Ministerie van Verkeer en Waterstaat

Directoraat-Generaal Rijkswaterstaat

Rijksinstituut voor Kust en Zee/RIKZ

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Inhoudsopgave

Preface

In the framework of the project “Investigating for chemicals in the future”, the North Sea Directorate has put the department of Rijkswaterstaat Institute for Coastal and Marine Management (RIKZ) in charge, to start a study on unknown chemicals. The object of this project is to identify the most important contaminants, which present a threat to the North Sea and the identification of gaps in policy, management and knowledge. In the project monitoring data are evaluated and a number of “new” substances are proposed as a potential threat for the North Sea.

On the 15th of September BKH Consulting Engineers has received the order to make a study on a selection of the brominated flame-retardants. This study will be directed on the whole track of brominated flame-retardants in the environment. From production and emission to immission, waste and effects.

The project is coordinated by Mr dr R.W.P.M. Laane of RIKZ. The project-leader of BKH is Mrs drs C.P. Groshart. The authors of the report are: Mr drs W.B.A. Wassenberg and Mrs drs C.P. Groshart.

Summary

General

Brominated flame-retardants are used for fire prevention and inhibition in polymers, rubber, textiles and wood. Flame retarded polymers are widely used in cars, consumer electronics, computers, electrical equipment and building materials. Dominant use of brominated flame-retardants in these materials is primarily based on their high specific flame retardancy and good mixing properties with polymers. Flame-retarded textiles are primarily used in upholstery of cars, trains, aircraft and other public facilities.

Current world-wide demand of brominated flame-retardants is estimated at 350,000 tonnes/y with tetrabromobisphenol A (TBBPA) as the major compound (45-50% of total demand). Further a wide range of brominated compounds such as diphenylethers, biphenyls and cyclo-aliphatics are used. For the next 4 years, overall production is believed to grow at a rate of ca. 8.5% per year.

Sources and emissions

It is estimated that in The Netherlands yearly 30,000 tonnes TBBPA and 5,000 tonnes hexabromocyclododecane (HBCD) are produced at Broomchemie in Terneuzen. Only a small fraction of these amounts, 1,700 and 400 tonnes/y respectively, are used in The Netherlands. Major other compound is decabromodiphenylether with an estimated demand of ca. 600 tonnes/y. A review of all produced and used amounts is given in table 1.

At the production site in Terneuzen approximately 15 tonnes TBBPA and 0.8 tonnes HBCD are emitted to the surface water annually. Corresponding emissions to the atmosphere are estimated at 8.4 and 0.4 tonnes/y respectively. TBBPA emissions due to compounding, processing and use of brominated polymers are relatively low. HBCD emissions due to evaporation losses during service life are however, significant (11 tonnes/y; see table 1). Emissions due to the use of other compounds are relatively low.

On an European scale, emissions of TBBPA and HBCD significantly increase as a result of the larger scale of compounding, processing and polymer use. For the other compounds it was assessed that only the use of tetra- and pentabromodiphenylether gives rise to emissions of 100 and 15 tonnes/y to the atmosphere (see table 1).

Environmental characteristics and toxicity in aquatic systems

Polybrominated biphenyls (PBBs) and diphenylethers (PBDEs), TBBPA and HBCD are characterised by low solubility in water (< 700 µg/l) and low vapour pressures ($10^{-4} – 10^{-9}$ Pa). Log K_{ow} values vary from 4.5 for low brominated compounds (TBBPA) to 10 for decabromodiphenylether. The volatility, however, declines sharply with rising bromine content. Accordingly, highly brominated compounds are estimated to be non-volatile and adsorb strongly to soil and sediment, whereas low brominated compounds will be more mobile in water and have a greater tendency to evaporate from surface water.

Laboratory results for PBBs reveal that bioaccumulation in aquatic biota and predatory birds is high for low brominated compounds (BCF = 100,000 – 300,000 l/kg) with high excretion half lives (> 30 days). Highly brominated compounds were hardly accumulated. Corresponding BCF values for PBDEs range from 50,000 l/kg for tetrabromodiphenylether to < 30 l/kg for the decabromo compound. TBBPA and HBCD also accumulate significantly, with BCF values of 3,000 and 18,000 l/kg in fish respectively. TBBPA is however rapidly excreted on depuration (half life < 24h).

From both field experiments and biodegradation tests can be concluded that PBBs are persistent under environmental conditions. Scarce biodegradation test results for PBDEs indicate a similar persistence in the environment. Laboratory evidence for photolytic debromination of PBBs and PBDEs could not be confirmed under environmental conditions. This means that the suspected conversion of non-mobile and non-accumulative compounds into the more soluble and bioaccumulative congeners is not likely to occur. Bioaccumulation studies with fish on the other hand, show that decabromodiphenylether may be slightly metabolised into hexa- to nonabromodiphenylethers. The highly bioaccumulative tetra- and penta congeners were however not identified. Biodegradation studies of TBBPA indicate that this compound is degraded slowly under environmental with half lives ranging from 50 – 100 days.

The scarce toxicity data available indicate that the toxicity of lower brominated compounds for freshwater and marine organisms lies around the solubility limit. These brominated flame-retardants therefore may present a risk to aquatic organisms.

Occurrence and behaviour in aquatic systems

Significantly increased levels of PBBs and PBDEs are found in sediments near production plants and polymer processing sites, with highest levels for highly brominated compounds. Levels in water were all below the detection limit. In all aquatic biota, the lower brominated substances are the dominant compounds. Historical PBDE levels in Swedish river systems seems to indicate that the environmental release of these compounds is declining, whereas high levels in sperm whales demonstrate that lower brominated diphenylethers already have reached the deeper regions of the Atlantic Ocean.

Policy

Although there has been a proposition in 1991 in the Netherlands to forbid the use of PBBs and PBDEs, this ban is still not enforced. There is an EC guideline in which PBBs are forbidden in textiles that make contact with the skin. Furthermore some PBBs and PBDEs are on the VROM list of dangerous substances, the EC first and second priority lists, the OSPAR list, the POP list and the PIC list. In the USA and Switzerland PBBs are forbidden. The industry participates in voluntary agreements (VIC) to diminish emission and waste.

Prognosis

Although it is anticipated that halogenated flame-retardants in waste materials will be forbidden by the EC in 2004, global demand for brominated flame-retardants is growing currently at an annual rate of 8.5%. This will result in a demand in 2004 of 500,000 tonnes/year, equivalent to a more than 3-fold increase relative to 1992. Within Western Europe, the commercial production of penta- and octabromodiphenylether recently has been stopped. Further it is expected that decaBB production will decline over the next years. It is not known whether also the use of these PBB and PBDE compounds has ceased or that these compounds are now supplied from outside the EU. On the other hand, the production of TBBPA and HBCD has significantly increased over the last years. These developments might indicate that compounds as PBBs and PBDEs are already substituted by other brominated products. Industry information to verify these matters was not available.

Conclusions and recommendations

From the results of this study can be concluded that especially lower brominated PBBs and PBDEs are widely spread in the environment, with a preference for bioaccumulation in aquatic biota. Current data on the release and distribution of higher brominated PBBs and PBDEs are limited, but suggest that these compounds will primarily bind to sediment and hardly will spread in aquatic systems or accumulate in biota.

For TBBPA and HBCD, adequate measurement data on environmental distribution are lacking. Emission distribution modelling results indicate however that TBBPA has comparable environmental properties as lower brominated PBDEs with the exception that it is slightly biodegradable and has a low excretion half life in fish. For HBCD is expected that it will bind strongly to sediment and bioaccumulate in fish.

Estimates for emissions to the environment demonstrate that significant TBBPA amounts may be released to surface water by discharge of treated wastewater. Emissions to air are predominantly caused by evaporation of HBCD, tetraBDE and pentaBDE during service life.

All emission estimates were based on generalised emission factors from relatively dated references. It is unknown to what extent these emission factors are representative for the current production processes and use. Due to uncertainties about the actual form in which brominated compounds are dissolved in water, it is further not known to what extent the computed emission estimates correspond with the actual emissions. For evaluation of the aquatic toxicity of selected compounds, only scarce data were available.

Considering the large emission estimates for low brominated compounds to surface water and atmosphere, their high tendency to spread in aquatic systems and the fact that their toxicity for aquatic organisms lies around the solubility limit, it is recommended to perform an additional study on these compounds with emphasis on collection and verification of recent emission factors and toxicity data.

Table 1
Overall emissions to the environment
(year 2000; tonnes/year)

	The Netherlands					European Union				
	Production and use	**Total emissions to the environment**				**Production and use**	**Total emissions to the environment**			
		Water	Air (v)	Air (d)	Solid waste		Water	Air (v)	Air (d)	Solid waste
Production										
Tetrabromobisphenol A	30000	14.7	6.30	2.10	774	30000	14.7	6.30	2.10	774
Hexabromocyclododecane	5000	0.82	0.02	0.35	132	5000	0.8	0.02	0.35	132
Decabromodiphenylether	-	-	-	-	-	3650	0.4	< 0.001	0.30	96
Nonabromodiphenylether	-	-	-	-	-	100	0.01	< 0.001	0.007	2.6
Decabromobiphenyl	-	-	-	-	-	1000	0.12	< 0.001	0.07	26
Compounding, processing and use										
Tetrabromobisphenol A	1700	0.28	0.10	1.70	15	40000	6.50	2.80	40	360
Hexabromocyclododecane	420	0.02	11	0.42	3.8	10000	0.55	260	10	91
Decabromodiphenylether	611	0.02	0.002	0.61	5.6	8070	0.32	0.02	8.10	74
Nonabromodiphenylether	33	< 0.001	< 0.001	0.03	0.3	441	0.02	0.01	0.44	4.0
Octabromodiphenylether	45	< 0.001	0.007	0.05	0.4	599	0.02	0.09	0.60	5.5
Heptabromodiphenylether	53	< 0.001	0.048	0.05	0.5	698	0.03	0.63	0.70	6.4
Hexabromodiphenylether	7	< 0.001	0.040	0.01	0.1	221	0.003	1.30	< 0.001	0.03
Pentabromodiphenylether	-	-	-	-	-	601	0.03	15	< 0.001	0.30
Tetrabromodiphenylether	-	-	-	-	-	371	0.26	101	< 0.001	1.85
Decabromobiphenyl	40	< 0.001	0.020	0.04	0.4	1000	0.04	0.50	1.00	9.2

air (v): as vapour; air (d): as dust particles

1. Introduction

1.1 Backgrounds

There are several families of flame-retardants based on bromine, chlorine, phosphorous, nitrogen, antimony oxides, metal salts and hydroxides. Brominated flame-retardants are used for flame retarding in polymers, rubbers, textiles and wood by giving these materials a higher fire safety level by inhibition or suppression of fire.

About the effects of brominated flame-retardants on the aquatic environment little information is available. This is alarming because several brominated flame-retardants are found in aquatic biota. To get an opinion on the consequences of the occurrence of these chemicals in the aquatic environment, the underlying report is composed. This report gives an overview of the available knowledge on 15 brominated flame-retardants in regard to the aquatic environment. Important criteria for selecting these chemicals were:

- they are used and/or produced in the Netherlands;
- they are on several attention lists;
- the production of these chemicals is growing;
- they are expected to be persistent and bioaccumulative;
- they are expected to present a danger to the environment.

This report is produced in the framework of the project “Investigating for chemicals in the future”.

