

2 Conclusions

2.1 DeBDE

Le DeBDE est largement utilisé comme retardateur de flamme dans les polymères. S'il entre en contact avec la population générale, c'est par l'intermédiaire des produits fabriqués à partir de ces polymères. L'exposition est très faible étant donné que le DeBDE n'est pas facile à extraire de ces polymères. La toxicité aiguë du DeBDE est très faible et son absorption au niveau des voies digestives est minime. On peut donc considérer comme insignifiant le risque que le DeBDE représente pour la population générale.

C'est sous forme particulaire que le DeBDE peut donner lieu à une exposition professionnelle. En se prémunissant contre les poussières au cours de la fabrication et de l'utilisation de ce produit, on peut efficacement en réduire les risques pour les travailleurs.

Le DeBDE est persistant et il se fixe sur les particules de matière présentes dans l'environnement; il est vraisemblable qu'il s'accumule dans les sédiments. En revanche, sa bioaccumulation est improbable. D'après les données disponibles, la photodécomposition du DeBDE en milieu aqueux dans l'environnement ne conduit pas à la formation de diphényléthers bromés inférieurs ni de bromodibenzofuranes, mais on est mal renseigné sur la décomposition de ce composé dans d'autres milieux.

On est également très peu renseigné sur la toxicité du DeBDE pour les êtres vivants dans leur milieu naturel.

2.2 Produits de décomposition

Il peut se former des PBDF et, dans une certaine mesure, des PBDD lorsque du DeBDE ou des produits qui en contiennent sont chauffés à 300-800 °C. Il faut se préoccuper des dangers que ces produits pourraient représenter,.

Lorsqu'elle est correctement conduite, l'incinération n'entraîne pas l'émission de quantités importantes de bromodioxines ou de bromodibenzofuranes. Si la combustion s'effectue dans des conditions non contrôlées, des PBDF et des PBDD peuvent prendre naissance en quantités indéterminées. Les risques qui pourraient en résulter pour l'homme et l'environnement seront étudiés dans un prochain Critère d'hygiène de l'environnement sur les PBDF et les PBDD.

On a observé la présence de PBDF dans le sang de travailleurs employés à la production de matières plastiques contenant du DeBDE. Toutefois aucun effet délétère sur leur santé n'a pu être attribué à ce type d'exposition. Moyennant des techniques appropriées, il est possible d'éviter l'exposition des travailleurs aux PBDF.

3 Recommandations

3.1 Recommandations générales

- Il convient que les travailleurs qui sont employés à la fabrication de DeBDE et de produits qui en contiennent soient protégés contre toute exposition par l'application de

mesures appropriées d'hygiène industrielle, la surveillance de l'exposition professionnelle et des moyens techniques appropriés.

- Il convient de minimiser l'exposition environnementale par un traitement approprié des effluents et des émissions produits par les industries qui utilisent ce composé ou des produits qui en contiennent. Le rejet des déchets industriels et des produits de consommation doit être réglementé afin de réduire au minimum la contamination de l'environnement par ce composé persistant et ses produits de décomposition.
- Les fabricants doivent faire en sorte que le DeBDE commercial contienne le minimum d'impuretés, en utilisant pour cela les meilleures techniques existantes. Une pureté d'au moins 97% est recommandée.
- On ne doit procéder à l'incinération qu'au moyen d'incinérateurs convenables, qui fonctionnent toujours dans les conditions optimales. Le brûlage des déchets par tout autre moyen risque d'entraîner la formation de PBDF et/ou de PBDD.

3.2 Etudes à effectuer

- Il conviendrait d'effectuer, sur les organismes appropriés, des études sur la biodisponibilité et la toxicité du DeBDE lié aux sédiments.
- Il importe d'assurer une surveillance permanente des concentrations dans l'environnement.
- La production de PBDF en situation réelle d'incendie doit faire l'objet d'études plus approfondies.
- Il importe d'étudier plus à fond la biodécomposition dans l'environnement ainsi que la photodécomposition de ce composé dans des milieux autres que l'eau.
- Il conviendrait d'étudier des méthodes pour le recyclage des polymères contenant du DeBDE et leurs conséquences.
- Il faudrait valider les méthodes d'analyse du DeBDE dans diverses matrices.

NONABROMODIPHENYLETHER

Le nonabromodiphényléther n'est ni produit ni utilisé. On ne dispose d'aucune donnée sur les points suivants:

- Transport, distribution et transformation dans l'environnement
- Concentrations dans l'environnement et exposition humaine
- Cinétique et métabolisme chez les animaux de laboratoire et l'homme
- Effets sur les mammifères de laboratoire et les systèmes d'épreuve *in vitro*
- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel
- Evaluations antérieures par des organismes internationaux.

1 Résumé et évaluation

Il n'existe aucune base de données sur laquelle se fonder pour une évaluation.

2 Recommandations

Il importe de réduire au minimum le taux de contami-nation des retardateurs de flamme bromés du commerce par le nonabromodiphényléther afin d'éviter une pollution de l'environnement et l'exposition humaine.

OCTABROMODIPHENYLETHER

L'octabromodiphényléther n'est ni fabriqué ni utilisé à l'état pur. On ne dispose d'aucune donnée sur les points suivants:

- Cinétique et métabolisme chez les animaux de laboratoire et l'homme
- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel
- Evaluations antérieures par des organismes internationaux.

1 Résumé et évaluation

1.1 Identité et propriétés physiques et chimiques

L'OBDE du commerce se présente sous la forme d'un mélange d'environ 11% de PeBDE/HxBDE, 44% de HpBDE, 31-35% d'OBDE, 10% de NBDE et 0,5% de DeBDE. D'après la structure chimique, il y a théoriquement 12 isomères de l'OBDE et 24 isomères de l'HpBDE.

Le point de fusion varie d'environ 80 °C à > 200 °C. La tension de vapeur est $< 10^{-7}$ mmHg, la solubilité dans l'eau est faible et le logarithme du coefficient de partage *n*-octanol/eau est > 5,5. Ces variations dans les propriétés physiques s'expliquent par des différences de composition des mélanges étudiés.

1.2 Production et usages

La consommation mondiale annuelle d'OBDE commercial est de 6000 tonnes, dont 70% sont utilisés comme retardateurs de flamme dans les résines ABS qui servent à la fabrication d'ordinateurs et d'armoires de bureau. L'OBDE vient au second rang des retardateurs de flamme dans l'ordre d'utilisation.

1.3 Transport, distribution et transformation dans l'environnement

On a trouvé des constituants de l'OBDE du commerce dans des sédiments aquatiques et des tissus adipeux humains. Certains de ces constituants à plus faible teneur en brome (HxBDE et PeBDE) ont été observés dans des biotes. On n'a pas décelé d'OBDE, mais on n'a cherché généralement ni le HpBDE ni le NBDE. Les constituants de l'OBDE commercial sont vraisemblablement persistants mais, lorsque le degré de substitution par le brome dépasse 6, la bioaccumulation devient de plus en plus improbable. On a trouvé chez la carpe un facteur de bioaccumulation de moins de 2 pour un OBDE commercial.

La pyrolyse de l'OBDE commercial, soit tel quel, soit ajouté à des polymères comme retardateur de flamme (avec ou sans Sb_2O_3) à 600 °C, produit des PBDF et, à beaucoup plus faibles concentrations, des PBDD. Le traitement des résines ABS avec de l'OBDE et du Sb_2O_3 dans différentes conditions révèle, que dans les conditions normales, il ne se forme que de faibles concentrations de PBDF. Lorsque les conditions sont mauvaises, les concentrations sont beaucoup plus élevées. En revanche, les concentrations de PBDD sont faibles dans les deux cas.

1.4 Concentrations dans l'environnement et exposition humaine

Dans des échantillons d'eau recueillis au Japon en 1987 et 1988, on n'a pas pu déceler d'OBDE ni de constituants de l'OBDE du commerce à plus faible teneur en brome. On a également analysé des échantillons de sédiments et dans environ 2-6% d'entre eux, on a observé la présence d'OBDE à des concentrations de 8-22 μg/kg de poids sec. Dans le sédiment, on a également trouvé des constituants moins substitués en brome.

Chez des poissons capturés au Japon en 1987 et en 1988, on n'a pas décelé d'OBDE.

Aux Etats-Unis d'Amérique, on a analysé en 1987 des échantillons de tissus adipeux humains à la recherche de PBDF et de PBDD. Les échantillons provenaient de 865 prélèvements associés de manière à former 48 homologues composites. Ce schéma d'échantillonnage composite reposait sur 9 divisions censitaires et 3 groupes d'âge. Dans ces échantillons, on a également constaté la

présence de PBDE et les premiers résultats ont montré que de l'OBDE était également présent dans 60% des cas avec une concentration estimative allant jusqu'à 8000 ng/kg.

1.5 *Cinétique et métabolisme chez les animaux de laboratoire et l'homme*

Aucune donnée disponible.

1.6 *Effets sur les mammifères de laboratoire et les systèmes d'épreuve* in vitro

L'OBDE du commerce présente une faible toxicité aiguë pour les mammifères de laboratoire. Il n'est pas irritant pour la peau et ne provoque qu'une légère irritation oculaire chez le lapin. Lors d'études toxicologiques à court terme (respectivement 4 et 13 semaines), on a observé, chez des rats à qui l'on en avait administré dans leur nourriture à raison de 100 mg/kg, une augmentation du poids du foie et des altérations microscopiques caractérisées par la présence, dans la région centro- et médio-lobulaire, de cellules parenchymateuses hypertrophiées contenant des structures granulaires. La gravité de ces lésions hépatiques était plus marquée aux doses élevées, c'est-à-dire 1000 et 10 000 mg/kg de nourriture. En outre, on a observé une hyperplasie de la thyroïde. La teneur en brome total de ces tissus a augmenté au cours de l'étude pour diminuer ensuite lentement au cours de la période de récupération. Les anomalies hépatiques étaient réversibles. Lors d'une étude toxicologique par inhalation au cours de laquelle on a fait respirer de la poussière micronisée d'OBDE aux animaux (8 h/jour, 14 jours de suite) on n'a pas observé d'effets à la concentration de 1,2 mg/m^3 mais à celle de 12 mg/m^3, on a observé des lésions hépatiques analogues à celles qui avaient été décelées après ingestion du produit.

Chez le rat, des doses relativement faibles d'OBDE du commerce accroissent d'activité du cytochrome P-450 et induisent les enzymes des microsomes hépatiques, comme l'UDP-glucuronyl-transférase et la benz[*a*]pyrène-hydroxylase. On a également constaté que ce produit avait un effet porphyrinogène sur les cultures de cellules hépatiques d'embryon de poulet.

L'étude du pouvoir tératogène de l'OBDE chez le rat a montré qu'à fortes doses (25,0 et 50,0 mg/kg de poids corporel), ce produit provoquait des résorptions ou un retard d'ossification en différents points du squelette ainsi que des malformations foetales. Les malformations observées aux doses de 25 mg/kg de poids corporel et au-delà étaient très vraisemblablement liées à la toxicité du produit pour la mère. Ces malformations n'ont pas été observées aux doses inférieures ou égales à 15,0 mg/kg de poids corporel. Chez le lapin, aucun signe d'activité tératogène n'a été observé, en revanche on a constaté une certaine foetotoxicité à la dose de 15 mg/kg de poids corporel qui était également toxique pour la mère. D'après les études de tératogénicité, la dose sans effets nocifs observables est de 2,5 mg/kg de poids corporel.

Lors de deux études, l'une de 28 jours et l'autre de 90 jours, on a constaté qu'une dose de 100 mg d'OBDE/kg de nourriture (soit l'équivalent de 5 mg/kg de poids corporel) ne produisait que des effets minimes sur le foie. On n'a pas cherché à établir la dose sans effets observables.

Toutes les épreuves de mutagénicité: synthèse non programmée de l'ADN, tests sur microorganismes *in vitro* et recherche d'échanges entre chromatides-soeurs sur cellules ovariennes de hamster chinois se sont révélées négatives.

On ne possède aucune donnée résultant d'études de cancérogénicité ou d'études à long terme.