1.2 Objectives

The objectives of this study with regard to the brominated flame-retardants are:

To give an analysis of the problems in the aquatic environment: a description of the load, occurrence, behaviour and effects and a analysis of the problems which indicate how the presence of the brominated flame-retardants may disturb the functioning of the different water systems by effects on sensitive organisms. Furthermore giving an overview of the national and international policy.

In this study the most recent information on brominated flame-retardants has been used. It is possible that in some attention areas the essential information is not yet available. In these cases recommendations for further research will be done.

The study is broadly set up. The next aspects will be handled. In chapter 2 the chemical characteristics of the brominated flame-retardants are described. In chapter 3 the production process is clarified and the use of these chemicals is described. In chapter 4 the sources of emissions, primarily to the aquatic environment, are estimated and specified. In chapter 5 and 6 the behaviour in the environment and the occurrence in the environment are described, respectively. In chapter 7 and 8 an overview is given of the toxicity data and the policy, respectively.

1.3 Limitations

In principle the study conforms itself to information that has a relation to aquatic systems. The situation around air or soil will be briefly described. Furthermore the emphasis lies on the situation in the Netherlands. In some cases the situation of the basins of Rhine, Meuse and Schelde will be commented. The information will be presented briefly. For more extensive information referred is to the concerned sources.

2. Physical chemical properties

2.1 Identification

In this study the risks of brominated compounds for the aquatic environment are evaluated in view of their use as a commercial flame-retardant. In regard to the current environmental concern about their extensive use (de Boer 1999, EU 1999 a,b,c), the environmental behaviour and effects of the following compounds are studied:

- Polybrominated biphenyls (PBB)
- Polybrominated diphenylethers (PBDE)
- Tetrabromobisphenols A (TBBPA) and its derivates
- Polybrominated cyclo-aliphatics (PBCA)

All groups have in common that they are based on large parent molecules. The bromine content e.g. number of bromine atoms in each compound is adjusted to the required level of flame retardancy (WHO, 1997). Theoretically, numerous congeners are possible within each group. However, commercial production is focused on a few major compounds (OECD, 1994; PGFR, 1999).

2.1.1 Polybrominated biphenyls (PBB)

In commercial production of decaBB (Adine 0102), biphenyl is brominated in a large excess of bromine. Due to incomplete bromination, also several lower brominated compounds can be formed (WHO, 1994a; Brinkman, 1980). The generalised formula for PBBs in figure 2.1 shows that PBBs can have variety of possible congeners, depending on the number and position of bromine atoms on the phenyl rings. The systematic numbering system, developed by Ballschmiter et al. (1992), for characterisation of polychlorinated biphenyl (PCB) congeners, has also been adopted for the corresponding PBBs congeners (Pijnenburg, 1995).

From the 209 possible PBB congeners, 101 compounds are listed in the Chemical Abstracts Service (CAS) register. PBBs are not known as natural product (WHO, 1994a). Typical compositions of commercially produced PBBs are given in Table 2.1.

Figure 2.1
Basic formulas of PBDEs and PBBs

PBDE (x=1-5, y=0-5)

PBB (x=1-5, y=0-5)

2.1.2 Polybrominated diphenylethers (PBDE)

As in production of PBBs, commercial products consist of a mixture of various PBDEs (Sellström, 1996). Polybrominated diphenylethers have not been reported to occur naturally in the environment, but related polybrominated phenoxy phenols have been found in several marine organisms, e.g. in Dysidea herbacca, Dysidea chlorea, and Phyllos pongio foliascents (WHO, 1994b). The bacteria Vibrio sp., associated with the sponge Dysidea sp. is capable of producing brominated diphenylethers (Vionov, 1991). Typical compositions of commercially produced PBDEs are given in Table 2.2.

Table 2.1
Composition of commercial PBB mixtures
(in weight-%) (WHO, 1994a)

PBB mixture	**Manu-facturer**	**Br**	**Number of bromine atoms**						
		%	10	9	8	7	6	5	4
Hexabromo-biphenyl									
Fire Master BP-6	Michigan Chemical	75				13.8	62.8	10.6	2
Fire Master BP-6					1	18	73	8	
Fire Master BP-6					33	63	4		
Fire Master BP-6					24.5	79	6		
Fire Master BP-6					7.7	74.5	5.6		
Fire Master RP-158 (1971)					12.5	72.5	9	4	
Fire Master 6244.A (1974)					13	77.5	5	4.5	
Hexabromo-biphenyl	RFR						25	67	4
2,2',4,4',6,6'	RFR						12	84	1
2,2',4,4',6,6'	Aldrich				2	24	70	4	
Composition range					12-25	60-80	1-11	2-5	
Octabromo-biphenyl									
Bromkal 80-9D	Kalk	81-83	9	65	25	1			
Bromkal 80					72	27	1		
XN-1902	Dow Chemical	82	6	47	45	2			
XN-1902	Dow Chemical		2	34	57	7			
Lot 102-7-72	Dow Chemical		6	60	33	1			
FR 250 13 A	Dow Chemical		8	49	3	1			
Octabromo-biphenyl	RFR		4	54	38				
2,2,2',3,3',5,5',6.6'	RFR		1	28	46	23	2		
Decabromo-biphenyl									
HFO 101	Hexcel	84	96	2					
Adine 0102	Ugine Kuhlmann	83-85	96	4					
Adine 0102	Ugine Kuhlmann		96.8	2.9	0.3				
Decabromo-biphenyl	RFR		71	11	7	4	4		
"DBB": Flammex B 10	Berk		96.8	2.9					

Table 2.2
Composition of commercial PBDEs (OECD, 1994; WHO 1994b; EU, 1996; EU, 1999a,b,c)

Product	**Composition (%)**						
	Tetra BDE	Penta BDE	Hexa BDE	Hepta BDE	Octa BDE	Nona BDE	Deca BDE
PeBDE	24-38	50-62	4- 8				
PeBDE	25-44	45-70	<13.3	<0.3	<0.2	<0.2	<0.8
OcBDE			10-12	43-44	31-35	9-11	0- 1
OcBDE		<1.1	<8,6	45-62	31-36	<13	<1.6
DeBDE*					<0.8	0.3-3	97-98
DeBPE**						<11	88-99
DeBPE**					0.85	21.8	77.4

*: Current commercial product **: no longer produced

2.1.3 Tetrabromobisphenol A and derivates

Commercial production of tetrabromobisphenol A is based on bromination of bisphenol A (TBBPA) in methylene chloride as a solvent. Product purity is typically >99.5%. Impurities generally consist of lower brominated TBBPA congeners (EU, 1996). Derivates of TBBPA are produced through moderate polymerisation of TBBPA (oligomer production) or by addition of (brominated) aromatic molecules at the hydroxyl positions of TBBPA. Approximately 20% of the total TBBPA production are converted into these derivates (WHO, 1995). Characteristics of major TBBPA compounds are given in table 2.3 to 2.6.

Table 2.3
Characteristics and physical properties of commercial TBBPA compounds (OECD, 1994; WHO, 1995, Hardy 1997)

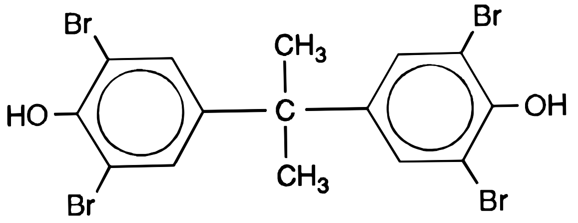
Substance	Tetrabromobisphenol A (TBBPA)
CAS number	79-94-7
Chemical formula	$C_{15}H_{12}Br_4O_2$
Molecular mass	543,93
Bromine (%)	59
Physical state	white crystalline powder
Chemical structure	
Synonyms	4,4'-isopropylidene-bis(2,6-dibromophenol); 2,2-bis(3,5-dibromo-4-hydroxy-phenyl)propane; phenol,4,4'-isopropylidenebis(dibromo); 3,3',5,5'- tetrabromobisphenol A; tetrabromodihydroxy diphenylpropane; Tetrabromodian
Technical products	Great Lakes BA-59-P; Saytex RB-100; Saytex RB-100 ABS; FR -1524; Bromdian; FG 2000; Fire Guard 2000; Firemaster BP 4A; Tetrabrom.

Table 2.4
Characteristics and physical properties of commercial TBBPA brominated epoxy oligomer (OECD, 1994; WHO, 1995)

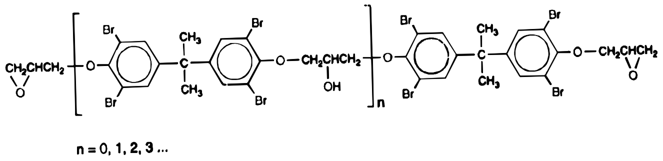
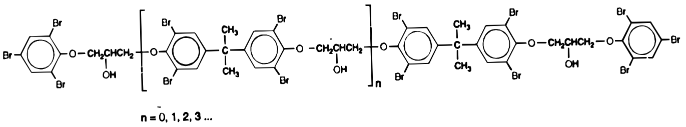
Substance	**TBBPA Brominated epoxy oligomer**
CAS number	-
Chemical formula	$(C_{15}H_{10}Br_4O_2 \,.\, C_3H_6O)_n \,.\, C_{21}H_{20}Br_4O_6$ (EP - type)
Molecular mass	1.300 - 40.000
Bromine (%)	50 – 52
Chemical formula	$(C_{15}H_{10}Br_4O_2 \,.\, C_3H_6O)_n \,.\, C_{15}H_{10}Br_6O_2$ (EC - type)
Molecular mass	1.400 – 3.000
Bromine (%)	55 – 59
Physical powder	Light yellow powder
Chemical structures EP – type EC – type	 
Synonyms	-
Technical products	-

Table 2.5
Characteristics and physical properties of commercial TBBPA Carbonate oligomer (BC-52) (OECD, 1994; WHO, 1995)

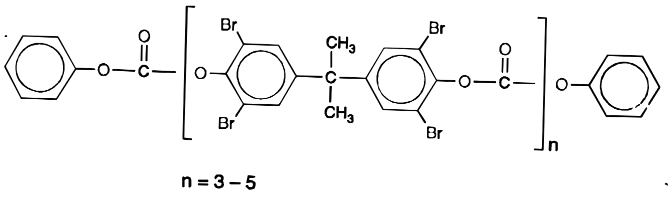
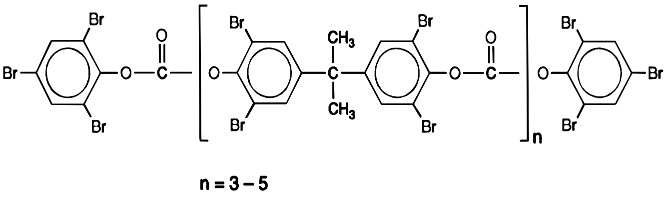
Substance	**TBBPA Carbonate oligomer (BC-52)**
CAS number	94334-64-2
Chemical formula	$(C_7H_5O_2) \,.\, (C_{16}H_{10}Br_4O_3)_x$ x = 3-5
Molecular mass	1920 – 3060
Bromine (%)	55
Physical state	White powder
Chemical structure	
Synonyms	-
Technical products	-

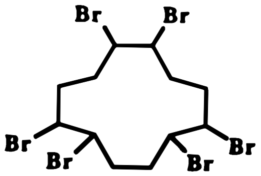
Table 2.6
Characteristics and physical properties of commercial TBBPA Carbonate oligomer (BC-58) (OECD, 1994; WHO, 1995)

Substance	TBBPA Carbonate oligomer (BC-58)
CAS number	71342-77-3
Chemical formula	$(C_7H_2Br_3O_3) . (C_{16}H_{10}Br_4O_3)_n . (C_6H_2Br_3)$ n = 3 - 5
Molecular mass	2400 – 3600
Bromine (%)	55
Physical state	White powder
Chemical structure	
Synonyms	-
Technical products	-

2.1.4 Polybrominated cyclo-aliphatics

Major non-aromatic brominated flame-retardant is hexabromocyclododecane (HBCD) which is produced through bromination of olefins in propanol (RIVM, 1993). This compound used to be produced in small quantities, but currently its use increases rapidly, especially for applications in foam insulation boards (Hardy, 1997). Characteristics of HBCD are given in table 2.7.