1.7 Effets sur l'homme

Aucune donnée disponible.

1.8 Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel

Données minimales.

2 Conclusions

2.1 OBDE

L'OBDE du commerce est un mélange d'hexa-, d'hepta-, d'octa- et de nonabromodiphényléthers, qui sont tous des composés rémanents, en grande partie fixée aux sédiments.

L'OBDE est très largement utilisé comme retardateur de flamme dans les polymères. Il peut y avoir contact avec la population générale par l'intermédiaire de produits fabriqués à partir de ces polymères. Il est peu probable qu'on puisse être exposé à de l'OBDE qui aurait été extrait de ces polymères.

L'OBDE présente une faible toxicité aiguë. On ne dispose d'aucune donnée sur sa fixation ou son élimination par l'organisme des mammifères. Il n'est ni tératogène ni mutagène. On ne dispose d'aucune donnée sur sa toxicité à long terme ni sur sa cancérogénicité.

On a relevé la présence, dans des tissus adipeux humains, de plusieurs constituants de l'OBDE commercial. Pour la population dans son ensemble, le risque d'intoxication aiguë est vraisemblablement faible. Il n'est pas possible d'évaluer les risques d'une exposition à long terme en raison de l'absence d'études toxicologiques pertinentes.

On ne dispose non plus d'aucune information qui permette de tirer des conclusions quant à l'exposition professionnelle à l'OBDE et à ses effets.

Les données relatives à la toxicité de l'OBDE pour les êtres vivants dans leur milieu naturel demeurent limitées. Il est possible que les constituants peu substitués en brome du mélange commercial subissent une bioaccumulation.

2.2 Produits de décomposition

Lors du chauffage de l'OBDE ou de produits qui en contiennent à des températures de 400-800 °C, il peut se former des PBDF et, dans une certaine mesure, des PBDD. Il importe de se préoccuper des dangers qui pourraient en résulter.

Il est improbable que la population générale soit exposée de façon notable aux impuretés de type PBDF, présentes dans les polymères contenant des retardateurs de flamme. Moyennant une incinération dans les règles, il ne devrait pas y avoir d'émission importante de bromodioxines ni de bromofuranes. Le brûlage sans précautions de produits qui contiennent de l'OBDE du commerce, peut donner naissance à des PBDF et des PBDD en quantités indéterminées. Ce problème et ses conséquences pour la santé humaine et l'environnement, seront abordés dans un prochain Critère d'hygiène de l'environnement consacré aux PBDF et aux PBDD.

3 Recommandations

3.1 Recommandations générales

- Il convient d'utiliser les meilleurs techniques possibles pour la fabrication de l'OBDE du commerce, afin de réduire au minimum la teneur en homologues hexabromés ou moins substitués, du fait de leur possibilité de bioaccumulation dans l'environnement.
- Les travailleurs qui sont employés à la fabrication de l'OBDE ou de produits qui en contiennent, doivent être protégés contre l'exposition à ces dérivés par des mesures d'hygiène industrielle, une surveillance de l'exposition professionnelle et des moyens techniques.
- Il convient de limiter au maximum la pollution de l'environnement grâce à un traitement approprié des effluents et des émissions provenant d 'industries qui utilisent le composé ou des produits qui en contiennent. Le rejet de produits industriels et de produits de consommation devra être réglementé de façon à réduire au minimum la pollution de l'environnement par ces composés rémanents et leurs produits de décomposition.
- L'incinération de produits qui contiennent des retardateurs de flamme à base d'OBDE, ne doit s'effectuer que dans des incinérateurs appropriés fonctionnant toujours dans des conditions optimales. Le brûlage par tout autre moyen risque de donner naissance à des PBDF ou des PBDD.

3.2 Etudes à effectuer

Comme la base de données toxicologiques actuelle est insuffisante pour permettre d'évaluer les dangers que représente l'OBDE du commerce pour l'homme et l'environnement, et pour en faciliter l'utilisation, il est recommandé d'entreprendre les études suivantes:

- Etudes, sur des organismes appropriés, relatives à la biodisponibilité et à l'écotoxicité des constituants de l'OBDE du commerce liés aux sédiments
- Surveillance généralisée de la concentration des constituants de l'OBDE du commerce dans l'environnement
- Etudes toxicologiques à long terme et études de cancérogénicité portant sur l'OBDE du commerce
- Surveillance de l'exposition professionnelle à l'OBDE du commerce
- Poursuite des études sur la formation de PBDF dans des conditions réelles d'incendie
- Poursuite des études sur la biodécomposition et la photodécomposition environnementales dans des milieux non aqueux
- Etudes de méthodes de recyclage des polymères contenant de l'OBDE et de ses conséquences
- Validation des méthodes d'analyse de l'OBDE dans diverses matrices
- Etudes sur la possibilité de migration à partir de divers types de polymères.

HEPTABROMODIPHENYLETHER

L'heptabromodiphényléther n'est ni produit ni utilisé.

Il n'existe pas de base de données relatives à l'HpBDE pur sur laquelle fonder une évaluation.

On ne dispose d'aucune donnée sur les points suivants:

- Cinétique et métabolisme chez les animaux de laboratoire et l'homme
- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel
- Evaluations antérieures par des organismes internationaux.

Du fait que l'HpBDE est le principal constituant de l'octabromodiphényléther du commerce, le résumé, l'évaluation , les conclusions et les recommandations relatives à l'OBDE du commerce, valent pour l'HpBDE "du commerce".

HEXABROMODIPHENYLETHER

L'hexabromodiphényléther n'est ni produit ni utilisé mais il constitue une impureté des bromodiphényléthers du commerce. Il convient d'en réduire la concentration au minimum afin d'éviter la contamination de l'environnement et l'exposition de l'homme.

Il n'existe pas de base de données sur laquelle fonder une évaluation.

On ne dispose d'aucune donnée sur les points suivants:

- Effets sur les mammifères de laboratoire et les systèmes d'épreuve *in vitro*
- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel

- Evaluations antérieures par des organismes internationaux.

PENTABROMODIPHENYLETHER

Le pentabromodiphényléther n'est ni produit ni utilisé.

On ne dispose d'aucune donnée sur les points suivants:

- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel
- Evaluations antérieures par des organismes internationaux.

1 Résumé et évaluation

1.1.1 Identité, propriétés physiques et chimiques

Le pentabromodiphényléther du commerce (PeBDE) est un mélange de tétra-, penta- et hexabromodiphényléther. Il contient approximativement 50-60% de PeBDE et 24-38% de TeBDE. D'après la structure chimique, il existe théoriquement 46 isomères du PeBDE et 42 isomères du TeBDE. Les principaux constituants des produits du commerce semblent être au nombre de 3, à savoir le 2,2',4,4',5'-PeBDE, le 2,2',4,4'-TeBDE et un analogue non identifié à 5 atomes de brome.

Le point de fusion se situe entre -7 et -3 °C et le point d'ébullition au-delà de 200 °C. La tension de vapeur est faible: $< 10^{-7}$ mmHg et la solubilité dans l'eau, négligeable. Le logarithme du coefficient de partage *n*-octanol/eau est > 6.

1.2 Production et usage

Le PeBDE est utilisé comme additif dans les résines époxy, les résines phénoliques, les polyesters et le polyuréthanne ainsi que les

textiles. la consommation mondiale est d'environ 4000 tonnes par an. C'est l'un des principaux bromodiphényléthers du commerce utilisés comme retardateurs de flamme.

1.3 Transport, distribution et transformation dans l'environnement

On trouve des constituants du PeBDE du commerce dans les biotes, les sédiments et les boues d'égouts. Il est vraisemblable que ces constituants soient rémanents et qu'ils aient tendance à la bioaccumulation. C'est ainsi que l'on a trouvé chez la carpe un facteur de bioconcentration de plus de 10 000.

L'étude de la pyrolyse du PeBDE du commerce a montré qu'il se forme au cours de ce processus des PBDF et des PBDD. La température optimale de formation de ces composés se situe entre 700 et 800°C. Lorsque la pyrolyse du PeBDE s'effectue en l'absence d'oxygène, il y a formation de polybromobenzènes, de polybromophénols et de PBDF.

1.4 Concentrations dans l'environnement et exposition humaine

Dans des échantillons de sédiments prélevés au Japon dans des cours d'eau et des estuaires, on a relevé des concentrations allant de 0 (< 2 µg/kg) jusqu'à 28 µg/kg de poids sec de PeBDE. En Suède, les sédiments de certains cours d'eau accusaient des concentrations allant jusqu'à 1200 µg de 2,2',4,4',5'-PeBDE/kg. Des boues d'égouts, analysées en Suède, contenaient également de ce PeBDE.

Des moules et poissons ont été prélevés aux fins d'analyse dans diverses zones littorales du Japon entre 1981 et 1985; dans deux échantillons de moules sur cinq, on a trouvé des concentrations de PeBDE qui étaient respectivement égales à 0,4 et 2,8 µg/kg de poids humide. En revanche, dans le poisson, on n'a pas décelé de PeBDE (limite de dosage < 0,2 µg/kg). On a fait état de concentrations de 1,9-22 µg/kg de poids frais dans des échantillons de foie de morue provenant de la mer du Nord. En Suède, on a trouvé des concentrations qui se situaient entre 7,2 et 64 µg de 2,2',4,4',5'-PeBDE/kg de graisse dans des poissons d'eau douce du genre corégone et dans des harengs de différentes provenances.

Du gras de phoque (*Phoca hispida* et phoque gris) prélevé en Suède en 1979-85, s'est révélé contenir des concentrations moyennes de 2,2',4,4',5'-PeBDE respectivement égales à 1,7 μg et 40 μg/kg de poids corporel.

En Suède, dans un mélange d'échantillons de muscles de lapins et d'élans ainsi que dans de la graisse de rognon de renne, on a constaté, en 1985-86, la présence de concentrations respectivement égales à < 0,3 μg, 0,64 μg et 0,26 μg de 2,2',4,4',5'-PeBDE/kg de graisse.

Dans des échantillons de muscles de balbuzard, obtenus en Suède en 1982-86, on a noté une concentration moyenne de 140 μg de 2,2,',4,4',5'-PeBDE/kg de graisse.

On a constaté qu'au cours des dernières décennies, la concentration de deux isomères du PeBDE avait augmenté d'un facteur 10 dans les oeufs de guillemots de la Baltique. On a également constaté que la concentration de ces isomères avait augmenté d'un facteur 4 dans des brochets provenant d'un lac du sud de la Suède. L'analyse de sédiments de la Baltique représentatifs de plusieurs années d'échantillonnage indique également qu'il y a eu une augmentation considérable de la pollution au cours de la dernière décennie.

On est très peu renseigné sur l'exposition humaine mais on peut estimer en gros, d'après la consommation de poisson des suédois, que la population de ce pays absorbe individuellement environ 0,1 μg de PeBDE par jour.

1.5 *Cinétique et métabolisme chez les animaux de laboratoire et l'homme*

La demi-vie du PeBDE n'a été étudiée qu'au niveau de la graisse périrénale chez le rat. On a ainsi obtenu une valeur comprise entre 25 et 47 jours, en fonction du sexe de l'animal et du type d'isomère en cause.

1.6 *Effets sur les mammifères de laboratoire et les systèmes d'épreuve* in vitro

Le PeBDE du commerce présente une faible toxicité aiguë par voie orale chez le rat; la toxicité par voie percutanée est également

faible chez le lapin. En exposant pendant une brève durée des rats par la voie respiratoire et en instillant du PeBDE à des lapins dans le sac conjonctival, on n'a obtenu que des effets modérés et passagers.

Des études toxicologiques à court terme sur des rats (4 semaines et 13 semaines respectivement) au cours desquelles du PeBDE a été administré aux animaux à des concentrations de 100 mg/kg de nourriture, ont révélé une augmentation du poids du foie et donné lieu à de légères anomalies histologiques. Ces anomalies consistaient en une hypertrophie des cellules du parenchyme hépatique, qui avaient un aspect granulaire et contenaient des "inclusions rondes" éosinophiles. On a constaté que la teneur en brome total du foie augmentait en fonction de la dose administrée et restait élevée pendant des périodes pouvant aller jusqu'à 24 semaines. On a également observé une légère hyperplasie thyroïdienne réversible.

Après administration par voie orale de doses quotidiennes de PeBDE ne dépassant pas 0,78 μmol/kg de poids corporel, on a observé l'induction des enzymes hépatiques et un accroissement de l'activité du cytochrome P-450 c. Les résultats des épreuves de tératogénicité et de mutagénicité se sont révélés négatifs.

Aucune étude toxicologique à long terme ou étude de cancérogénicité n'a été publiée.

1.7 Effets sur l'homme

Pas de données disponibles.

1.8 Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel

On ne dispose que d'un minimum de données.

2 Conclusions

2.1 PeBDE

Le PeBDE du commerce (mélange de 24-38% de tétra-, 50-60% de penta- et 4-8% d'hexabromodiphényléther) est rémanent et il s'accumule chez les êtres vivants dans leur milieu naturel.

Le PeBDE du commerce est largement utilisé, incorporé à des polymères, comme retardateur de flamme. Lorsqu'il entre en contact avec la population, c'est par l'intermédiaire de produits fabriqués à partir de ces polymères. Il est improbable qu'il puisse y avoir exposition après extraction du produit de ces polymères. Il peut y avoir exposition de l'homme au PeBDE par l'intermédiaire de la chaîne alimentaire, étant donné que la substance a été décelée chez divers animaux vivant dans leur milieu naturel, animaux qui servent de nourriture à l'homme, comme les poissons, les fruits de mer, etc. On constate depuis au moins deux décennies que les concentrations augmentent chez les poissons et les oiseaux de Suède.

Le PeBDE du commerce présente une faible toxicité aiguë. On ne possède aucune donnée sur la fixation et l'élimination de ce produit chez les mammifères. On ne dispose pas non plus d'études sur la reproduction d'animaux exposés à cette substance, ni sur sa toxicité à long terme ou sa cancérogénicité.

Il n'est pas possible, à partir des données disponibles, d'évaluer le risque qu'il représente pour la population générale.

On ne possède pas non plus de données qui permettent d'établir le niveau d'exposition professionnelle ou de se prononcer sur les effets du PeBDE ?? du commerce.

On ne dispose que de données limitées sur la toxicité du PeBDE du commerce pour les êtres vivants dans leur milieu naturel.

2.2 Produits de décomposition

Lorsqu'on chauffe du PeBDE ou des produits qui en contiennent à une température de 400-800 °C, il se forme des PBDF et, dans une certaine mesure, des PBDD. Il faudra examiner les risques qui pourraient en découler.

Il est peu probable que la population générale soit exposée de façon notable aux PBDF produits par des polymères contenant du PeBDE comme retardateur de flamme. Si elle est convenablement effectuée, l'incinération n'entraîne pas l'émission de quantités importantes de bromodioxines ou de bromofuranes. En revanche, le brûlage inconsidéré de produits qui en contiennent peut donner naissance à des quantités indéterminées de PBDF ou de PBDD. Dans un futur Critère d'hygiène de l'environnement consacré à ces deux

substances, l'importance de ce problème pour l'homme et l'environnement sera examinée.

3 Recommandations

3.1 Recommandations générales

La rémanence du PeBDE du commerce dans l'environnement et son accumulation dans les êtres vivants militent contre l'utilisation de ce produit. Toutefois, s'il l'on continue à l'utiliser, il faudra prendre les précautions suivantes:

- Les travailleurs qui sont employés à la production de PeBDE ou de polymères qui en contiennent, doivent être protégés contre toute exposition, par des mesures appropriées d'hygiène industrielle, la surveillance de l'exposition professionnelle et des moyens techniques convenables.
- Il convient de minimiser l'exposition environnementale par un traitement approprié des effluents et des émissions produits par les industries qui utilisent ce composé ou des produits qui en contiennent. Le rejet des déchets industriels et des produits de consommation doit être réglementé afin de réduire au minimum la contamination de l'environnement par ce composé qui persiste et s'accumule et par ses produits de décomposition.
- On ne doit procéder à l'incinération qu'au moyen d'incinérateurs convenables fonctionnant toujours dans des conditions optimales. Le brûlage des déchets par tout autre moyen risque d'entraîner la formation de produits de décomposition toxiques.

3.2 Etudes à effectuer

- Il faut poursuivre la surveillance des concentrations dans l'environnement.
- Il conviendrait de valider les méthodes de dosage du PeBDE dans diverses matrices.

- Du fait que la base de données toxicologiques actuelle est insuffisante pour permettre d'évaluer des risques pour l'homme et l'environnement du PeBDE du commerce et en justifier l'utilisation, il conviendrait d'entreprendre les études suivantes:
  - études complémentaires de cancérogénicité et études toxicologiques et écotoxicologiques:
  - poursuite des travaux sur la formation de PBDF dans les conditions réelles d'incendie;
  - étude de méthodes pour le recyclage des polymères contenant du PeBDE et de leurs conséquences;
  - études sur les possibilités de migration à partir de produits contenant des retardateurs de flamme.

TETRABROMODIPHENYLETHER

Le tétrabromodiphényléther n'est ni produit ni utilisé.

Il n'existe aucune donnée sur les points suivants:

- Effets sur les mammifères de laboratoire et les systèmes d'épreuve *in vitro*
- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel
- Evaluations antérieures par des organismes internationaux.

1 Résumé et évaluation

1.1 Identité, propriétés physiques et chimiques

Le tétrabromodiphényléther du commerce est constitué d'un mélange de 41% de tétra-, 45% de penta-, et 7% d'hexabromodiphényléthers plus environ 7% d'un PBDE de structure inconnue.

D'après la structure chimique, le tétrabromodiphényléther a théoriquement 42 isomères. On ne dispose pratiquement d'aucune donnée sur les propriétés physiques et chimiques de ce composé, à part le logarithme du coefficient de partage *n*-octanol/eau, qui est 5,87-6,16.

1.2 Production et usages

D'après un rapport, la production (et l'usage) du TeBDE aurait été d'environ 1000 tonnes en 1987 au Japon. Autant qu'on sache, il n'existe actuellement aucune production sous le nom de tétrabromodiphényléther, mais le composé est présent dans la proportion de 24 à 38% dans le pentabromodiphényléther du commerce.

1.3 Transport, distribution et transformation dans l'environnement

On a trouvé des constituants du TeBDE du commerce dans des biotes, des sédiments et des boues d'égouts. Il est probable que les constituants du TeBDE du commerce (qui contiennent des quantités à peu près équivalentes de PeBDE) aient un caractère rémanent et subissent une bioaccumulation.

L'étude de la pyrolyse du TeBDE du commerce montre qu'à 800 °C, il se forme des PBDF et des PBDD, mais uniquement les homologues inférieurs.

1.4 Concentrations dans l'environnement et exposition humaine

Au Japon, on a trouvé du TeBDE dans les sédiments de cours d'eau à des concentrations de 12-31 µg/kg de poids sec et en Suède, à des concentrations allant jusqu'à 840 µg/kg (perte au feu). La présence de TeBDE a été également constatée en Suède dans des boues d'égouts à la concentration de 15 µg/kg.

Au Japon, on a constaté, dans des moules et des poissons de différentes provenances, la présence de TeBDE à des concentrations allant de < 0,1 à 14,6 µg de 2,2',4,4'-TeBDE/kg de poids humide. En Suède, on a capturé dans des cours d'eau diverses espèces de poissons que l'on a analysés à la recherche de 2,2',4,4'-TeBDE. Les concentrations moyennes allaient de 0 (< 0,1 mg/kg) à 100 mg/kg de graisse. L'analyse a montré qu'il existait au moins une source de pollution locale dans un certain cours d'eau. Des corégones, des

ombles arctiques et des harengs pêchés en différents lieux de Suède entre 1986 et 1987 se sont révélés contenir des concentrations de TeBDE respectivement égales à 15, 400 et 59-450 μg de 2,2',4,4'-TeBDE/kg de graisse. En Allemagne, des poissons provenant de différents cours d'eau en contenaient jusqu'à 1 mg/kg de graisse.

Dans les harengs et les foies de morues pêchés dans la partie méridionale, centrale et septentrionale de la mer du Nord, au cours de la période 1983-89, on a noté une tendance à la diminution des concentrations de TeBDE de la région méridionale à la région septentrionale. Dans les harengs, la concentration allait de 8,4 à 100 μg de 2,2',4,4'-TeBDE/kg de graisse.

Dans le tissu musculaire d'oiseaux nichant et hivernant en mer Baltique, en mer du Nord et au Spitzberg, on a relevé des concentrations de 2,2',4,4'-TeBDE de 80-370 μg/kg de graisse. Chez des balbuzards capturés en Suède au cours de la période 1982-86, on a mesuré des concentrations moyennes de 1800 μg/kg de graisse.

En Suède, on constate une tendance à l'augmentation des concentrations de 2,2',4,4'-TeBDE dans les sédiments de la Baltique, les poissons d'eau douce et les oeufs d'oiseaux de mer.

Dans la graisse de phoques de la mer Baltique et du Spitzberg on a observé des concentrations de 10-730 μg/kg de graisse. Chromatographiquement, le PBDE est analogue au Bromkal 70-5. Sur des échantillons groupés de graisse de phoques de l'espèce *Phoca hispida* et de phoques gris, prélevés en Suède au cours de la période 1979-85, on a mesuré des concentrations respectivement égales à 47 μg et 650 μg de 2,2',4,4'-TeBDE/kg.

Dans des échantillons groupés de muscles de mammifères terrestres, par exemple des lapins, des élans et des rennes, obtenus en 1985-86 en Suède, on a observé des concentrations moyennes respectivement égales à < 2, 0,82, et 0,18 μg de 2,2',4,4'-TeBDE/kg de graisse.

En Allemagne, on a trouvé dans quatre échantillons de lait de vache, des concentrations de 2,5-4,5 μg de PBDE/kg de matière grasse, sous la forme de Bromkal 70DE. Dans le même pays et sous cette même forme, on a retrouvé du PBDE dans le lait de 25 femmes à des concentrations de 6,2-11,1 μg/kg de matière grasse.

Une estimation approximative de l'exposition de la population suédoise, calculée en fonction de la consommation de poisson en Suède, donne une absorption individuelle de 0,3 μg de TeBDE/jour.

1.5 Effets sur les mammifères de laboratoire et les systèmes d'épreuve in vitro

Il n'existe pas de données sur le TeBDE lui-même, cependant on dispose de données de toxicité aiguë et de toxicité à court terme pour le PeBDE du commerce qui contient 41% de TeBDE.

1.6 Cinétique et métabolisme chez les animaux de laboratoire et l'homme

On ne possède qu'un minimum de données.

1.7 Effets sur l'homme

Il n'existe aucune donnée.

1.8 Effets sur les autres vivants au laboratoire et dans leur milieu naturel

Il n'existe aucune donnée.

2 Conclusions

2.1 TeBDE

Les constituants du TeBDE du commerce (mélange à 41% de 2,2',4,4'-tétra-; 45% de 2,2',4,4',5'-penta; 7% d'hexa-, et 7-8% de polybromodiphényléther de structure inconnue) persistent dans l'environnement et s'accumulent chez les êtres vivants dans leur milieu naturel.

Constituant du pentabromodiphényléther, le TeBDE est très souvent incorporé à des polymères comme retardateur de flamme. La population générale peut entrer en contact avec cette substance par l'intermédiaire de produits fabriqués à partir de ces polymères. Il est improbable qu'il puisse y avoir exposition par suite de l'extraction du composé de ces polymères. Il peut y avoir exposition humaine au

TeBDE par l'intermédiaire de la chaîne alimentaire car on a décelé la présence de ce composé chez des animaux dans leur milieu naturel, animaux qui servent de nourriture à l'homme comme les poissons, les fruits de mer, etc. En Suède, on observe depuis les deux dernières décennies une augmentation des concentrations de ce composé chez les poissons et les oiseaux.