Table 2.7
Characteristics and physical properties of Hexabromocyclododecane (HBCD) (OECD, 1994; WHO, 1997, Hardy 1997)

Substance	Hexabromocyclododecane (HBCD)
CAS number	25637-99-4 or 3194-55-6
Chemical formula	$C_{12}H_{18}Br_6$
Molecular mass	642
Bromine (%)	75
Physical state	White powder
Chemical structure	
Synonyms	-
Technical products	-

2.2 Physico-chemical characterisation

2.2.1 Polybrominated biphenyls (PBB)

Chemical and physical data for commercial PBBs in table 2.8 demonstrate that properties vary strongly with the PBB product. All PBBs have a very low vapour pressure. Their volatility can vary over a wide range, but is still significantly lower than that of corresponding PCBs (WHO, 1994a; (Pijnenburg, 1995).

The solubility of all PBBs in water is very low and decreases with the bromine content. Determination of the water solubility of these hydrophobic compounds is difficult to perform due to preferent adsorption on particles. Solubility in water can further vary due to co-solubilisation by other substances/pollutants (WHO, 1994a). For instance, PBBs were found to be 200 times more soluble in landfill leachate than in distilled water. Most PBBs have a log K_{ow} values >7, and are therefore regarded as superlipophilic compounds (Prins, 1996).

Brominated compounds have a lower solubility in water than corresponding chlorinated compounds (Pijnenburg, 1995). PBBs show further an unusual chemical stability and resistance to acids, bases, reduction, oxidation or heat. In that sense PBBs are chemically comparable to PCBs. However, chlorine atoms are stronger bound to polybiphenyl than bromine atoms (WHO, 1994a). As for PCBs, chemical stability of PBBs varies strongly with halogenation and substitution patterns (Safe, 1984). Unlike PCBs, the reactivity of PBBs has not been well studied and documented in the literature (de Boer, 1999).

Table 2.8
Chemical and physical data of commercial PBB products (WHO 1994 a;Pijnenburg, 1995)

Compound	**HexaBB**	**0ctaBB**	**NonaBB**	**DecaBB**
CAS no	36355-01-8	2858-07-7	69278-62-2	13654-09-6
Commercial product	FM BP-6	XN-1902	Bromkal 80-9D	Adine 0102
Molecular formula	$C_{12}H_4Br_6$	$C_{12}H_2Br_8$	$C_{12}H_lBr_9$	$C_{12}\ Br_{10}$
Molecular mass	627	785	864	943
Melting point (°C)	72	200- 250	220-290	380-386
			360-380	
			385	
Decomposition Point (°C)	300-400	435	435	395; >400
Temperature (°C)		250 - 350 °C	300 °C	341 - 388 °C
Volatility (weight loss)		1% - 50%	1 - 2%	<10% - 25%
Vapour Pressure (Pa)	25°C 0.000007	-	-	< 0.0000006
	90°C 0.01			
	140°C 1			
	222°C 100			
Solubility H20 (25°C ; ìg /1)	11 – 610	30-40	Insoluble	<30
- distilled	0.32			
- deionized	0.06			
- as pure BB 153	30			
Soluble in (28°C; g/kg)	CCl4 300	Ether 18	Insoluble	CCl4: 10
	Benzene 750	Benzene 81		
	Chloroform 400			
	Toluene 970			
	Dioxane 150			
Log K_{ow}	7.20	-	-	8.58

2.2.2 Polybrominated diphenylethers (PBDE)

Due to the central oxygen atom, there is less similarity in the molecular structure between PBDEs and PBB than between PBBs and PCBs (WHO, 1994b). Commercial PBDEs are rather stable compounds with boiling points ranging between 310 and 425°C and with low vapour pressures (WHO, 1994b; Sellström, 1996; EU 1999a, b, c) (see Table 2.9).

The volatility of PBDEs and their solubility in water is very low, especially that of higher brominated diphenylethers. The commercial PBDEs are lipophilic substances with increasing log K_{ow} values at higher bromine content (WHO,1994b).

Table 2.9
Chemical and physical data of commercial PBDE mixtures (WHO, 1994b)

Compound	**TetraBDE**	**PentaBDE**	**0ctaBDE**	**DecaBDE**
CAS no	40088-47-9	32534-81-9	32536-52-0	1161-19-5
Molecular formula	$C_{12}H_6Br_40$	$C_{12}H_5\ Br_50$	$C_{12}H_2Br_8O$	$C_{12}Br_{10}0$
Molecular mass	486	565	801	959
Melting point (°C)	-	-7 – -3	200	290-306
			79- 89	
			75-125	
			170-220	
Decomposition Point (°C)	-	> 200	-	320 – 425
Volatility (% weight loss)	-	-	-	1% at 319 °C
				5% at 353 °C
				10% at 370 °C
				50% at 414 °C
				90% at 436 °C
Vapour Pressure (10^{-6} Pa)	250 – 330	29 – 73	0.12 – 0.23	4.6 at 25 °C
				270 at 250 °C
				550 at 278 °C
				1360 at 306 °C
Solubility H_20 (25°C; ìg/l)	10.9	2.4	0.5	20-30
Well soluble in (25°C; g/kg)	-	Methanol 10	Toluene 190	O-xylene 8.7
			Benzene 200	
			Styrene 250	
Log K_{ow}	5.9 – 6.2	6.6 – 7.0	6.3 – 8.9	6.3 – 10.0

2.2.3 Tetrabromobisphenol A (TBBPA) and derivates

Tetrabromobisphenol A

Tetrabromobisphenol A is a white colourless crystaline compound with low solubility in water and extreme low vapour pressure (see table 2.10). Due to its high log K_{ow} value (4.5-5.3), it is preferably bound to soil or sediment. Only low levels in surface water are detected (<0.05 µg/l; WHO, 1995). Levels in ambient air near production sites contained only minor TBBPA traces (<2 $\mu g/m^3$; WHO 1995).

In soil, tetrabromobisphenol A is aerobically degradable with typical half-lives of 50 to 100 days. Anaerobic degradation rates are comparable (WHO, 1995). Due to its high hydrophobicity, TBBPA has a high potential for bioaccumulation in aquatic organisms, but is seldom detected in biological species due to rapid excretion (WHO, 1995, IUCLID, 1996).

TBBPA Epoxy oligomer

At standard temperature and pressure, TBBPA Epoxy oligomer EP-type (epoxy end-capped) is a light yellow powder with a molecular weight of 1,300-40,000 and a reactive epoxy group at the hydroxyl ends of the molecule. Physico-chemical data are not available. However, based on the high molecular weight and properties of similar organic compounds, it is expected that water solubility and vapour pressure will be extremely low. Furthermore it is assessed that the bioavailability of large molecules like this is extremely low ((WHO, 1995; Hardy, 1997).

The other congener, the EC-type is a light yellow powder and has non-reactive tribromophenol groups at both ends of the molecule (WHO,1995). Typical molecular weight is 1,400-3,000. Standard physico-chemical data are not available (OECD,1994). With respect to its behaviour in the environment, similar properties as for the EP-type congener are expected.

TBBPA Carbonate oligomer BC 52 and BC 58

Both congeners are white powders with high melting points (210-260 °C). Typical molecular weights vary from 1,900 to 3,600, depending on the number of monomers. Data on other relevant properties are lacking (WHO, 1995; OECD, 1994). For the BC 52 (methoxy) congener, a water solubility of 1,000 mg/l is reported. Compared with solubilities of similar compounds, this value seems too high to be realistic. The solubility of tribromophenol substituted compound (BC 58) in water is negligible (WHO, 1995; OECD, 1994).

Table 2.10
Chemical and physical properties of TBBPA compounds (OECD, 1994; WHO, 1995, Hardy 1997)

Substance	Unit	Tetrabromobisphenol A (TBBPA)
Melting point	(°C)	181 – 182
Boiling point	(°C)	316
Vapour pressure	(10^{-6} Pa)	<133 at 20°C
Weight loss		95% at 500°C
Solubility in water	(µg/l)	720 at 20°C
		4,160 at 25°C
		1,770 at 35°C
Solubility in solvents	(g/l)	styrene <10 at 25°C
		toluene 64 at 25°C
		methanol 920 at 25°C
		aceton 2.400 at 25°C
Log K_{ow}		4.5 – 5.3

Table 2.10
Chemical and physical properties of TBBPA compounds (OECD, 1994; WHO, 1995, Hardy 1997) continued

Substance	**Unit**	**TBBPA Brominated epoxy oligomer**
Melting point	(°C)	n.a.
Boiling point	(°C)	n.a.
Decomposition point	(°C)	n.a.
Weight loss		n.a.
Log K_{ow}		n.a.
Substance	**Unit**	**TBBPA Carbonate oligomer (BC-52)**
Melting point	(°C)	210 – 230
Boiling point	(°C)	n.a.
Vapour pressure	(10^{-6} Pa)	n.a.
Weight loss		25% at 475°C
Solubility in water	(mg/l)	< 1,000 at 25°C
Log K_{ow}		n.a.
Substance	**Unit**	**TBBPA Carbonate oligomer (BC-58)**
Melting point	(°C)	230 – 260
Boiling point	(°C)	n.a.
Vapour pressure	(10^{-6} Pa)	n.a.
Weight loss		25% at 475°C
Solubility in water	(mg/l)	Negligible
Log K_{ow}		n.a.

2.2.4 Hexabromocyclododecane (HBCD)

Hexabromocyclododecane is a white crystaline compound with low vapour pressure and water solubility (4 µg/l; Hardy, 1997; OECD, 1994). Due to its high log K_{ow} value (5.81-7.0), it will strongly bind to soil and sediment (WHO, 1997). Due to its high hydrophobicity, it has a high bioaccumulation potential. However, HBCD is readily metabolised and excreted in rats. (Hardy, 1997).

Table 2.11
Chemical and physical properties of HBCD (OECD, 1994; WHO, 1994, Hardy 1997)

Substance	**Unit**	**Hexabromocyclododecane (HBCD)**
Melting point	(°C)	170 – 180
Boiling point	(°C)	n.a.
Decomposition point	(°C)	>200
Vapour pressure	(10^{-6} Pa)	62.7
Weight loss		50% at 280°C
Solubility in water	(ìg/l)	3.4 – 8
Log K_{ow}		5.81-7.0

2.3 Congeners

2.3.1 Polybrominated biphenyls (PBB)

All PBBs have a very low vapour pressure. Their volatility can vary over a wide range, but it is still significantly lower than that of corresponding PCBs. Most PBBs have a log K_{ow} values >7, and have a lower solubility in water than corresponding chlorinated compounds (Pijnenburg, 1995). PBBs show further an unusual chemical stability and resistance to acids, bases, reduction, oxidation or heat. In that sense PBBs are chemically comparable to PCBs. However, chlorine atoms are stronger bound to polybiphenyl than bromine atoms. As for PCBs, chemical stability varies strongly with halogenation and substitution patterns (WHO, 1994a; Safe, 1984).