On manque d'information au sujet des études toxicologiques à court et à long terme, des études de cancérogénicité ou sur la reproduction qui auraient pu être faites. En outre, on ne dispose pas de données sur la cinétique et le métabolisme du produit chez les animaux de laboratoire et l'homme.

Il n'est pas possible d'évaluer le risque pour la population générale sur la base des données disponibles.

On ne dispose pas non plus de données suffisantes pour déterminer les niveaux d'exposition professionnelle ni pour se prononcer sur les effets du TeBDE.

Il n'existe aucune donnée sur la toxicité de TeBDE du commerce pour les êtres vivants dans leur milieu naturel.

2.2 Produits de décomposition

Lorsqu'on chauffe du TeBDE à 800°C, il se forme des PBDF et des PBDD. Il faudra étudier les dangers que cela peut comporter.

Il n'est guère probable que la population générale soit exposée de façon importante aux PBDF qui se forment lorsque l'on chauffe des polymères contenant du TeBDE comme retardateur de flamme. Si l'incinération est effectuée correctement, elle n'entraîne pas l'émission de bromodioxines ni de bromofuranes en quantités importantes. Le brûlage inconsidéré de produits contenant du TeBDE peut conduire à la formation de PBDF ou de PBDD en quantités indéterminées. Dans un futur Critère d'hygiène de l'environnement consacré aux PBDF et aux PBDD, l'importance de ce problème pour l'homme et l'environnement sera examinée.

3 Recommandations

3.1 Recommandations générales

Du fait de sa rémanence dans l'environnement et de son accumulation chez les êtres vivants, il est recommandé de ne pas utiliser le TeBDE. Cependant si son usage se poursuit, il faudra prendre les précautions suivantes:

- Les travailleurs qui sont employés à la production de TeBDE et de produits qui en contiennent, doivent être protégés contre toute exposition grâce à des mesures appropriées d'hygiène industrielle, par la surveillance de l'exposition professionnelle et par des mesures techniques adéquates.
- Il convient de minimiser l'exposition environnementale par un traitement approprié des effluents et des émissions provenant des industries qui utilisent ce composé ou des produits qui en contiennent. Le rejet des déchets industriels et des produits de consommation doit être réglementé afin de réduire au minimum la contamination de l'environnement par ce composé persistant et cumulatif et ses produits de décomposition.
- On ne doit procéder à l'incinération de produits contenant un retardateur de flamme à base TeBDE qu'au moyen d'incinérateurs convenables fonctionnant toujours dans des conditions optimales. Le brûlage des déchets par tout autre moyen risque d'entraîner la formation de produits de décomposition principalement formés de furanes.

3.2 Etudes à effectuer

- Il importe d'assurer une surveillance permanente des concentrations dans l'environnement.
- Il faudrait valider les méthodes d'analyse du TeBDE dans diverses matrices.
- Comme la base de données toxicologiques actuelle est insuffisante pour permettre d'évaluer le danger que le TeBDE représente pour l'homme et l'environnement, il

faudra, si on continue à utiliser ce produit, effectuer les travaux suivants:

- études toxicologiques et écotoxicologiques supplémentaires et études de cancérogénicité;
- poursuite des études sur la formation de PBDF dans les conditions réelles d'incendie;
- étude des méthodes de recyclage des polymères contenant du TeBDE et de ses conséquences;
- recherches sur la possibilité de migration à partir de produits contenant des retardateurs de flamme.

TRIBROMODIPHENYLETHER

Le tribromodiphényléther n'est ni produit ni utilisé.

On ne dispose d'aucune donnée sur les points suivants:

- Transport, distribution et transformation dans l'environnement
- Cinétique et métabolisme chez les animaux de laboratoire et l'homme
- Effets sur les mammifères de laboratoire et les systèmes d'épreuve *in vitro*
- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel
- Evaluations antérieures par des organismes internationaux.

1 Résumé et évaluation

Il n'existe pas de base de données sur laquelle fonder une évaluation.

2 Recommandations

Il convient de réduire au minimum la contamination des produits du commerce par du tribromodiphényléther afin d'éviter la pollution de l'environnement et l'exposition humaine.

Il faut éviter d'utiliser des produits commerciaux susceptibles d'entraîner la pollution du milieu.

DIBROMODIPHENYLETHER

Le dibromodiphényléther n'est ni produit ni utilisé.

On ne dispose d'aucune donnée sur les points suivants:

- Cinétique et métabolisme chez les animaux de laboratoire et l'homme
- Effets sur l'homme
- Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel
- Evaluations antérieures par des organismes internationaux.

1 Résumé et évaluation

Il n'existe pas de base de données sur laquelle fonder une évaluation.

2 Recommandations

Il convient de réduire au minimum la contamination des produits du commerce par du dibromodiphényléther afin d'éviter la pollution de l'environnement et l'exposition humaine.

Il faut éviter d'utiliser des produits commerciaux susceptibles d'entraîner la pollution du milieu.

MONOBROMODIPHENYLETHER

Il n'existe aucune donnée sur les points suivants:

- Cinétique et métabolisme chez les animaux de laboratoire et l'homme
- Effets sur l'homme
- Evaluations antérieures par des organismes internationaux.

1 Résumé et évaluation

1.1 Propriétés physiques et chimiques

Il y a trois isomères possible du monobromodiphényléther.

Le *p*-bromodiphényléther se présente à la température ambiante sous la forme d'un liquide dont le point d'ébullition est de 305-310 °C. Le calcul montre que sa solubilité dans l'eau est de 48 mg/litre. Le logarithme de son coefficient de partage *n*-octanol/eau se situe entre 4 et 5. Sa tension de vapeur est de 0,0015 mmHg à 20 °C.

1.2 Production et usages

Le MBDE n'est pas utilisé comme retardateur de flamme. Un rapport sur sa production est paru en 1977, mais on ne lui connaît pas d'usage.

1.3 Transport, distribution et transformation dans l'environnement

Sa demi-vie d'évaporation à partir de l'eau est de l'ordre de plusieurs centaines de jours.

Placé dans une culture de 7 jours ensemencé avec des microorganismes présents dans des eaux usées domestiques, il ne subit pas de biodécomposition importante, mais il est dégradé à 90% dans des boues d'égouts activées. D'après la seule étude consacrée à sa dégradation par les bactéries terricoles, il semblerait que celles-ci, tout au moins une souche particulière, soient incapables d'utiliser le MBDE comme seule source de carbone.

1.4 Concentrations dans l'environnement et exposition humaine

On a décelé la présence de MBDE dans des échantillons d'eau superficielle prélevés à proximité de sites industriels aux Etats-Unis d'Amérique; toutefois, une enquête analogue menée au Japon n'a pas donné de résultats. On en a également décelé aux Etats-Unis d'Amérique dans des eaux souterraines à proximité d'une usine. Aux Etats-Unis d'Amérique, on a décelé la présence de MBDE dans des sédiments et des biotes aquatiques.

1.5 Cinétique et métabolisme chez les animaux de laboratoire et l'homme

Il n'existe pas de donnée.

1.6 Effets sur les mammifères de laboratoire et les systèmes d'épreuve in vitro

Le MBDE n'est pas tératogène, mais on ne possède aucune donnée sur la toxicité aiguë ni la toxicité à court et à long terme de ce composé; aussi est-il impossible de procéder à une évaluation.

1.7 Effets sur l'homme

Il n'existe aucune donnée.

1.8 Effets sur les autres êtres vivants au laboratoire et dans leur milieu naturel

Chez un poisson, *Lepomis macrochirus*, la CL_{50} à 96 heures serait de 4,9 mg/litre, avec une concentration sans effets observables de moins de 2,8 mg/litre. La CL_{50} à 48 heures pour la puce d'eau est de 0,36 mg/litre avec une concentration sans effets observables de moins de 0,046 mg/litre.

2 Conclusions et recommandations

Le monobromodiphényléther n'agit pas comme retar-dateur de flamme. Il peut s'accumuler chez les êtres vivants dans leur milieu naturel et on en a décelé la présence dans divers secteurs de

l'environnement. Il semblerait qu'il puisse subir une biodécomposition.

Ces données sont trop limitées pour qu'on puisse parvenir à des conclusions quant aux niveaux d'exposi-tion et aux effets que ce composé peut avoir sur la population générale et les êtres vivants dans leur milieu naturel.

Il n'existe aucune base de données toxicologiques qui plaide en faveur de l'utilisation de ce produit.

Il faut éviter toute utilisation susceptible de conduire à une pollution de l'environnement.

RESUMEN, EVALUACIÓN, CONCLUSIONES Y RECOMENDACIONES

ÉTER DE DECABROMODIFENILO

1 Resumen y evaluación

1.1 Identidad y propiedades físicas y químicas

El éter de decabromodifenilo (DeBDE) comercial suele tener una pureza del 97-98%, con un 0,3-3,0% de éteres de difenilo nona- y octabromados. La impureza más importante es el éter de nonabromodifenilo (NBDE). A diferencia de los otros éteres de difenilo polibromados, el DeBDE tiene un solo isómero.

El punto de fusión es de unos 300 °C y la descomposición se produce por encima de los 400 °C. La solubilidad en agua es de 20-30 μg/litro y el logaritmo del coeficiente de reparto *n*-octanol/agua es superior a 5. La presión de vapor es $< 10^{-6}$ mm de Hg a 20 °C.

1.2 Producción y aplicaciones

Entre los éteres de difenilo bromados (del mono- al deca-), el éter de decabromodifenilo es el más importante de fabricación comercial en cuanto a producción y aplicaciones.

A partir del decenio de 1970 se ha elaborado DeBDE comercial cada vez más puro. Su producción mundial es de unas 300 000 toneladas al año. Se utiliza como aditivo pirorretardante en numerosos plásticos, sobre todo en el poliestireno de gran resistencia al impacto, en el tratamiento de tejidos utilizados en pasamanería, telas de automóviles y tiendas de campaña.

1.3 Transporte, distribución y transformación en el medio ambiente

La fotodegradación del DeBDE tiene lugar en disolventes orgánicos con radiación ultravioleta (RUV) o la luz del sol y produce éteres de difenilo con un número menor de átomos de bromo y dibenzofuranos bromados. También se produce fotodegradación, en menor grado, en el agua bajo la acción de la luz del sol; sin embargo, no se ha detectado la presencia de éteres de difenilo menos bromados ni tampoco de dibenzofuranos bromados.

En función del tipo de polímero y del disolvente de extracción se obtiene una concentración de DeBDE que está casi en el límite de detección o es inferior a él.

Debido a que la solubilidad en agua y la presión de vapor son extremadamente bajas, es probable que el transporte del DeBDE se produzca sobre todo mediante adsorción sobre partículas. Es persistente y se acumula fácilmente en el sedimento y en el suelo.

No se dispone de datos acerca de su biodisponibilidad a partir del sedimento y del suelo. En un estudio realizado en la trucha irisada no se detectó bioacumulación en la carne, la piel o las vísceras durante más de 48 horas. No es probable la bioacumulación del DeBDE, debido a su peso molecular relativamente alto.

A la larga, los productos que contienen DeBDE comercial se eliminan en vertederos o mediante incineración. El DeBDE, en último término, se puede lixiviar de los vertederos. Se pueden producir dibenzofuranos polibromados (PBDF) y mezclas de dibenzofuranos y dibenzodioxinas halogenados en incendios de los vertederos o por una incineración incompleta. Los productos que contienen DeBDE comercial pueden contribuir a estas emisiones.

La pirólisis del propio DeBDE comercial y de los polímeros (HIPS, PBT, polipropileno industrial) con DeBDE en presencia de oxígeno produjo PBDF, detectándose en menor grado dibenzodioxinas polibromadas (PBDD). La formación máxima de PBDF tiene lugar a 400-500 °C, pero se puede producir a temperaturas de hasta 800 °C; el Sb_2O_3 ejerce una función catalítica en la formación de PBDF y PBDD.

La formación de PBDF y PBDD y las cantidades encontradas dependen de la temperatura, el contenido de oxígeno y la duración

de la pirólisis. En ausencia de oxígeno, se forman sobre todo polibromobencenos y polibromonaftalenos.