2.3.2 Polybrominated diphenylethers (PBDE)

Because of the presence of an oxygen atom, there is less similarity in the molecular structure between PBDEs and PCBs than between PBBs and PCBs. The wide spread use of polychlorinated diphenylethers is not known (WHO, 1994b).

2.3.3 Tetrabromobisphenol A (TBBPA)

Commercial use of chlorinated bisphenol A compounds and their environmental properties are not known (WHO, 1995).

2.3.4 Hexabromocyclododecane (HBCD)

Data on commercial use and environmental properties of chlorinated cycloaliphatics are lacking (WHO, 1996).

2.4 References

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3. Production and use

3.1 Major compounds and producers

The brominated flame-retardant industry currently consists of around 10 major companies that produce in total 50 chemicals, of which 30 compounds are used commercially. A summary of major brominated flame-retardants is given in table 3.1 (EU, 1996)

Table 3.1
Major additive and reactive brominated flame-retardants (EU, 1996)

Additive compounds	Reactive compounds
Aliphatic Compounds	
Tetrabromoethylene Pentabromoethane 1.1.2.2-Tetrabromoethane 1.2.3.4-Tetrabromoethane Octabromohexadecane Hexabromocyclohexane Tetrabromocyclododecane Hexabromocyclododecane	Bromoform Vinyl bromide Ethylene bromohydrine Dibromopentyl glycol
Aromatic Compounds	
Pentabromodiphenylether Octabromodiphenylether Decabromodiphenylether Decabromobiphenyl Hexabromobenzene Pentabromoethylbenzene 1.2-Dibromoethylbenzene Tetradecabromodiphenoxybenzene	Tetrabromobisphenol A Tetrabromophthalic anhydride Tribromophenol Pentabromophenol Dibromostyrene

From the chemicals listed in table 3.1, the most widely used groups of brominated flame-retardants are (OECD, 1994):
- Tetrabromobisphenol A (TBBPA) and derivates;
- Polybrominated diphenylethers (PBDE);
- Polybrominated biphenyls (PBB)
- Polybrominated (cyclo)aliphatics (PBCA)

Main application areas for above mentioned chemicals are the electrical engineering and electronics sector (consumer electronics, computers etc), transportation sector (upholstery) and building and construction sector. Generally, applications can be divided into the use in plastics (polymers) and textiles (upholstery). A summary of the major producers of brominated flame-retardants is given in tables 3.2 (EU, 1996):

Table 3.2
Major producers of brominated flame-retardants (EU, 1996)
*: not specified

Country	**Producer**	**Location**
The Netherlands	Broomchemie	Terneuzen
Great Britain	Great Lakes Chemical Ltd Warwick Int. Specialities Ltd	Aycliffe Leeds
France	Albemarle CECA Atochem / Ferro	Thann Port-de-Bouc
Israel	Dead Sea Bromines	*
USA	Albemarle Great Lakes Chemical Corp.	*
Japan	Tosoh / Matsunaga / Nippo	*

PBBs are exclusively produced by CECA Atochem, which also produces major quantities of decaBDE. Warwick Specialities is the only producer of pentaBDE, which is mainly used for flame retardation of upholstery and textiles in the UK

(EU, 1996). Broomchemie in Terneuzen produced until recently octaBDE, but nowadays the brominated flame-retardant production is focused on TBBPA and HBCD (RIVM, 1993; Eurobrome, 1999).

3.2 Production processes

3.2.1 General

The production of polybrominated biphenyls, diphenylethers, bisphenol A and cyclo-aliphatics is based on the bromination of the parent molecules with elemental bromine. All production processes, with exception of TBBPA production which is operated continuously, are operated batch-wise and have the same general process characteristics. A generalised process description is given in figure 3.1. Detailed descriptions of the individual production processes are given in Annex 2.1 (EU 1996, RIVM 1993).

3.2.2 Bromination

For production of the brominated chemicals, the parent compounds are dissolved into a reaction solvent. In PBB- and PBDE-production liquid bromine is used as reaction solvent. In TBBPA production methylene chloride is used for this. In special cases a catalyst is added to the reaction mixture. The reagent mixture is heated in a closed reaction vessel at temperatures between 40 and 60°C, the latter being the boiling point of bromine. The reactor is equipped with a reflux condensor, which operates at 10-20°C, to recycle bromine vapours. Non-condensable reaction products such as hydrogen bromide are removed in serial scrubbing towers. In TBBPA production, hydrogen bromide is converted into bromine by hydrogen peroxide addition.

At the end of each process cycle, a solvent is added to the reaction mixture to dissolve the polybrominated products. Excess bromine is distilled from the reaction vessel, condensed and recycled for subsequent use in following production cycles. After completion of the bromine recovery, the reaction mixture is mixed with water to dissolve hydrogen bromide and other water soluble products. The reaction mixture is subsequently decanted to separate solvent and water layers. Wastewater is sent to the production site's effluent treatment plant.

3.2.3 Product recovery

Solid polybrominated product is primarily separated from the solvent by centrifugation. Solvent traces in the product are removed by vacuum drying. Evaporated solvent is condensed and recycled for subsequent use. Dried product is grinded and pneumatically conveyed into storage silos for subsequent packaging and transport.

3.2.4 Hydrogen bromide recovery

Uncondensed bromine and hydrogen bromide from the reflux condensors are removed in serial scrubbing towers, equipped with water or an organic solvent. In this step a typical HBr liquor of 47-48% is produced, which is used in the production of other brominated compounds. Tail gases from the scrubbers are treated in a caustic scrubber before discharge into the atmosphere.

3.2.5 Wastewater treatment

Wash water from the decanter contains unreacted bromine, hydrogen bromide and suspended particles of the brominated product. For removal of suspended particles, the wastewater is usually treated by sedimentation and/or filtration. Subsequently the wastewater is transferred to the central wastewater treatment plant to undergo biological treatment. In special cases an additional flocculation/sedimentation step is required to remove catalyst particles, if used. Residues from the sedimentation, decantation, flocculation and filtration steps and waste activated sludge from the biological treatment plant are dewatered and landfilled or incinerated (RIVM, 1993).

3.3 Flame-retardant systems

3.3.1 Halogenated flame-retardants

Halogenated flame-retardants can consist of fluorinated, chlorinated, brominated and iodinated compounds. The effectiveness of halogen-containing flame-retardants, which is based on the emission of HX molecules, increases as follows: F < Cl < Br < I. Fluorine and iodine based compounds are not used as flame-retardants because both types do not interfere sufficiently with the combustion process. Fluorine, which is bound too strong to carbon, will only result in minor HF emissions. Iodine, which it is bound too loose to carbon, will cause uncontrolled HI emissions. Chlorinated flame-retardants release HCl over a wide temperature range, resulting in low HCl concentrations. Therefore relatively high loadings are required (Troitzsch, 1998).

Brominated compounds are most effective since its bonding to carbon enables it to interfere at a more specific point in the combustion process. It is assumed that HBr is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone. The temperature zone at which this occurs, is far below the ignition temperature of the polymer. For a summary on flame-retardation mechanisms see Annex 2.3.

Bromine atoms can be bound either aliphatically or aromatically to the retardant's base molecule. The more effective aliphatic bromine compounds break down more easily and are therefore less temperature resistant than aromatic compounds. Flame-retardants with aromatic bromine atoms have the highest market share. They can be subdivided into several classes based on the aromatic structure. The overall suitability depends on plastic characteristics and the method of incorporation. For incorporation of flame-retardants, distinction can be made between reactive and additive compounds and synergetic systems of both types (Troitzsch, 1998).

3.3.2 Reactive flame-retardants

As a reactive compound, the flame-retardant is built chemically into the base molecule of the polymer and becomes part of the polymer structure. This prevents possible leaching and/or volatilisation of the flame-retardant. In addition, they have no plasticising effect and do not affect the thermal stability of the polymer. They are mainly used in plastic fibres in which they can easily be incorporated, especially polyesters, epoxy resins, and polyurethanes.

3.3.3 Additive flame-retardants

These compounds are mixed with the plastic either before, during, or more frequently, after polymerisation. Due to this type of physical mixing, leaching and volatilisation may occur under specific circumstances. Additive flame-retardants are mainly used in plastics. If they are compatible with the plastic, they also act as a plasticiser, otherwise they are considered as fillers.

3.3.4 Synergetic flame-retardant systems.

Specific combinations of additive and reactive flame-retardants can produce an synergistic effect. When used alone, synergists show no or negligible effectiveness. The synergetic effect occurs when they are used together with specific flame-retardants. These flame-retardants/ synergist systems have achieved great importance in practical use because they are usually less expensive than singularly used flame-retardants. A frequently used system is the combination of antimony trioxide and brominated flame-retardants.

3.4 Major applications

Most important industry sectors where brominated flame-retardants are used, are the electrical engineering and electronics sector, wires and cables, transportation and the building & construction sector. Major application areas are summarised in table 3.3.

Table 3.3
Major application areas for flame-retardants (Troitzsch, 1998)

Industry sector	Applications
Electrical Engineering and Electronics	Consumer electronics housings and backplates Office electronics housings and backplates Printed circuit boards Appliances
Motor vehicles	Wire & cable Upholstery
Rail vehicles	Compartment linings and coverings Insulation Upholstery
Aircraft	Panels Carpets Flooring
Building and construction	Thermal insulation for roofs, facades, walls Sheeting for roofs Floor coverings Ducting & conduits Panels, linings and coverings

The electrical engineering and electronics sector is the largest application area for brominated flame-retardants. In 1998, approximately 60% of the global demand of 300,000 tonnes was used in this sector (CW, 1998a). When this use is related to the regional consumption of electrical engineering and electronics (E&E) plastics, it shows that specific use of brominated flame-retardants in European E&E plastics is considerably lower than in the USA and Japan (see table 3.4).

Table 3.4
Use of brominated flame-retardants (BFR) in (E&E applications)

1998	W-Europe	USA	Japan	
Total plastics[1]	28000	27500	11000	Kton/y
E&E plastics[1]	2500	2500	1000	Kton/y
BFR's[2]	39	57	39	Kton/y
BFR / E&E	0,016	0,023	0,039	Ton/ton

1: APME 1999a and OECD 1994
2: computed from CW 1998a

The lower use of brominated flame-retardants in European E&E plastics is largely caused by
less stringent fire safety requirements for consumer electronics in Europe. As a consequence of international discussions on fire safety standardisation, it is expected that use of (brominated) flame-retardants in E&E applications in Europe will increase in the future (APME, 1999b).

Typical consumption data for the use of individual brominated flame-retardants in plastics are given in table 3.5. From this table it can be seen that the use of tetrabromobisphenol A (TBBPA) derivatives and polybrominated diphenylethers (PBDE's) account for >80% of the total flame-retardant use (OECD, 1994).

Table 3.5
Use of brominated flame-retardants in various plastics in Japan (1992)

BROMINE COMPOUNDS	BFR use (tonnes)	ABS*	PS	EPS	PE	PP	PVC	PC	PBT	PET	PA	EPOXY	PHENOL	UPE	PU
Decabromodiphenylether	8,000	x	x		x	x	x	x	x	x	x	x	x	x	x
Octabromodiphenylether	1,000	x	x		x								x		
Tetrabromobisphenol A	15,000	x	x					x				x	x	x	
TBBPA PC oligomer	3,000	x						x	x	x			x		
TBBPA epoxy oligomer	4,000	x	x						x				x		
Hexabromocyclododecane	1,000		x	x					x	x					x
Other compounds	5,000	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Examples of final products		1, 2	1, 2	6	4	2	4, 6	1, 2	2, 3	3	3	3, 5	5	5, 6	7

1: business machine housing; 2: electrical appliance housing; 3: electronics parts; 4: wire and cables; 5: circuit boards; 6: building materials; 7: cushioning materials
*: see Annex 1

Furthermore it is shown that decabromodiphenylether is used in nearly all applications. This can be explained by the fact that, of all brominated chemicals, decabromodiphenylether is most economical in relation to its bromine content (OECD, 1994).

3.5 Demands and developments

3.5.1 Historic demands

In 1992, global demand for brominated flame-retardants amounted to 150,000 tonnes, being approximately 25% of the overall flame-retardant market of 600,000 tonnes. Demands for brominated compounds are coming mainly from 3 regions:

- North America (40%);
- Western Europe (25%)
- Japan (25%).

The rest is supposed to be consumed in China and the other Asian countries (OECD, 1994).

Within the above mentioned regions, consumption varies greatly from country to country. Some non-producing countries such as Belgium, Canada, Germany, Italy, the Scandinavian countries, Spain and Switzerland only import brominated flame-retardant chemicals and incorporate them in products used domestically. Producing countries like USA, UK, France, the Netherlands and Israel compound their chemicals into polymers for domestic and foreign use, or export them for compounding in foreign countries. Tetrabromobisphenol A and derivatives were responsible for 33% of the 1992 world market whereas brominated diphenylethers accounted for 27%. Both groups of chemicals are produced and used world wide (OECD, 1994).

Polybrominated biphenyls, in particular hexa-, octa- and decabromobiphenyls, were produced world-wide during the 1970s in amounts of several thousand tonnes/year. As a result of the Michigan disaster in 1974, when hexaBB was accidentally mixed with cattle feed, major environmental and health concern was risen to the use of these compounds (de Boer, 1999). HexaBB production in the USA ceased in 1974, whereas the production of octaBB and decaBB continued until 1979. German production of Bromkal 80-9D, a mixture of highly brominated PBBs, ceased by mid 1985, whereas the PBB production in UK was already stopped in 1977. In France, the production of decaBB (Adine 0102), declined from approximately 2,000 tonnes/year in the 1980s to a current amount of several hundred tonnes/year, mainly used in France, UK, Spain and the Netherlands (de Boer, 1999).

3.5.2 Global developments

Market figures for brominated flame-retardants from 1998 indicate that global demand has doubled from 150,000 to 300,000 tonnes between 1992 and 1998. This equals an average annual growth rate of 12.2% (CW, 1998a). This figure is in good agreement with growth estimates from the industry in 1992 (EU, 1996). For the next 5-6 years it is estimated that annual growth in global demand will vary from 8 to 9 % (Roskill, 1999). Historic growth of the USA domestic market for brominated flame-retardants (8.0%) was significantly lower than global growth. In 1998 the domestic market demand in the USA amounted to approximately 95,000 tonnes/year, which means an 60% increase relative to 1992. For the period 1998-2004, the annual growth of the domestic brominated flame-retardants market is supposed to be slightly higher (8.5%) (CMR, 1999a).

Separate data for brominated flame-retardant demand in western Europe and Japan are not available. On basis of equal economical growth e.g. consumption growth as in the USA, it is assumed that the market growth in the 1992-1998 period is more or less the same as for the USA market. Due to current environmental constraints, the annual growth for the next 5-6 years is estimated to be slightly lower than in the USA (8.0%). Overall global flame-retardant market (brominated and non-brominated) increased at an annual rate of 6.0%, corresponding with an overall increase of approximately 40%) (1992 –1998). It is estimated that this market will grow 5-6% annually for the next 5-6 years (CW, 1998b).

An overall summary of historic and projected data is given in table 3.6. A graphical presentation of the brominated flame-retardants demands is given in figure 3.2. The amounts in table 3.6 refer to demands and not to production, which implies that demands in a specific region do not necessarily correspond with regional production.

From table 3.6 can be concluded that between 1992 and 1998:

- BFR demands in Japan and western Europe increased to 60,000 tonnes;
- BFR demands in non-OECD countries increased from 14,000 to 85,000 tonnes.

Furthermore, it is demonstrated that at future growth rates:

- the global BFR market will be increased by 60% in 2004;.
- in 2004 the major BFR market will be in the USA and non-OECD countries;

Table 3.6
Demand estimates for brominated flame-retardants (1992-2004)

	Brominated Flame Retardants (BFR)					Total FR	
	W-Europe	USA	Japan	Other*	World	World	
1992	38,000	60,000	38,000	14,000	150,000	600,000	tonnes/y
1998	60,000	95,000	60,000	85,000	300,000	850,000	tonnes/y
2004 **	95,000	155,000	95,000	145,000	490,000	1,170,000	tonnes/y
Growth							
1992-1998	8.0	8.0	8.0	35	12.2	6.0	% / y
1998-2004**	8.0	8.5	8.0	9.3	8.5	5.5	% / y

*: non-OECD (China / other Asian countries) **: projected figures FR: flame-retardant

From market estimates in 1998 it was further assessed that between 1992 and 1998 the global demand for tetrabromobisphenol A (TBBPA) had increased from 50,000 to 145,000 tonnes per year, corresponding with an average annual growth of 19%. (CMR, 1999b). Investment decisions in the USA indicate that TBBPA production will further increase (CMR, 1999b). Similar developments are observed for brominated flame-retardants production in the Netherlands, where overall production increased from 17,000 tonnes (1991) to 37,000 tonnes in 1996. This growth was mainly due to increased TBBPA production (Eurobrome, 1999)

Global TBBPA demand growth for the 1998-2004 period is estimated at 8-9% annually (Chemexpo, 1999). A graphical presentation of TBBPA demand in relation to the overall brominated flame-retardants demand is given in figure 3.3. From demand developments can be assessed that the TBBPA market share has increased from 33% in 1992 to 50% in 1998.

3.5.3 Competition with non-brominated flame-retardants

According to OECD estimates, the world demand in 1992 for flame-retardants chemicals was about 600,000 tonnes and could be divided into the following products (see table 3.7)

Table 3.7
World demand for flame-retardants (tonnes/year)

Base chemical	1992	1998	2004
Aluminium	170,000	*	*
Bromine	150,000	300,000	490,000
Phosphorous	100,000	*	*
Chlorine	60,000	*	*
Antimony	50,000	*	*
Nitrogen	30,000	*	*
Other	40,000	*	*
Total	600,000	850,000	1,170,000

*: not available

Figure 3.2
Brominated flame retardants demand

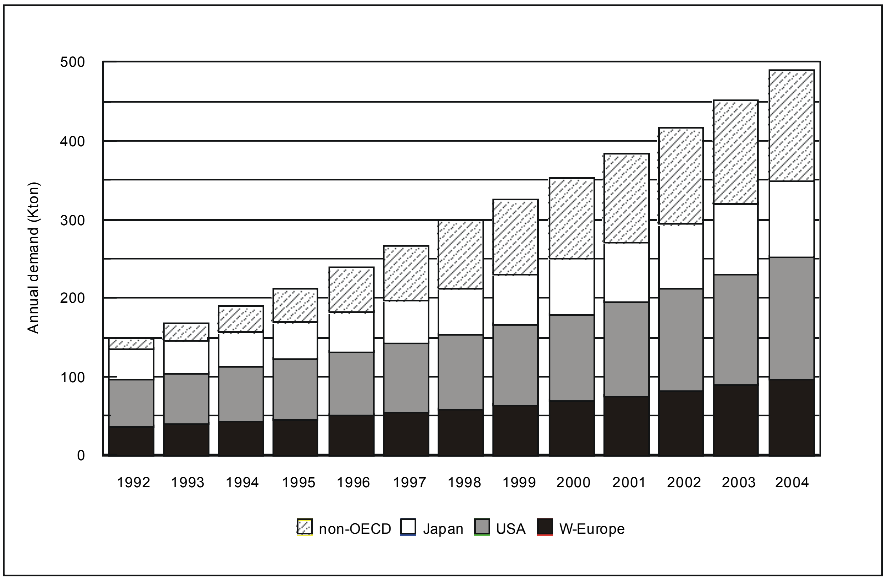
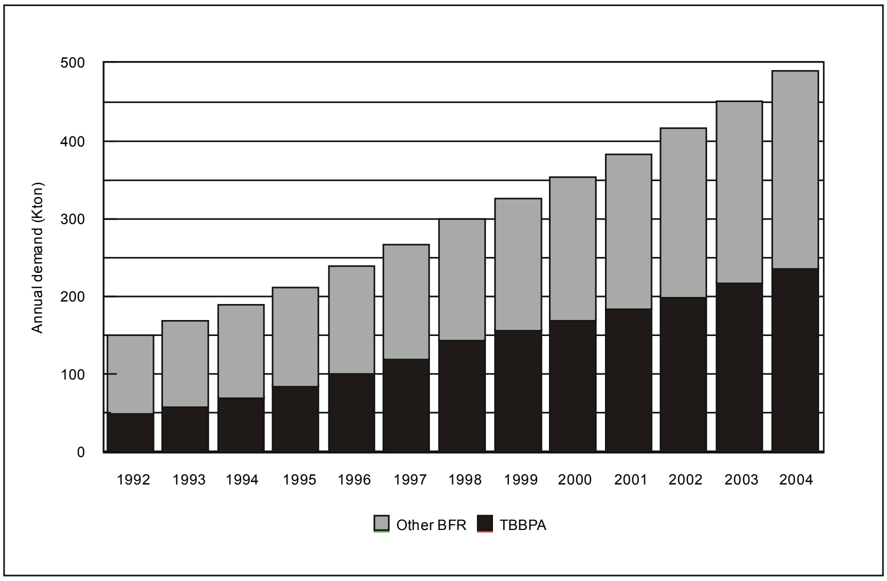


Figure 3.3
Global demand for brominated flame retardant



Comparison of the 1998 demands for brominated flame-retardants with total flame-retardants demands demonstrates that the relative share of brominated flame-retardants increased from 25% (1992) to 35% in 1998. In 2004, the market share of brominated flame-retardants is expected to be ca 40%. Comparison of demand growths for brominated and non-brominated flame-retardants shows that growth in flame-retardants is slightly dominated by brominated compounds (see figures 3.4 and 3.5).

3.5.4 Specific demands in the European Union

PBBs

Estimates for the annual PBB demand in Western Europe are contradictory. Within the framework of OSPAR (OSPAR, 1999) reference is made to 1,000 tonnes, while manufacturer's communication indicates an amount of several hundreds tonnes (de Boer, 1999).

PBDEs

Figures for the overall PBDE demand in Western Europe are given in table 3.8. These figures are based on 1994 estimates from the brominated flame-retardant producers within the frame-work of the OECD, and refer to the total of all brominated diphenylethers.