1.4 Niveles medioambientales y exposición humàna

En la vecindad de las instalaciones de fabricación se han identificado concentraciones de DeBDE de hasta 25 $\mu g/m^3$. No se detectó en las muestras de agua recogidas en el Japón durante el perfodo de 1977-91. Sin embargo, se observó en el sedimento de ríos recogido en el Japón durante el mismo perfodo a concentraciones de hasta unos 12 mg/kg de peso seco. En los Estados Unidos se encontró DeBDE (hasta 1 g/kg) en el sedimento de los ríos cercanos a una fábrica. No se detectó su presencia en las muestras de peces recogidas en el Japón, aunque en una muestra de mejillones se observó una concentración ligeramente superior al nivel de detección. Aunque no se encontró en las muestras de tejido adiposo humano recogidas en el Japón, en los Estados Unidos se observó en 3 de 5 muestras de este tipo de tejido.

La exposición humana al DeBDE se puede producir en el curso de la fabricación y la formulación en polímeros. La exposición de la población general al DeBDE es insignificante.

En la determinación de la exposición en el trabajo a los productos de degradación del DeBDE durante la fabricación, formulación o utilización se puso de manifiesto que las muestras de aire próximas al cabezal del extrusor contenían concentraciones elevadas de PBDF. En el aire de la sala de trabajo se encontraron niveles más bajos. Se detectó asimismo en muestras del material de limpieza. Se ha demostrado que la aplicación de buenas técnicas industriales reduce la exposición ocupacional al PBDF.

No es probable una exposición significativa de la población general a las impurezas de PBDF de los polímeros con características pirorretardantes.

1.5 Cinética y metabolismo en animales de laboratorio y en el ser humano

El DeBDE tiene una escasa absorción desde el tracto gastrointestinal y se excreta con rapidez tras su inyección.

Los resultados de los estudios metabólicos en ratas utilizando DeBDF marcado con ^{14}C indicaron una semivida para su desaparición del organismo de menos de 24 horas, siendo la ruta principal de eliminación tras la ingestión oral la vía fecal. En la orina o el aire expirado no se encontró una actividad apreciable de ^{14}C (inferior al 1%).

Las ratas alimentadas con 0,1 mg/kg de peso corporal al día, durante un período de hasta dos años, no mostraron acumulación de DeBDF en el suero, los riñones, los músculos o los testículos, como se comprobó mediante una determinación del bromo total. La acumulación de bromo en el hígado alcanzó un nivel estacionario a los 30 días y desapareció en un período de 10 días después del tratamiento. Tras 180 días de tratamiento, el nivel de bromo en el hígado de las ratas tratadas no era superior al de las testigo. En el tejido adiposo se acumuló una concentración baja de bromo total, que se mantenía tras 90 días con una alimentación sin DeBDE; se desconoce la naturaleza del bromo acumulado. Habida cuenta de que el DeBDE representaba sólo el 77% de la mezcla comercial utilizada, el "bromo" podría proceder del NBDE o el OBDE.

1.6 *Efectos en los animales de laboratorio y en sistemas de prueba* in vitro

La toxicidad aguda del DeBDE en los animales de laboratorio es baja. La sustancia no es irritante para la piel o los ojos de los conejos. No es cloracnegénico en la piel de los conejos, ni tampoco sensibilizador cutáneo humano.

Se realizaron pruebas de toxicidad aguda y de comedogenicidad de los productos de la combustión del poliestireno pirorretardante con DeBDE y Sb_2O_3. La DL_{50} por vía oral del hollín y la carbonilla fue > 2000 mg/kg de peso corporal.

No se observó inducción de efectos adversos en los estudios de toxicidad a corto plazo realizados en ratas y ratones con niveles de DeBDE (pureza > 97%) de 100 g/kg (4 semanas) ó 50 g/kg de alimentos (13 semanas, equivalente a 2500 mg/kg de peso corporal de la rata). En un estudio de reproducción de una sola generación en ratas no se observaron efectos adversos con niveles de dosis de 100 mg/kg de peso corporal. El DeBDE no produjo efectos teratogénicos en los fetos de las ratas que recibieron dosis de

100 mg/kg de peso corporal. Con 1000 mg/kg de peso corporal se detectaron malformaciones como el retraso de la osificación. En varias pruebas realizadas no se ha observado que tenga efectos mutagénicos.

En un estudio de carcinogenicidad en ratas y ratones, se administraron concentraciones de DeBDE (pureza 94-99%) de hasta 50 g/kg de alimentos. Se observó un aumento en el número de adenomas hepáticos (pero no de carcinomas) de las ratas macho que recibieron 25 g/kg y en las ratas hembra con 50 g/kg. En ratones macho tratados con 25 g/kg se detectó una frecuencia mayor de adenomas y carcinomas hepatocelulares (combinados) y con ambos niveles de dosis un aumento de adenomas/carcinomas (combinados) de las células foliculares del tiroides. En los ratones hembra no se apreció ningún incremento de la frecuencia de tumores. Se obtuvo una prueba equívoca de carcinogenicidad en ratas macho y hembra y en ratones macho sólo con dosis de 25-50 g de DeBDE/kg de alimentos. Dado que los resultados de todas las pruebas de mutagenicidad han sido negativos, se puede concluir que el DeBDE carece de carcinogenicidad genotóxica. IARC (1990) concluyó que las pruebas de carcinogenicidad del DeBDE en los animales de experimentación eran limitadas. Los niveles de dosificación muy elevados, la falta de genotoxicidad y las pruebas mínimas de carcinogenicidad ponen de manifiesto que el DeBDE, a las concentraciones de exposición actuales, no representa un riesgo de carcinogénesis para el ser humano.

1.7 Efectos en el ser humano

No se detectaron signos de sensibilización cutánea en una prueba realizada con 200 personas expuestas al DeBDE.

En un estudio de morbilidad realizado con el personal del extrusor que mezcla polibutilenterftalato que contiene DeBDE, con la consiguiente exposición potencial al PBDD y al PBDF durante 13 años, no se observaron efectos nocivos, aun cuando se detectaron en sangre 2,3,7,8-TeBDF y -TeBDD. Los resultados de los estudios inmunológicos pusieron de manifiesto que el sistema inmunitario de las personas expuestas no se había visto negativamente afectado después de 13 años.

1.8 Efectos en otros organismos en el laboratorio y en el medio ambiente

Las CE_{50}s para el crecimiento de tres algas unicelulares marinas fueron superiores a 1 mg de DeBDE/litro. No se dispone de más información sobre los efectos del DeBDE en otros organismos en el laboratorio y en el medio ambiente.

2 Conclusiones

2.1 DeBDE

El DeBDE se utiliza ampliamente en polímeros como aditivo pirorretardante. El contacto de la población general se produce a través de productos fabricados con dichos polímeros. La exposición es muy escasa, puesto que no es fácil extraer el DeBDE de los polímeros. La toxicidad aguda es muy baja y la absorción del tracto gastrointestinal mínima. Así pues, el riesgo para la población general se puede considerar insignificante.

La exposición en el trabajo se da con el DeBDE en forma de partículas. El control del polvo durante la fabricación y el empleo reducirá el riesgo para los trabajadores de manera suficiente.

El DeBDE es persistente y se une a partículas del medio ambiente; es fácil que se acumule en el sedimento, pero no es probable su bioacumulación. Aunque las pruebas disponibles indican que la fotodegradación ambiental en agua no producen éteres de difenilo o dibenzofuranos con menor número de átomos de bromo, apenas se conoce nada sobre la degradación en otros medios.

La información sobre la toxicidad del DeBDE para los organismos del medio ambiente es mínima.

2.2 Productos de degradación

Se puede producir PBDF y, en cierta medida, PBDD cuando se somete el DeBDE, o los productos que lo contienen, a temperaturas de 300-800 °C. Hay que estudiar los posibles peligros asociados a estos productos.

La incineración controlada de manera adecuada no produce una emisión de cantidades significativas de dioxinas o furanos bromados.

Cualquier combustión no controlada de productos con DeBDE puede dar lugar a una formación no cuantificada de PBDF/PBDD. De su importancia para el ser humano y el medio ambiente se ocupará un futuro número de Criterios de Salud Ambiental.

Se ha detectado PBDR en la sangre de las personas que trabajan en la producción de plásticos con DeBDE. No se han observado efectos adversos relacionados con esta exposición. Con un buen control técnico se puede evitar la exposición de los trabajadores al PBDF.

3 Recomendaciones

3.1 Generales

- Las personas que trabajan en la fabricación de DeBDE y productos que lo contienen deben estar protegidas de la exposición mediante la aplicación de medidas adecuadas de higiene industrial, la vigilancia de la exposición en el trabajo y controles técnicos.
- Hay que reducir al mínimo la exposición ambiental mediante el tratamiento adecuado de efluentes y emisiones industriales que contienen el compuesto o sus productos. Se debe controlar la eliminación de los residuos industriales y los productos de consumo para que sea mínima la contaminación del medio ambiente con esta sustancia persistente y sus productos de degradación.
- Los fabricantes deben reducir al mínimo los niveles de impurezas en los productos comerciales de DeBDE, utilizando las mejores técnicas disponibles. Se recomienda una pureza del 97% o superior.
- La incineración sólo se debe realizar en incineradores adecuados que funcionen siempre en condiciones óptimas. La quema por otros medios puede dar lugar a la formación de PBDF y PBDD.

3.2 Otros estudios

- Se deberán realizar en los organismos pertinentes nuevos estudios sobre la biodisponibilidad y la toxicidad del DeBDE unido al sedimento.
- Hay que mantener una vigilancia constante de los niveles en el medio ambiente.
- Se debe investigar con más detalle la formación de PBDF en incendios reales.
- Hay que estudiar más a fondo la biodegradación en el medio ambiente y la fotodegradación en compartimentos distintos del agua.
- Se debe investigar los posibles métodos y las consecuencias del reciclaje de polímeros que contienen DeBDE.
- Hay que validar métodos analíticos para el DeBDE en diversos aglomerantes.

ÉTER DE NONABROMODIFENILO

El éter de nonabromodifenilo no se fabrica ni se utiliza. No se dispone de datos sobre los aspectos siguientes:

- Transporte, distribución y transformación en el medio ambiente
- Niveles medioambientales y exposición humana
- Cinética y metabolismo en animales de laboratorio y en el ser humano
- Efectos en los animales de laboratorio y en sistemas de prueba *in vitro*
- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente
- Evaluaciones anteriores por parte de órganos internacionales.

1 Resumen y evaluación

No hay ninguna base de datos sobre la cual realizar una evaluación.

2 Recomendaciones

Los niveles de contaminación de los pirorretardantes bromados comerciales que contienen éter de nonabromodifenilo deberían ser mínimos a fin de evitar la contaminación del medio ambiente y la exposición humana.

ÉTER DE OCTABROMODIFENILO

El éter de octabromodifenilo puro no se fabrica ni se utiliza. No se dispone de datos sobre los aspectos siguientes:

- Cinética y metabolismo en animales de laboratorio y en el ser humano
- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente
- Evaluaciones anteriores por parte de órganos internacionales.

1 Resumen y evaluación

1.1 Identificación y propiedades físicas y químicas

El éter de octabromodifenilo (OBDE) comercial es una mezcla formada por alrededor del 11% de PeBDE/HxBDE, 44% de HpBDE, 31-35 % de OBDE, 10% de NBDE y 0,5% de DeBDE. En función de su estructura química, existen 12 posibles isómeros del OBDE y 24 del HpBDE.

El punto de fusión oscila entre unos 80 °C y > 200 °C. La presión de vapor es < 10^{-7} mm de Hg. La solubilidad en agua es

baja y el logaritmo del coeficiente de reparto *n*-octanol/agua es > 5,5. Las variaciones anteriores obtenidas en los datos físicos pueden deberse a diferencias de composición en las mezclas probadas.

1.2 Producción y aplicaciones

El consumo anual de OBDE comercial en todo el mundo es de 6000 toneladas, el 70% del cual se utiliza como pirorretardante en ABS para la producción de computadores y cabinas comerciales. El OBDE es el segundo más utilizado de los pirorretardantes de PBDE.

1.3 Transporte, distribución y transformación en el medio ambiente

Se han detectado componentes de OBDE comercial en el sedimento acuático y en la grasa humana. En la biota se han encontrado algunos componentes de menor número de átomos de bromo (HxBDE y PeBDE) del producto comercial. No se ha observado OBDE, pero normalmente no se ha investigado la presencia de HpBDE y NBDE. Es fácil que persistan los componentes comerciales de OBDE, pero a medida que el número de átomos de bromo aumenta por encima del HxBDE disminuye la probabilidad de bioacumulación. En la carpa se ha encontrado un factor de bioacumulación inferior a 2 para un producto de OBDE comercial.

En la pirólisis a 600 °C del producto comercial como tal o de polímeros que lo contienen como aditivo pirorretardante (con Sb_2O_3 o sin él) se ha puesto de manifiesto la producción de PBDF y, en grado mucho menor, PBDD. El tratamiento de ABS con OBDE/Sb_2O_3 en diferentes condiciones permitió demostrar que, en el caso de tratamiento normal, sólo se formaban pequeñas concentraciones de PBDF. En condiciones de uso excesivo, las concentraciones fueron mucho más elevadas. Las concentraciones de PBDD fueron bajas en ambos casos.

1.4 Niveles medioambientales y exposición humana

En una serie de muestras recogidas en el Japón durante 1987 y 1988 no se detectó OBDE ni los componentes de menor número de átomos de bromo del producto comercial. También se analizaron

muestras del sedimento y se encontró OBDE en alrededor del 2-6% de las muestras a concentraciones que oscilaban entre 8 y 22 μg/kg de peso seco. En el sedimento se observó asimismo la presencia de componentes de menor número de átomos de bromo

No se detectó OBDE en las muestras de peces recogidas en el Japón durante 1987 y 1988.

En los Estados Unidos se investigó la presencia de PBDF Y PBDD en muestras de grasa humana recogidas en 1987. Las muestras procedían de 865 personas combinadas para formar 48 grupos compuestos análogos. La composición se basó en 9 divisiones de censo y 3 grupos de edad. En estas muestras también se identificó PBDE y los datos preliminares indicaron la presencia de OBDE con una frecuencia del 60% y una concentración estimada de hasta 8000 ng/kg.

1.5 Cinética y metabolismo en animales de laboratorio y en el ser humano

No se dispone de datos.

1.6 Efectos en los animales de laboratorio y en los sistemas de prueba in vitro

La toxicidad aguda del producto comercial en los animales de laboratorio es baja. No es irritante cutáneo y sólo produce una ligera irritación ocular en los conejos. En los estudios de toxicidad a corto plazo (4 semanas y 13 semanas) se observó que en las ratas que recibieron dosis de 100 mg/kg de alimentos se produjo un mayor peso del hígado y cambios microscópicos caracterizados por un aumento de tamaño de las células parenquimáticas hepáticas de la zona centrolobular y media que contienen estructuras granulares. Estos cambios hepáticos fueron más graves con dosis más elevadas, es decir, 1000 y 10 000 mg/kg de alimentos. A esto hay que añadir que se observó hiperplasia en el tiroides. El contenido total de bromo en los tejidos aumentó durante el estudio y disminuyó lentamente durante un período de recuperación. Los cambios hepáticos fueron reversibles. En un estudio de inhalación con polvo de OBDE micronizado (8 horas al día durante 14 días consecutivos) no se observaron efectos con exposiciones a 1,2 mg/m^3, pero a 12 mg/m^3

se produjeron en el hígado los cambios descritos en los estudios de administración oral.

El OBDE comercial a dosis relativamente bajas produjo en ratas un aumento del citocromo P450 y la inducción de enzimas microsómicas hepáticas, como la UDP-glucuronil transferasa y la benzo[α]pireno hidroxilasa. El OBDE comercial indujo efectos porfirinogénicos en cultivos de células hepáticas de embrión de pollo.

Su potencial teratogénico se probó en ratas; con dosis elevadas (25,0 y 50,0 mg/kg de peso corporal) se detectaron procesos de resorción y osificación retardada de diferentes huesos, así como malformaciones fetales. Las malformaciones observadas tras la administración de dosis de 25 mg/kg de peso corporal y superiores probablemente se debieron en buena parte a la toxicidad materna. Estos cambios no se advirtieron a dosis de 15,0 mg/kg de peso corporal o inferiores. No se obtuvieron pruebas de actividad teratogénica en los conejos, pero se observó fetotoxicidad a una dosis tóxica para las madres de 15 mg/kg de peso corporal. En los estudios de teratogenicidad se puso de manifiesto la ausencia de efectos a una dosis de 2,5 mg/kg de peso corporal.

En estudios de 28 días y 90 días realizados en ratas se observó que 100 mg de OBDE por kg de alimentos (equivalentes a 5 mg/kg de peso corporal) producían efectos mínimos en el hígado. No se estableció un nivel sin efectos. Los resultados de las pruebas de mutagenicidad, incluso con un ensayo de ADN fuera de programa, los ensayos microbiológicos *in vitro* y un ensayo de intercambio de cromátidas hermanas con células de ovario de hámster chino fueron negativos.

No se dispone de resultados de pruebas de carcinogenicidad a largo plazo.

1.7 *Efectos en el ser humano*

No se dispone de datos.

1.8 *Efectos en otros organismos en el laboratorio y en el medio ambiente*

Los datos disponibles son mínimos.

2 Conclusiones

2.1 OBDE

El OBDE comercial es una mezcla de éteres de hexa-,hepta-, octa-, y nonabromodifenilo, todos ellos persistentes en el medio ambiente, fundamentalmente unidos al sedimento.

El OBDE se añade con mucha frecuencia a los polímeros como aditivo pirorretardante. El contacto de la población general tiene lugar mediante los productos fabricados con estos polímeros. No es probable la exposición por extracción de los polímeros.

La toxicidad aguda del OBDE es baja. No se dispone de información sobre su absorción y eliminación en los mamíferos. No es teratogénico ni mutagénico. No se dispone de estudios de toxicidad y carcinogenicidad a largo plazo.

En el tejido adiposo humano se han identificado varios componentes del OBDE comercial. El riesgo grave para la población general probablemente es bajo. No es posible evaluar el riesgo de exposición prolongada, debido a la falta de los estudios de toxicidad correspondientes.

La falta de información no permite sacar conclusiones sobre la exposición en el trabajo al OBDE o sus efectos.

La información sobre la toxicidad del OBDE para los organismos en el medio ambiente es limitada. Los componentes de la mezcla de OBDE comercial con menor número de átomos de bromo podrían dar lugar a una bioacumulación en los organismos.

2.2 Productos de degradación

Puede formarse PBDF, y en cierto grado PBDD, cuando el OBDE o los productos que lo contienen se calientan a 400-800 °C. Hay que investigar los posibles peligros relacionados con esta transformación.

No es probable que la exposición de la población general a las impurezas de PBDF en los polímeros pirorretardantes sea significativa. La incineración adecuadamente controlada no debería producir la emisión de cantidades importantes de dioxinas y furanos bromados. Cualquier combustión no controlada de productos que

contienen OBDE comercial puede dar lugar a la producción de cantidades no cuantificadas de PBDF/PBDD. Su importancia para el ser humano y el medio ambiente será objeto de estudio en un futuro EHC sobre el PBDF/PBDD.

3 Recomendaciones

3.1 Generales

- En la fabricación de OBDE comercial se deben utilizar las mejores técnicas disponibles, a fin de reducir al mínimo los niveles de hexabromodifenilo y los compuestos análogos de menor número de átomos de bromo, debido a su posible bioacumulación en el medio ambiente.
- Los trabajadores que intervienen en la fabricación de OBDE y de los productos que contienen el compuesto deben estar protegidos de la exposición mediante la aplicación de medidas de higiene industrial adecuadas, la vigilancia de la exposición en el trabajo y controles técnicos.
- Se debe reducir al mínimo la exposición ambiental mediante el tratamiento adecuado de los efluentes y las emisiones en las industrias que utilizan el compuesto o sus productos. Hay que controlar la eliminación de desechos industriales y de los productos de consumo, a fin de reducir al mínimo la contaminación del medio ambiente con este material persistente y los productos de su degradación.
- La incineración de materiales con aditivos pirorretardantes a base de OBDE se debe realizar sólo en incineradores adecuados que funcionen siempre en condiciones óptimas. La combustión por cualquier otro medio puede dar lugar a la producción de PBDF y PBDD.

3.2 Otros estudios

Habida cuenta de que la base de datos toxicológica actual no es adecuada para evaluar los peligros del OBDE comercial para el ser humano y el medio ambiente y a fin de mejorar su uso se deberían realizar los siguientes estudios:

- Investigaciones sobre la biodisponibilidad y la ecotoxicidad de los componentes del OBDE comercial unidos al sedimento utilizando los organismos pertinentes.
- Mayor vigilancia de los niveles en el medio ambiente de los componentes de OBDE comercial.
- Estudios de toxicidad y carcinogenicidad a largo plazo del OBDE comercial.
- Vigilancia de la exposición en el trabajo al OBDE comercial.
- Otras investigaciones sobre la formación de PBDF en incendios reales.
- Nuevos estudios sobre biodegradación y fotodegradación en el medio ambiente en compartimentos diferentes del acuático.
- Investigación de posibles métodos y consecuencias del reciclaje de polímeros que contienen OBDE.
- Validación de métodos analíticos para el OBDE en varios aglomerantes.
- Investigaciones sobre la posibilidad de migración a partir de diferentes tipos de polímeros.

ÉTER DE HEPTABROMODIFENILO

El éter de heptabromodifenilo no se fabrica ni se utiliza.

No existe una base de datos sobre la que hacer una evaluación del HpBDE.

No se dispone de datos sobre los aspectos siguientes:

- Cinética y metabolismo en animales de laboratorio y en el ser humano
- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente
- Evaluaciones previas por parte de órganos internacionales.

Dado que el HpBDE es el principal componente del éter de octabromodifenilo comercial, el resumen, evaluación, conclusiones y recomendaciones del OBDE comercial son aplicables al HpBDE "comercial".

ÉTER DE HEXABROMODIFENILO

Aunque el éter de hexabromodifenilo no se fabrica ni se utiliza, es posible encontrarlo como contaminante de los éteres bromados del difenilo comerciales. Se debe reducir al mínimo tales niveles del éter de hexabromodifenilo para evitar la contaminación del medio ambiente y la exposición humana.

No existe una base de datos sobre la que hacer una evaluación.

No se dispone de datos sobre los aspectos siguientes:

- Efectos en mamíferos de laboratorio y en sistemas de ensayo *in vitro*
- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente
- Evaluaciones previas por parte de órganos internacionales.

ÉTER DE PENTABROMODIFENILO

El éter de pentabromodifenilo no se fabrica ni se utiliza.

No se dispone de datos sobre los aspectos siguientes:

- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente

- Evaluaciones previas por parte de órganos internacionales.

1 Resumen y evaluación

1.1 Identificación y propiedades físicas y químicas

El éter de pentabromodifenilo comercial (PeBDE) es una mezcla de éteres de tetra-, penta-, y hexabromodifenilo. Contiene aproximadamente un 50-60% de PeBDE y un 24-38% de TeBDE. Habida cuenta de su estructura química, hay seis posibles isómeros del PeBDE y 42 del TeBDE. Los productos comerciales parecen estar formados por tres componentes principales, a saber, 2,2',4,4',5'-PeBDE, 2,2',4,4'-TeBDE y un compuesto análogo no identificado con cinco átomos de bromo.

El punto de fusión es de -7 a -3 °C y el de ebullición superior a 200 °C. La presión de vapor es baja: $< 10^{-7}$ mm de Hg; la solubilidad en agua es insignificante. El log del coeficiente de reparto *n*-octanol/agua es > 6.

1.2 Producción y aplicaciones

El PeBDE se utiliza como aditivo de resinas epoxi, resinas fenólicas, poliésteres y poliuretano, así como de materiales textiles. El consumo mundial es de unas 4000 toneladas anuales. Es uno de los principales éteres bromados del difenilo pirorretardantes comerciales.