Table 3.8
Production and import of polybrominated diphenylethers in EU (WHO, 1994b)

Year	Production (tonnes)	Imports (tonnes)	Total (tonnes)
1986	4,300	4,300	8,600
1987	3,600	3,500	7,100
1988	4,100	4,900	9,000
1989	3,800	7,100	10,900

A confidential industry source confirmed that total EU usage in 1999 was still in the range of 10,000-11,000 tonnes/year. Furthermore, production of octaBDE within the EU would have ceased in 1999 (EU, 1999b). Taking the demand and distribution figures from table 3.8 as a basis for the 2000 demand in Europe, the current demands for individual PBDEs are as follows:

Table 3.9
Demands of individual PBDE in Europe (EU, 1999b,c)

2000	**%**	**Tonnes/y**
DecaBDE	75	8250
Octa BDE	15	1650
PentaBDE	5	1100
Total	100	11000

Figure 3.4
Global demand for flame retardant

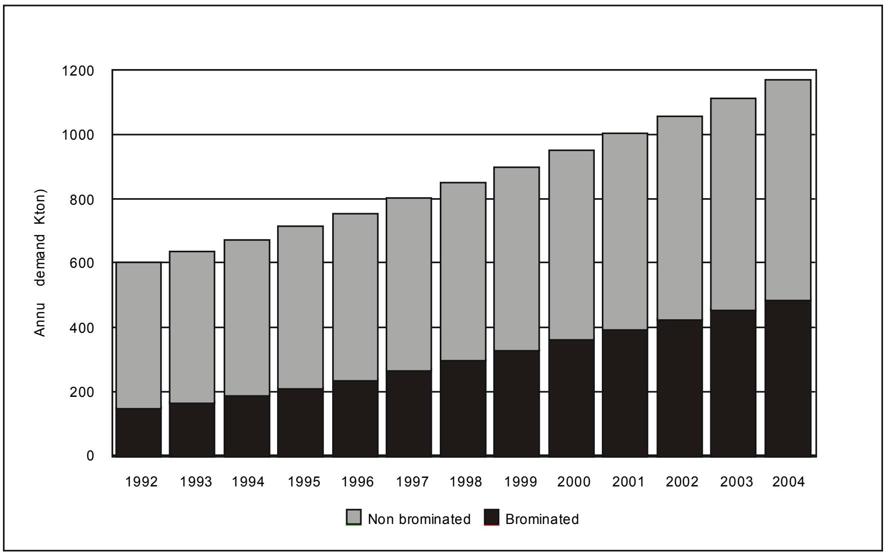
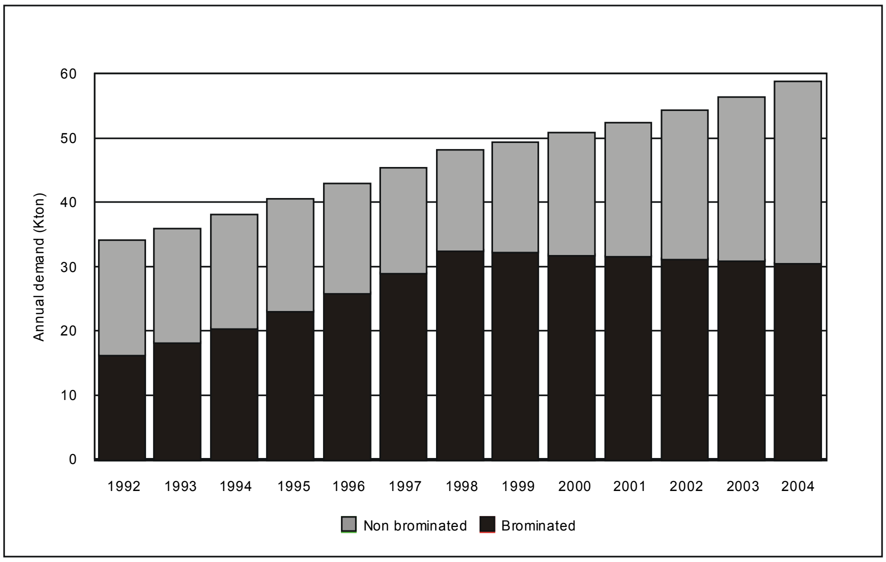


Figure 3.5
Global demand growt for flame retardant



TBBPA derivates and HBCD
Separate data for current TBBPA demand in Europe are not available. With a global TBBPA demand of approximately 170,000 tonnes/year in 2000 and a market share of 25% (WHO, 1995), the European demand is estimated at about 40,000 tonnes/year. From IUCLID data it is established that Broomchemie is also the major HBCD producer in the EU. According to Eurobrom, Broomchemie's current production is 5,000 tonnes/year (Greenpeace, 1999). Furthermore, significant HBCD amounts are imported via Belgium. Imported amounts are estimated to be in the same order as the produced amounts, so that the total HBCD demand in the EU is estimated at approximately 10,000 tonnes/year.

3.5.5 Specific demands in the Netherlands

PBBs and PBDEs
According to the Netherlands Flame Retardants Project Group, in 1998 the PBBs and PBDEs use was restricted to decaBB, decaBDE and octaBDE in E&E plastics and amounted to 790 tonnes. Due to confidentiality requirements, no specification was made for individual compounds. Only 4 tonnes of related products were supplied to the Netherlands internal market. The balance between the 790 and 4 tonnes is either exported as flame-retardant , in master batches or as flame-retarded polymer (PGFR, 1999a).

TBBPA derivates and HBCD
Specific data on the use of other brominated flame-retardants in the Netherlands were not available (PGFR,1999b). In order to estimate the overall use of these compounds, individual figures were derived from Western European demands on basis of the proportional production of (flame-retarded) plastics in the Netherlands.

With an overall European use of 70,000 tonnes of brominated flame-retardants in 2000 and a plastic market share in the Netherlands of 4.25% (APME, 1999a), the proportional Netherlands brominated flame-retardants market is estimated at 3,000 tonnes/year. Accordingly, annual TBBPA and HBCD demands are estimated at 1,700 and 420 tonnes, respectively. A summary of the individual demands is given in table 3.10.

Table 3.10
Estimated of BFR use in plastics (2000; in tonnes/year)

2000	W-Europe	The Netherlands
BFR retarded plastics	400,000	17,000
BFR in plastics	70,000	3,000[1]
TBBPA and derivates	40,000	1,700[1]
HBCD	10,000	420[1]
PBDE's	11,000	750[2]
DecaBB	<1,000	<40[1, 2]
Other compounds	8,000	90[3]

1: proportional to plastic demand 2: PGFR 1999a 3: balance

3.6 Production in the Netherlands

PBBs and PBDEs
According to recent EU risk assessment studies there is no current production of PBBs or PBDEs in the Netherlands (EU, 1996; EU, 1999b,c).

TBBPA derivates and HBCD
Individual production figures are not available (PGFR, 1999b). From Broomchemie company information annual TBBPA production in 1996 is estimated at approx. 22,000 tonnes (RIVM, 1993; Eurobrome, 1999). With an annual growth estimate of 8.5%, the TBBPA production in 2000 will be around 30,000 tonnes/year. From recent information about an environmental permit for production extension, current HBCD production at Broomchemie is estimated at 5,000 tonnes/year (Greenpeace, 1999).

3.7 Use in polymer processing

For incorporation into plastics, flame-retardants are processed at special companies/sites where they are compounded and integrated into plastic materials. An overall summary of the manufacture of flame-retarded materials is given in figure 3.6 (OECD, 1994).

3.7.1 Compounding

In this step, brominated flame-retardants and synergists are mixed together with pigments etc. to form a masterbatch which is sent to the polymer processor. Masterbatches can consist of solid and liquid mixtures, depending on the end application. Furthermore, base materials such as virgin plastics can be mixed in the compounding stage, to form typical mixtures containing up to 50% flame-retardant (EU, 1996).

Dry compounding usually consists of mechanical processes, where powder ingredients are thoroughly mixed at ambient temperature and pressure (20°C and 1 atmosphere). Mixtures are subsequently extruded at 200 - 220°C and pelletised. Product pellets are fluidised with air to remove fines. Dust containing air is treated in cyclones before discharge to air. Other relevant processes for potential emissions are the storage and (un)loading sections.

According to the properties of the brominated compounds (low water solubility and vapour pressure) major emission will be dust emission from dry product during transport, handling and mixing. Due to product saving and human health incentives, these losses are already minimised to a great extend, through fully closed process equipment. Another emission path will be the cleaning of mixing equipment, which is generally used in a batch wise mode. After each different batch, mixing vessels and equipment are cleaned with water. Wash water is discharged to wastewater treatment plant for removal of solid particles. Furthermore, water is used to clean storage buildings and handling equipment (EU, 1996).

3.7.2 Polymer processing

In this stage, flame-retardant chemicals, compound mixtures or masterbatches are incorporated into plastics by means of thermal treatment (moulding). Process temperatures typically range from 200 to 300ºC, depending on plastic properties, desired product quality and incorporation method. Incorporation is either performed by moulding injection, extrusion or compression. All processes are performed in fully closed equipment. Process vapours, generated at 200-300°C, are condensed. The condensate is treated in a decanter.

The organic fraction is separated and incinerated. Wastewater is discharged to the sewer. Wastewater from the rinsing process equipment, is discharged to the wastewater treatment plant for removal of spilled flame-retardant and possible waste materials coming from the moulding, extrusion and compression processes (EU, 1996).

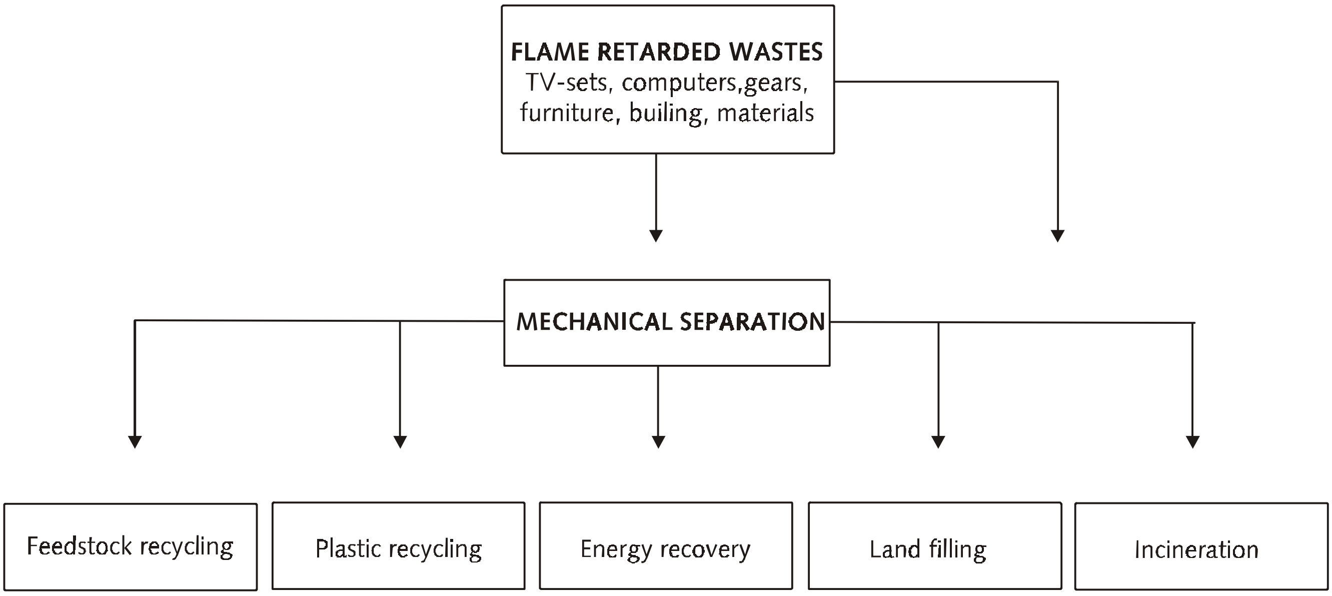
3.8 Waste disposal

3.8.1 General

Flame-retarded wastes are either generated in the form of used consumer goods or as industrial waste materials. Flame-retarded waste materials consist mainly of plastic waste materials from cars, computers and consumer electronics such as TV sets, audio equipment, etc.

Being a constituent of regular industrial, company and municipal waste, these flame-retarded waste materials are currently disposed of with these waste streams. In 1998 however, in the Netherlands a waste disposal directive came into force with respect to separate collection and treatment of white and brown goods (VROM, 1998).
According to this directive, flame-retarded plastics used in brown and white goods, must be separated and disposed of by controlled landfilling or incineration. It is estimated that, by diverting these brown and white goods from municipal waste incineration, the brominated pollutants content in bottom and fly ash can be lowered by approx. 90%. However, due to the short implementation period of the new directive, flame-retarded plastics are still largely disposed of through landfilling and incineration of (unseparated) municipal waste (VROM, 1998). A review of waste disposal and recovery techniques is given in figure 3.7.

Figure 3.7
Review of disposal methods for flame retarded wastes



3.8.2 Incineration of flame-retarded wastes

A significant disadvantage of brominated flame-retardants is that PBDDs and PBDFs may be formed during thermal treatment or waste incineration. These brominated compounds are estimated to be just as toxic as their chlorinated congeners PCDD and PCDFs, but little is still known about the actual toxicity of PBDDs and PBDFs (WHO, 1994a,b). Most research reports indicate that maximal PBDF or PBDD production is observed at temperatures between 400 and 600°C, depending on the type of brominated flame-retardant. However, highly toxic 2,3,7,8-substituted compounds were measured only in low concentrations (WHO, 1994b).

Another study showed that at 600°C, flame-retarded plastics with decaBDE or PBDE produced toxic 2,3,7,8-TeBDD and TeBDFs in incineration ashes at levels of 0.01-7 and 0.01-6 mg/kg respectively. At temperatures >800°C, concentrations of these compounds decreased below the detection limit (0.01 mg/kg). Pyrolysis experiments further demonstrated that PBDEs produce greater amounts of brominated dioxins and furans than PBBs. In this respect PBDEs can be considered more toxic than PBBs (Lahaniatis, 1991).

Quarts flask pyrolysis in N_2/H_2 atmosphere at 1100°C demonstrated that flame-retardants in printed circuit boards and electronic components still produce small amounts of toxic 2,3,7,8-TeBDFs in incineration ashes (29 µg/kg; Dumler-Gradl, 1995). Therefore, as with PCBs, thermal destruction of PBB and PBDE containing wastes should be carefully controlled. For PCBs, a residence time of 2 seconds at temperatures >1000°C is recommended. Since PBDDs and PBDFs are not detected at temperatures >800°C, a similar approach might be effective for adequate destruction of PBDEs and PBBs (WHO, 1994a).

Brominated dioxines and furanes can also be formed in plastic processing, as shown in a study with 78 TV's and 34 personal computers. Composed samples of plastics, flame-retarded with PBDEs and PBBs, already contained traces of

PBDFs and PBDDs. When only PBBs were used, these levels further increased during plastic recycling. In that sense, possible formation of PBDFs and PBDDs should also be included in the overall toxicity and risk assessment of PBBs and PBDEs (Riess, 1998).

Laboratory pyrolysis experiments with PBDEs and PBBs show that PBDFs and PBDDs are formed in various concentrations, depending on the nature of PBDEs and PBBs, polymer matrix, processing temperature, presence of oxygen and type of moulding equipment used (Lahaniatis, 1991). Antimony oxide, frequently used as a synergist in flame-retardant systems, can further play a catalytic role in formation of PBDFs and PBDDs (WHO, 1994b).

3.8.3 Waste separation and recycling

According to draft EU directives on banning integral disposal of hazardous compounds in solid wastes e.g. municipal solid waste (EU, 1998), industry initiatives are being developed to source separate brominated wastes and recycle these waste materials. Most initiatives are focused on separate collection of electrical/electronical goods and mechanical removal of flame-retarded plastics. Separated plastics are crushed to pellets (recyclate) for reuse or separate disposal.

Currently, mechanical waste separation and recovery is in a starting phase in the Netherlands (VROM,1998). Quantitative information on the (re)use of recyclates in the Netherlands is lacking, but from industry information can be concluded, that large amounts of these recyclates are imported to / exported from the Netherlands (APME, 1999a). For final reuse and treatment of recyclates, currently various pilot plant projects are performed on environmental sustainable recovery of plastic wastes and brominated constituents. Either by direct recycling and reuse of flame-retarded plastics, by extraction of flame-retardants from plastic wastes (feedstock recycling and/or bromine recovery) or by energy recovery in controlled incineration of recyclates (EBFRIP,1999) .

3.9 Potential alternatives

Due to present environmental concerns, there is a growing need to reduce the use of brominated flame-retardants, either by decreasing loading rates or by replacement with non-brominated alternatives. Brominated compounds also have the disadvantage that, to increase the bromine efficiency, heavy metal compounds such as Sb_2O_5 (in reactive systems) and Sb_2O_3 (in additive systems) are required (Shelley,1993).

For good fire resistance and low formation of toxic gases, currently special flame-retardants are available that contain only 25% bromine and which are used at loadings of 4-6%, whereas regular compounds contain up to 80% Br and are used in loadings of 15-25%. Intumescents, based on nitrogen and phosphorus compounds, also exhibit a low smoke release and are used in wiring and electronic housing applications, where smoke poses an immediate threat. However, they are far more costly than brominated compounds (Shelley, 1993).

Furthermore, there are various reactive brominated flame-retardants, which are chemically bound into the polymer's structure, thereby minimizing the environmental release of flame-retardants. For example, there is a 25% pelletized mixture of antimony pentoxide, bromine and polypropylene (PP) which is added to PP fibres for application in textiles, carpets and thin films. Furthermore, dibromostyrene (DBS) is used to make copolymers for adhesives and coatings. DBS can also be used for flame-retardation in poly olefins. Because reactive compounds are very polymer specific, their application is generally limited. (Hairston, 1995).

Non-halogenated flame-retardants, mainly based on phosphorus, aluminium trihydrate (ATH) and magnesium hydroxide, do not have the disadvantage of potential formation of toxic by products. The additive flame-retardant ATH is multifunctional, cheap, and widely used as a filler and plasticizer. It is particularly used in carpet underlay (Hairston, 1995). Despite high loading requirements (20-70 wt-%), these inorganics are widely used for their ability to suppress smoke generation and avoid the production of toxic off-gasses. However, at high loadings, inorganic compounds will compromise mechanical properties. (Shelley, 1993).

For construction applications, inert glass fabrics are available. Construction materials woven with Advantex glass yarn, can withstand high temperatures without the release of toxic off gases. Furthermore, there are no emissions of persistent and bioaccumulative compounds during production, compounding and use (Hairston, 1995).

3.10 Conclusions and recommendations

With respect to the use of brominated flame-retardants it was established that between 1992 and 1998 global demand for these compounds has roughly doubled. Indicative production data of Broomchemie in Terneuzen over the same period are in line with this estimate. However, industry information for verification of these developments is not available. For a conclusive insight in current amounts of types of brominated flame-retardants in Europe and the Netherlands, an extended market survey by a specialised company is recommended.

Furthermore, over the 1992-1998 period a threefold increase in demand for TBBPA was noticed. Qualitative information from Eurobrome, the parent company of Broomchemie, seems to confirm this development. Reasons for this large demand increase are not known. It can be either the consequence of autonomic growth, or it may be caused by a pro-active substitution of environmentally suspected PBDEs. Last assumption is supported by the fact that production of octaBDE recently has ceased in Europe.

Conclusive data on the use of individual brominated flame-retardants in the Netherlands are not available. According to proportional estimates from European figures, the overall brominated flame-retardants use in the Netherlands is estimated at 3,000 tonnes/year, largely consisting of TBBPA, HBCD and PBDEs. Production of major brominated flame-retardants is restricted to TBBPA and HBCD, with estimated capacities of 30,000 and 5,000 tonnes/year in 2000.

Quantitative data are lacking on waste disposal methods for materials containing brominated flame-retardants. According to existing EU waste disposal regulations it is however expected that integral disposal of halogenated e.g. brominated materials in municipal solid waste will be banned by 2004. In the future this will either result in a complete substitution of brominated flame-retardants by alternative compounds or in complete source separation and recycling of brominated waste materials.

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4. Emissions to aquatic environment

4.1 Industrial sources

4.1.1 Production

The production of brominated flame-retardants in The Netherlands is restricted to the production of approx. 30,000 tonnes/y tetrabromobisphenol A and 5,000 tonnes/y hexabromocyclododecane at the Broomchemie plant in Terneuzen (PGFR, 1999). Production in the EU further includes decabromodiphenylether and decabromobiphenyl in France. A review of production amounts is given in table 4.1.

Table 4.1
Production and processing amounts in the Netherlands and EU (tonnes/years;EU 1999a,b,c; EU 1996)

	Production		Industrial processing	
	Netherlands	EU	Netherlands	EU
Tetrabromobisphenol A	30000	30000	1700	40000
Hexabromocyclododecane	5000	5000	420	10000
Decabromodiphenylether	-	3750	625	8250
Octabromodiphenylether	-	-	125	1650
Pentabromodiphenylether	-	-	-	1100
Decabromobiphenyl	-	1000	40	1000

From the generalised process descriptions from 1992, the following emission sources/ activities were identified (EU, 1996; RIVM, 1993):

1. wash out of reactor after each production cycle;
2. wash out and centrifugation of raw reaction production;
3. product grinding and packaging.

For a review of process units, see the generalised process scheme in Chapter 3 (figure 3.1).

Reactor wash out
According to the EU Technical Feasibility Study, the net product loss to wastewater is estimated at 0.5 kg/tonne product (EU, 1996).

Product wash (centrifuge)
From RIVM (1993) it was assessed that after completion of the bromine distillation, solvent is added to the reaction mixture to recover the product. Subsequently water is added to dissolve water soluble impurities. This mixture is centrifuged to recover the solid product from the solvent/water mixture, which is subsequently treated in decanters to recover the solvent. The solvent fraction, still containing significant amounts of solids, is distilled and condensed for recovery. The solid residue is discharged to a landfill or incinerated in a hazardous waste incineration plant. Product loss is estimated at 25 kg/tonne (solid waste) and 0.5 kg/tonne to wastewater, generated in the decanter before the solvent recovery (RIVM, 1993).

Product grinding and packaging
After the centrifuged solids are dried, the coarse product is grinded into the desired particle size and transported to the storage/packaging department. Dust emissions from product grinding and product packaging are treated in bagfilters. According to EU (1996), the product loss after dust recovery amounts to 0.07 kg/tonne product. Product losses to wastewater due to cleaning floors and equipment are estimated at 0.5 kg/tonne product. A summary of source emissions and resulting emission factors after in-plant treatment of ventilation gases and process liquids is given in table 4.2.