1.3 Transporte, distribución y transformación en el medio ambiente

Se han detectado componentes del PeBDE comercial en muestras de biota, sedimento y fangos cloacales. Es fácil que sean persistentes y tengan capacidad de bioacumulación. En las carpas se ha encontrado un factor de bioacumulación para el PeBDE superior a 10 000.

En los estudios de pirólisis con PeBDE comercial se observó la formación de PBDF y PBDD. La temperatura óptima de formación osciló entre 700-800 °C. Cuando la pirólisis de PeBDE tenía lugar en ausencia de oxígeno se formaban polibromobencenos, polibromofenoles y PBDF.

1.4 Niveles medioambientales y exposición humana

En muestras obtenidas de ríos y estuarios del Japón se detectaron niveles que variaban entre la ausencia de PeBDE (< 2 μg/kg) y 28 μg/kg de peso seco. En Suecia, la concentración en muestras de sedimento de algunos ríos alcanzó un valor de hasta 1200 μg de 2,2',4,4',5'-PeBDE/kg. También en el análisis de fangos cloacales de Suecia se puso de manifiesto la presencia de PeBDE.

En los mejillones y peces recogidos en diferentes costas del Japón durante el período de 1981-85 se encontraron concentraciones de 0,4 y 2,8 μg de PeBDE/kg de peso húmedo de dos de cinco muestras de mejillones. No se detectó PeBDE en los peces (límite de determinación < 0,2 μg/kg). Se informó de concentraciones de 1,9-22 μg/kg de peso fresco en muestras de hígado de bacalao procedente del mar del Norte. En Suecia se encontraron concentraciones de 7,2 a 64 μg de 2,2',4,4',5'-PeBDE/kg de grasa en corégonos de agua dulce y en arenques recogidos en diversos lugares.

En una mezcla de grasa de focas oceladas y focas grises recolectada en Suecia entre 1979 y 1985 se encontró una concentración media de 1,7 μg y 40 μg de 2,2',4,4',5'-PeBDE/kg de grasa, respectivamente.

En mezclas de muestras de músculo de conejo y ratón y en muestras de sebo de reno recogidas en Suecia de 1985 a 1986 se determinó una concentración < 0,3 μg, 0,64 μg y 0,26 μg de 2,2',4,4',5'-PeBDE/kg de grasa, respectivamente.

Las muestras de músculo de quebrantahuesos recogidas en Suecia en 1982-86 contenían una concentración media de 140 μg de 2,2',4,4',5'- PeBDE/kg de grasa.

En los últimos decenios se han multiplicado por diez los niveles de dos isómeros del PeBDE en los huevos de arao del Báltico. La concentración de dichos isómeros en los lucios de un lago de la región meridional de Suecia también ha experimentado un aumento (del cuádruple). Se ha observado asimismo un aumento considerable en los muestreos realizados en el sedimento del Báltico en distintos años durante el último decenio.

Aunque se dispone de una información muy escasa sobre la exposición humana, una estimación aproximada de la exposición de

la población sueca a través del consumo de pescado parece indicar una absorción diaria de 0,1 μg de PeBDE/persona.

1.5 Cinética y metabolismo en animales de laboratorio y en el ser humano

La semivida del PeBDE sólo se ha investigado en la grasa perirrenal de ratas. La semivida media osciló entre 25 y 47 días, en función del sexo del animal y del tipo de isómero.

1.6 Efectos en mamíferos de laboratorio y en sistemas de ensayo in vitro

La toxicidad aguda por vía oral del PeBDE comercial en ratas es baja; la toxicidad dérmica en conejos es también escasa. La exposición de ratas a inhalación durante períodos breves y la aplicación de PeBDE al saco conjuntival de conejos produjo sólo efectos transitorios leves.

En los estudios de toxicidad a corto plazo realizados en ratas (4 y 13 semanas), las concentraciones de 100 mg/kg de alimentos produjeron un aumento del peso del hígado y ligeras alteraciones histológicas. Los cambios consistieron en el agrandamiento de las células parenquimáticas hepáticas, que tenían un aspecto granular y contenían "cuerpos redondos" eosinófilos. Se produjo en el hígado un aumento de la cantidad total de bromo dependiente de la dosis y los niveles se mantuvieron durante un período largo, de hasta 24 semanas. Se observó una hiperplasia tiroidea ligera de carácter reversible.

Tras la administración oral de PeBDE en dosis diarias bajas, del orden de 0,78 μmoles/kg de peso corporal, se detectó la inducción de enzimas hepáticas y un aumento de concentración del citocromo P450. Los resultados de la pruebas de teratogenicidad y mutagenicidad fueron negativos.

No se ha informado de estudios de carcinogenicidad a largo plazo.

1.7 Efectos en el ser humano

No se dispone de datos.

1.8 Efectos en otros organismos en el laboratorio y en el medio ambiente

Se dispone de muy pocos datos.

2 Conclusiones

2.1 PeBDE

El PeBDE comercial (mezcla de varios éteres: 24-38% de tetra-, 50-60% de penta- y 4-8% de hexabromodifenilo) es persistente y se acumula en los organismos y en el medio ambiente.

El PeBDE comercial de utiliza ampliamente incorporado a polímeros como aditivo pirorretardante. El contacto de la población general tiene lugar a través de los productos fabricados con estos polímeros. No es probable la exposición debida a su extracción de ellos. Se puede producir exposición humana al PeBDE mediante la cadena alimentaria, puesto que se ha detectado su presencia en organismos del medio ambiente que son artículos alimenticios humanos, como peces, crustáceos, etc. En los dos últimos decenios se han determinado cantidades crecientes en los peces y las aves de Suecia.

La toxicidad aguda del PeBDE comercial es baja. No se dispone de información acerca de su absorción y eliminación en los mamíferos. Tampoco se han realizado estudios sobre la reproducción, la toxicidad a largo plazo y la carcinogenicidad.

De los datos disponibles no se puede determinar el riesgo de la población general.

Se carece de la información necesaria para sacar conclusiones sobre los niveles de exposición en el trabajo o los efectos del PeBDE comercial.

Se dispone de una información limitada sobre la toxicidad del PeBDE comercial para los organismos en el medio ambiente.

2.2 Productos de degradación

Al calentar el PeBDE (o los productos que lo contienen) a 400-800 °C se producen PBDF, y en cierta medida el PBDD. Habría que ocuparse de los posibles peligros derivados de su formación.

La exposición de la población general al PBDF de los polímeros pirorretardantes con PeBDE probablemente carece de importancia. La incineración controlada de forma adecuada no produce una emisión de cantidades significativas de dioxinas y furanos bromados. La combustión no controlada de productos con PeBDE puede dar lugar a la formación de cantidades no cuantificadas de PBDF/PBDD. En un futuro EHC sobre PBDF y PBDD se prestará atención a su importancia para el ser humano y el medio ambiente.

3 Recomendaciones

3.1 Generales

Dada su persistencia en el medio ambiente y la acumulación en organismos no se debería utilizar PeBDE comercial. Sin embargo, si se va a seguir usando hay que tener en cuenta los puntos siguientes:

- Se debe proteger de la exposición a los trabajadores que intervienen en la fabricación de PeBDE y de los productos que contienen el compuesto mediante medidas adecuadas de higiene industrial, vigilancia de la exposición en el trabajo y controles técnicos.
- Hay que reducir al mínimo la exposición ambiental mediante el tratamiento adecuado de efluentes y emisiones de las industrias que utilizan el compuesto o sus productos. Se debe controlar la eliminación de desechos industriales y de productos de consumo para evitar en lo posible la contaminación del medio ambiente con este producto persistente y acumulable, así como con sus productos de degradación.
- La incineración de materiales pirorretardantes con PeBDE sólo se debe realizar en incineradores adecuados que funcionen siempre en condiciones óptimas. La quema por otros medios dará lugar a la formación de productos de descomposición tóxicos.

3.2 Otros estudios

- Se requiere una vigilancia permanente de sus niveles en el medio ambiente.
- Se deben validar métodos de determinación del PeBDE en diversos aglomerantes.
- Habida cuenta de que la base de datos toxicológicos actual no es adecuada para evaluar los peligros del PeBDE comercial para el ser humano y el medio ambiente y, a fin de mejorar su uso, se deberían realizar los siguientes estudios:
  - estudios adicionales toxicológicos, carcinogénicos y ecotoxicológicos;
  - nuevas investigaciones sobre la formación de PBDF en condiciones de incendios reales;
  - investigación de posibles métodos de reciclaje de polímeros que contienen PeBDE y sus consecuencias;
  - investigaciones sobre la posibilidad de migración a partir de diferentes tipos de polímeros.

ÉTER DE TETRABROMODIFENILO

El éter de tetrabromodifenilo no se fabrica ni se utiliza.

No se dispone de datos sobre los aspectos siguientes:

- Efectos en mamíferos de laboratorio y en sistemas de ensayo *in vitro*
- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente
- Evaluaciones previas por parte de órganos internacionales

1 Resumen y evaluación

1.1 Identificación y propiedades físicas y químicas

El éter de tetrabromodifenilo comercial está formado por una mezcla de éteres: 41% de tetra-, 45% de penta- y 7% de hexabromodifenilo y alrededor del 7% de PBDE de estructura desconocida. En función de su estructura química, hay 42 posibles isómeros del éter de tetrabromodifenilo. Prácticamente se carece de datos sobre sus propiedades físicas y químicas, a excepción del logaritmo del coeficiente de reparto *n*-octanol/agua, que es 5,87-6,16.

1.2 Producción y aplicaciones

Hay un informe de la producción (utilización) de unas 1000 toneladas de TeBDE en el Japón en 1987. No se tiene conocimiento de producción alguna en la actualidad como éter de tetrabromodifenilo, pero está presente en el éter de pentabromodifenilo comercial en cantidades que oscilan entre el 24 y el 38%.

1.3 Transporte, distribución y transformación en el medio ambiente

En muestras de biota, sedimento y fangos cloacales se han encontrado componentes del TeBDE comercial. Es probable que éstos (con cantidades aproximadamente iguales de PeBDE) sean persistentes y bioacumulables.

En estudios de pirólisis con TeBDE comercial se puso de manifiesto que a 800 °C se formaban PBDF y PBDD. No se encontraron estos compuestos con más átomos de bromo.

1.4 Niveles medioambientales y exposición humana

Se detectó TeBDE en el sedimento de ríos del Japón en concentraciones de 12-31 μg/kg de peso seco y en Suecia a niveles de hasta 840 μg/kg de pérdida por incineración. También se encontró TeBDE en fangos cloacales de Suecia a concentraciones de 15 μg/kg.

Los mejillones y peces recogidos en diferentes lugares del Japón contenían TeBDE en concentraciones que oscilaban entre < 0,1 y 14,6 μg de 2,2',4,4'-TeBDE/kg de peso seco. En Suecia se

recogieron diferentes tipos de peces en diversos ríos para analizar la concentración de 2,2',4,4'-TeBDE. Las concentraciones medias variaron entre la no detectable (< 0,1 mg/kg) y 110 mg/kg de grasa. En los análisis se puso de manifiesto la existencia de por lo menos una fuente local de contaminación en un río determinado. Los corégonos, las truchas alpinas y los arenques recogidos en distintos lugares de Suecia en 1986-87 contenían concentraciones de 15, 400 y 59-450 μg de 2,2',4,4'-TeBDE/kg de grasa respectivamente. Los peces recogidos en ríos de Alemania contenían hasta 1 mg de TeBDE/kg de grasa.

En el arenque y en el hígado de bacalao procedentes de las regiones meridional, central y septentrional del mar del Norte durante el período 1983-89, se encontró una tendencia decreciente en la concentración del TeBDE en dirección sur-norte. En el arenque se detectaron concentraciones de 8,4-100 μg de 2,2',4,4'-TeBDE/kg de grasa.

En el tejido muscular de aves que se reproducen e invernan en el mar Báltico, el mar del Norte y Spitzbergen se determinaron concentraciones de 80 a 370 μg de 2,2',4,4'-TeBDE/kg de grasa. Los quebrantahuesos recogidos en Suecia entre 1982 y 1986 contenían concentraciones medias de 1800 μg/kg de grasa.

Se ha indicado que hay una tendencia creciente de las concentraciones de 2,2',4,4'-TeBDE en los sedimentos del mar Báltico, los peces de agua dulce y los huevos de aves marinas de Suecia.

En la grasa de las focas recogidas en el mar Báltico y en Spitzbergen se determinaron concentraciones de 10-73 μg de 2,2',4,4'-TeBDE/kg de grasa. El perfil cromatográfico del PBDE fue semejante al del Bromkal 70-5. En mezclas de muestras de grasa de focas oceladas y focas grises recogidas en Suecia en 1979-85 se encontraron concentraciones de 47 μg y 650 μg de 2,2',4,4'-TeBDE/kg de grasa, respectivamente.

Las mezclas de muestras de músculo de mamíferos terrestres, por ejemplo conejos, ratones y renos, recogidas en Suecia en 1985 y 1986 pusieron de manifiesto concentraciones medias de < 2, 0,82 y 0,18 μg de 2,2',4,4'-TeBDE/kg de grasa, respectivamente.

En cuatro muestras de leche de vaca recogidas en Alemania se encontraron niveles de 2,5-4,5 μg de PBDE/kg de grasa, medida

como Bromkal 70DE. En la leche de 25 mujeres de Alemania se encontró PBDE, como Bromkal 70DE, en concentraciones que oscilaron entre 6,2 y 11,1 μg/kg de grasa.

Una estimación aproximada de la exposición a través del consumo de pescado entre la población sueca parece indicar una absorción diaria de 0,3 μg de TeBDE/persona.

1.5 Efectos en los mamíferos de laboratorio y en los sistemas de ensayo in vitro

No hay datos sobre el propio TeBDE, pero se dispone de datos sobre toxicidad aguda y a corto plazo del PeBDE comercial con un contenido de TeBDE del 41%.

1.6 Cinética y metabolismo en animales de laboratorio y en el ser humano

Se dispone de muy pocos datos.

1.7 Efectos en el ser humano

Se carece de datos.

1.8 Efectos en otros organismos de laboratorio y del medio ambiente

Se carece de datos.

2 Conclusiones

2.1 TeBDE

Los componentes del TeBDE comercial (una mezcla de un 41% de 2,2',4,4'-tetra-; 45% de 2,2',4,4',5'-penta-; 7% de hexa- ; y 7-8% de éteres de difenilo polibromados de estructura desconocida) son persistentes y se acumulan en organismos del medio ambiente.

El TeBDE, como componente del éter de pentabromodifenilo, se incorpora con profusión a polímeros como aditivo pirorretardante. El contacto de la población general se produce a través de productos fabricados con estos polímeros. No es probable la exposición por extracción a partir de los mismos. Es posible la exposición humana

al TeBDE, mediante la cadena alimentaria, porque se ha detectado su presencia en organismos del medio ambiente que forman parte de la alimentación humana, como por ejemplo peces, crustáceos, etc. Durante los dos últimos decenios se han determinado concentraciones crecientes en los peces y las aves de Suecia.

Apenas se dispone de información acerca de la toxicidad/ carcinogenicidad a corto y largo plazo y de estudios de reproducción.

No se puede determinar el riesgo para la población general en función de los datos disponibles.

No se dispone de la información necesaria para poder sacar conclusiones sobre los niveles de exposición en el trabajo o los efectos del TeBDE.

Tampoco hay datos acerca de la toxicidad del TeBDE comercial para los organismos del medio ambiente.

2.2 *Productos de degradación*

Cuando el TeBDE se calienta a 800 °C se forman PBDF y PBDD. Hay que prestar atención a los posibles peligros relacionados con éstos.

La exposición de la población general al PBDF de los polímeros pirorretardantes con TeBDE probablemente carece de importancia. La incineración con los controles adecuados no produce una emisión de cantidades importantes de dioxinas y furanos bromados. Cualquier combustión sin control de productos que contienen TeBDE puede dar lugar a la formación de cantidades no cuantificadas de PBDF/PBDD. Un futuro número de EHC se ocupará de su importancia para el ser humano y el medio ambiente.

3 Recomendaciones

3.1 *Generales*

Dada su persistencia en el medio ambiente y la acumulación en organismos, se recomienda que no se utilice TeBDE. Sin embargo, si se va a seguir usando hay que tener en cuenta los puntos siguientes:

- Se debe proteger de la exposición a los trabajadores que intervienen en la fabricación de TeBDE y de los productos que contienen el compuesto, mediante medidas adecuadas de higiene industrial, vigilancia de la exposición en el trabajo y controles técnicos.
- Hay que reducir al mínimo la exposición ambiental mediante el tratamiento adecuado de efluentes y emisiones de las industrias que utilizan el compuesto o sus productos. Se debe controlar la eliminación de desechos industriales y de productos de consumo para evitar en lo posible la contaminación del medio ambiente con este producto persistente y acumulable, así como con sus productos de degradación.
- La incineración de materiales pirorretardantes con TeBDE sólo se debe realizar en incineradores adecuados que funcionen siempre en condiciones óptimas. La quema por otros medios dará lugar a la formación de productos de degradación del furano tóxicos.

3.2 Otros estudios

- Se requiere una vigilancia permanente de sus niveles en el medio ambiente.
- Se deben validar métodos de determinación del TeBDE en diversos aglomerantes.
- Habida cuenta de que la base de datos toxicológicos actual no es adecuada para evaluar los peligros del TeBDE comercial para el ser humano y el medio ambiente, si se va a continuar con su uso se deberían realizar los siguientes estudios:
  - estudios adicionales toxicológicos, carcinogénicos y ecotoxicológicos;
  - nuevas investigaciones sobre la formación de PBDF en condiciones de incendios reales;
  - investigación de posibles métodos de reciclaje de polímeros que contienen TeBDE y sus consecuencias;

- investigaciones sobre la posibilidad de migración a partir de diferentes tipos de polímeros.

ÉTER DE TRIBROMODIFENILO

El éter de tribromodifenilo no se fabrica ni se utiliza. No se dispone de datos sobre los aspectos siguientes:

- Transporte, distribución y transformación en el medio ambiente
- Cinética y metabolismo en animales de laboratorio y en el ser humano
- Efectos en mamíferos de laboratorio y en sistemas de ensayo *in vitro*
- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente
- Evaluaciones anteriores por parte de órganos internacionales.

1 Resumen y evaluación

No hay una base de datos sobre la cual realizar una evaluación.

2 Recomendaciones

Se debe reducir al mínimo la contaminación de los productos comerciales con éter de tribromodifenilo, a fin de evitar la del medio ambiente y la exposición humana.

Hay que evitar el uso de los productos comerciales capaces de contaminar el medio ambiente.

ÉTER DE DIBROMODIFENILO

El éter de dibromodifenilo no se fabrica ni se utiliza.

No se dispone de datos sobre los aspectos siguientes:

- Cinética y metabolismo en animales de laboratorio y en el ser humano
- Efectos en el ser humano
- Efectos en otros organismos en el laboratorio y en el medio ambiente
- Evaluaciones anteriores por parte de órganos internacionales.

1 Resumen y evaluación

No hay una base de datos sobre la cual realizar una evaluación.

2 Recomendaciones

Se debe reducir al mínimo la contaminación de los productos comerciales con éter de dibromodifenilo, a fin de evitar la del medio ambiente y la exposición humana.

Hay que evitar el uso de los productos comerciales capaces de contaminar el medio ambiente.

ÉTER DE MONOBROMODIFENILO

No se dispone de datos sobre los aspectos siguientes:

- Cinética y metabolismo en animales de laboratorio y en el ser humano
- Efectos en el ser humano.
- Evaluaciones anteriores por parte de órganos internacionales.

1 Resumen y evaluación

1.1 Propiedades físicas y químicas

El éter de monobromodifenilo tiene tres posibles isómeros.

El éter de *p*-bromodifenilo a temperatura ambiente es un líquido con un punto de ebullición de 305-310 °C. Se estima que su solubilidad en agua es de 48 mg/litro. El log del coeficiente de reparto *n*-octanol/agua es de 4 a 5. La presión de vapor a 20 °C es de 0,0015 mm de Hg.

1.2 Producción y aplicaciones

El MBDE no se utiliza como pirorretardante. En 1977 apareció un informe sobre su producción, pero se desconoce su empleo.

1.3 Transporte, distribución y transformación en el medio ambiente

La semivida de volatización a partir del agua es del orden de centenares de días.

Aunque el MBDE no se degradó de manera significativa en un cultivo de siete días con microorganismos de las aguas residuales domésticas, se ha informado que en los fangos cloacales activados lo hace en un 95%. En un estudio aislado se puso de manifiesto que una cepa de bacterias del suelo no era capaz de degradar el MBDE como única fuente de carbono.

1.4 Niveles medioambientales y exposición humana

Se ha detectado MBDE en muestras de agua superficial recogidas en las cercanías de zonas industriales de los Estados Unidos, pero no se obtuvieron estos resultados en un estudio semejante realizado en el Japón. Se encontró asimismo en agua del suelo de un lugar próximo a una instalación industrial de los Estados Unidos. También se ha detectado en el sedimento acuático y en la biota acuática de los Estados Unidos.

1.5 Cinética y metabolismo en animales de laboratorio y en el ser humano

No se dispone de datos.

1.6 Efectos en mamíferos de laboratorio y en sistemas de ensayo in vitro

El MBDE no es teratogénico, pero se carece de datos sobre su toxicidad aguda, a corto plazo y a largo plazo, y por consiguiente no se puede realizar su evaluación.

1.7 Efectos en el ser humano

No se dispone de datos.

1.8 Efectos en otros organismos en el laboratorio y en el medio ambiente

Se ha informado que la CL_{50} en 96 h para *Lepomis macrochirus* es de 4,9 mg/litro, con una concentración sin efectos observados de menos de 2,8 mg/litro. La CL_{50} en 48 horas para la pulga de agua fue de 0,36 mg/litro, con un NOEC de menos de 0,046 mg/litro.

2 Conclusiones y recomendaciones

El éter de monobromodifenilo no tiene propiedades pirorretardantes. Puede acumularse en los organismos del medio ambiente y se ha detectado en diferentes compartimentos ambientales. Algunas pruebas indican que es biodegradable.

La reducida información de que se dispone impide sacar conclusiones sobre los niveles de exposición y los efectos sobre la población general y los organismos.

No existe una base de datos toxicológicos que apoye su uso.

Se debe evitar todo empleo que provoque la contaminación del medio ambiente.

Manganese (No. 17, 1981)
Mercury (No. 1, 1976)[a]
Mercury - environmental aspects (No. 86, 1989)
Mercury, inorganic (No. 118, 1991)
2-Methoxyethanol, 2-ethoxyethanol, and their acetates (No. 115, 1990)
Methylene chloride (No. 32, 1984)
Methyl ethyl ketone (No. 143, 1992)
Methyl isobutyl ketone (No. 117, 1990)
Methylmercury (No. 101, 1990)
Methyl parathion (No. 145, 1992)
Mirex (No. 44, 1984)
Mutagenic and carcinogenic chemicals, guide to short-term tests for detecting (No. 51, 1985)
Mycotoxins (No. 11, 1979)
Mycotoxins, selected: ochratoxins, trichothecenes, ergot (No. 105, 1990)
Nephrotoxicity associated with exposure to chemicals, principles and methods for the assessment of (No. 119, 1991)
Neurotoxicity associated with exposure to chemicals, principles and methods for the assessment of (No. 60, 1986)
Nickel (No. 108, 1991)
Nitrates, nitrites, and *N*-nitroso compounds (No. 5, 1978)[a]
Nitrogen, oxides of (No. 4, 1977)[a]
2-Nitropropane (No. 138, 1992)
Noise (No. 12, 1980)[a]
Organophosphorus insecticides: a general introduction (No. 63, 1986)
Paraquat and diquat (No. 39, 1984)
Pentachlorophenol (No. 71, 1987)
Permethrin (No. 94, 1990)
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