Table 4.2
Emission factors during production, processing and service life (kg/tonne;EU 1999a,b,c; EU 1996; RIVM 1993)

	Source emissions		**Waste water treatment**			**Direct to atmosphere**		**Solids recovery**
	Waste water	**Process air**	**Effluent**	**Sludge**	**Vapour**	**Dust**	**Vapour**	
Production process								
Reactor wash out	0.50	-	EUSES	EUSES	EUSES	-	-	-
Product wash (centrifuge)	25.5	-	EUSES	EUSES	EUSES	-	-	25 (sw)
Product grinding/ packaging	0.50	9.5 (d)	EUSES	EUSES	EUSES	0.07 (bf)	-	9.43 (pr)
Compounding								
Raw material handling	0.50	4.5 (d)	EUSES	EUSES	EUSES	0.5 (va)	-	4.0 (sw)
Extrusion (200°C)	-	0.10 (g)	-	-	-	-	-	0.10 (fs)
Pellet packaging	-	5.0 (d)	-	-	-	0.5 (cyc)	-	4.5 (sw)
Polymer processing								
Moulding (200 – 300°C)	-	0.10 (g)	-	-	-	-	-	0.10 (fs)
Service life (evaporation)	-	-	-	-	-	-	VP	-

WWTP: wastewater treatment plant
EUSES: wwtp modelling
VP: proportional to vapor pressure
sw: solid waste
fs: floatation sludge va : ventilated air
pr: product recycle cyc : after cyclone
bf : after bag filters d: dust
g: gaseous

Wastewater treatment
Wastewater from reactor cleaning, product wash and floor cleaning etc. is treated in a central wastewater treatment plant. For estimation of the environmental fate of TBBPA and HBCD during wastewater treatment, distribution computations were made with EUSES (EU modelling programme for prediction of the behaviour of substances in the environment (TGD, 1998)). The distribution of TBBPA and HBCD over effluent, sludge and aeration air (vapour) are given in table 4.3.

For treatment of TBBPA containing wastewater, the results show that TBBPA is only partially removed (ca. 70%) and that 14% of the ingoing emission load is directed to the atmosphere. Distribution results for treatment of HBCD wastewater indicate that only 0.3% is discharged to the atmosphere and that more compound is retained by the sludge. Mass balances based on the yearly TBBPA and HBCD production, reveal that annually ca. 15 tonnes TBBPA is discharged with the effluent and that 6.3 tonnes are emitted into the air. In addition to this, 2.1 tonnes of dust are released from the dust filters. Similar computations for HBCD result in significantly less emissions to surface water (0.8 tonne/y) and atmosphere (0.020 tonne/y). Dust emissions for HBCD amount to 350 kg/y.

Table 4.3
Emissions at production site in the Netherlands (year 2000; tonnes/year)

	Source emissions		Waste water treatment			Direct to atmosphere		Solid waste
	Waste water	Process air	Effluent	Sludge	Vapour	Vapour	Dust	
Tetrabromobisphenol A			32.6%	53.4%	14.0%			
Reactor wash out	15	-	4.89	8.01	2.10	-	-	-
Product wash (centrifuge)	765	-	4.89	8.01	2.10	-	-	750
Product grinding/ packaging	15	285	4.89	8.01	2.10	-	2.1	-
Total	795	285	14.7	24.0	6.3	-	2.1	750
Hexabromocyclododecane			10.9%	88.8%	0.3%			
Reactor wash out	2.50	-	0.273	2.220	0.008	-	-	-
Product wash (centrifuge)	128	-	0.273	2.220	0.008	-	-	125
Product grinding / packaging	2.50	47.5	0.273	2.220	0.008	-	0.35	-
Total	133	48	0.82	6.66	0.02	-	0.35	125

Extrapolating these figures to EU scale, then the TBBPA and HBCD will remain the same because Broomchemie is the only producer of both compounds within the EU. Emissions will further occur at the decaBDE and decaBB production plants in France. For emission computations of decabromodiphenylether, a distinction was made between deca- and nonabromodiphenylether in the commercial product. Distribution computations show however that the relative emissions to effluent, sludge and air are identical for both compounds (see table 4.4).

Based on the annual production amounts of decabromodiphenylether (3,750 tonnes) yearly approximately 450 kg commercial product will be emitted with the effluent. The major part of the emissions are removed through sludge disposal (ca. 5 tonnes/y). Emissions to the atmosphere are negligible. Accordingly, the emissions at the decabromobiphenyl production are estimated at ca. 120 kg to effluent and 1,400 kg through disposal of sludge.

Table 4.4
Emissions at production site in the EU
(year 2000; tonnes/year)

	Source emissions		Waste water treatment			Direct to atmosphere		Solid waste
	Waste water	Process air	Effluent	Sludge	Vapour	Vapour	Dust	
Tetrabromobisphenol A			32.6%	53.4%	14.0%			
Reactor wash out	15	-	4.89	8.01	2.10	-	-	-
Product wash (centrifuge)	765	-	4.89	8.01	2.10	-	-	750
Product grinding / packaging	15	285	4.89	8.01	2.10	-	2.1	-
Total	795	285	14.7	24.0	6.3	-	2.1	750
Hexabromocyclododecane			10.9%	88.8%	0.3%			
Reactor wash out	2.50	-	0.273	2.220	0.008	-	-	-
Product wash (centrifuge)	128	-	0.273	2.220	0.008	-	-	125
Product grinding / packaging	2.50	47.5	0.273	2.220	0.008	-	0.35	-
Total	133	47.5	0.818	6.660	0.023	-	0.35	125
Decabromodiphenylether			8.0%	92.0%	0.0%			
Reactor wash out	1.8	-	0.146	1.679	0.000	-	-	-
Product wash (centrifuge)	93.1	-	0.146	1.679	0.000	-	-	91
Product grinding / packaging	1.8	34.7	0.146	1.679	0.000	-	0.26	-
Total	96.7	34.7	0.438	5.037	0.000	-	0.26	91
Nonabromodiphenylether			8.0%	92.0%	0.0%			
Reactor wash out	0.05	-	0.004	0.046	0.0000	-	-	-
Product wash (centrifuge)	2.6	-	0.004	0.046	0.0000	-	-	2.5
Product grinding / packaging	0.05	1.0	0.004	0.046	0.0000	-	0.007	-
Total	2.7	1.0	0.012	0.138	0.000	-	0.007	2.5
Decabromobiphenyl			8.1%	91.9%	0.0%			
Reactor wash out	0.50	-	0.041	0.460	0.000	-	-	-
Product wash (centrifuge)	26	-	0.041	0.460	0.000	-	-	25
Product grinding / packaging	0.50	9.5	0.041	0.460	0.000	-	0.07	-
Total	27	10	0.122	1.379	0.000	-	0.07	25

4.1.2 Compounding and polymer processing

Compounding

Major emission sources in compounding are the handling, feeding and mixing of raw materials which are predominantly processed in powder form. Mixing is believed to be performed in fully closed equipment. Dust emissions from the mixing equipment are treated in filters and filtered air is recycled (EU, 1996). According to the TGD, the emission factor for raw material handling is estimated at 0.5% product loss e.g. 5 kg/tonne. For recovery of emitted dust it is assumed that approximately 90% settles and that 10% is discharged to the atmosphere, resulting in a net emission factor of 0.5 kg/tonne. For recovery of the settled dust, it is estimated that 90% is removed mechanically and discharged to a waste disposal site. The remaining 10% (ca. 0.5 kg/tonne product) is removed by flushing and will end up in wastewater (EU, 1999b,c).

During extrusion, where the powder mixture is melted into pellets, some evaporation of brominated compounds may occur. Emitted vapours are condensed at ambient temperatures. On basis of the low vapour pressures of brominated compounds, a maximal emission factor of 0.1 kg/tonne is estimated. Condensation of vapours result in a mixture of water and nonpolar compounds which is separated in a flotation unit. The resulting flotation sludge is discharged to a specialised waste disposal site. Product pellets are treated in a cyclone to remove dust particles. The emission factor for this source is estimated to be 0.5 kg/tonne (EU, 1996).

Polymer processing
Analogous to the extrusion process, the emission factor for moulding is set to 0.1 kg/tonne product in the form of flotation sludge.

4.2 Service life

During the life of flame-retarded polymers, additive flame-retardants have the potential to evaporate from the plastic. According to UCD (1994). the overall emission factor can be estimated by the following formula:

Annual loss (in %) = $1.1.10^6 * P * N$

P = Vapour pressure (mmHg)
N = Service life of product (year)

The maximal emission from this source is equivalent to the total amount of flame-retardant in use at a certain time. In case of a life cycle of 10 years, the total amount in use equals 10 times the average production capacity over the last ten years. A review of evaporation emission factors is given in Annex 3.1.

4.3 Overall emissions to the environment

In order to evaluate the contributions of the various emission sources in the production, compounding and service life stage, emissions from the individual stages are summarized in table 4.5. The TBBPA emissions to the Netherlands environment are largely related to the production stage. Total emissions amount to 25 tonnes/y divided into 15.0 tonnes to the surface water, 6.4 tonnes as vapour to the atmosphere and 3.8 tonnes as dust particles. Besides these emissions, 790 tonnes of TBBPA containing wastes are produced. Emissions caused during handling, storage and treatment of these wastes are not included in this study.

Total HBCD emissions to the Netherlands environment amount to 12.5 tonnes/y. As shown in table 4.5 the main part of HBCD emissions (10.9 tonnes) are generated as vapour during service life. This amount is released as diffuse emissions due to continuous evaporation from flame-retarded materials during use. As such, these emissions are uncontrollable. For the other compounds used in the Netherlands it is demonstrated that emissions are negligible compared to the TBBPA and HBCD emissions (see Annex 3.2).

If the overall emissions are considered on an European scale, then it shows that due to large scale compounding of TBBPA (40,000 tonnes), emissions to water will increase by 6.5 tonnes. Vapour emissions during wastewater treatment will increase by 2.7 tonnes/y. Further, due to extra dust emissions at compounding sites the emission of dust particles will be 42 tonnes in the EU, and thereby becoming the major emission source for TBBPA.

EU emission loads for HBCD reveal that, due to the use of 10,000 tonnes HBCD, the evaporation losses during service life will increase to 260 tonnes/year, being by far the largest HBCD emission source. Emissions of the other flame-retardants during production, compounding and polymer processing mainly consist of 0.4 and 1.0 tonne/y of decabromodiphenylether and decabromobiphenyl in dust emissions to atmosphere. Additionally, about 14 tonnes/y pentabromodiphenylether and 100 tonnes/y tetrabromo-diphenylether are emitted to the atmosphere as a consequence of evaporation losses during service life (see table 4.5).

4.4 Transboundary emissions

4.4.1 Atmospheric deposition

No data are available on the atmospheric deposition of gaseous or dust emissions in the Netherlands or in the EU. Neither is known in what way and to what extent released emissions are susceptible to wet or dry deposition.

4.4.2 Hydrological transport

Data on emission levels or emissions loads in rivers, entering or leaving the Netherlands, are also not known.

4.5 Evaluation

4.5.1 Basic process and emission data

In order to obtain as much as possible representative estimates for emissions during production and use of brominated flame-retardants, the Netherlands and European brominated flame-retardants manufacturers have been contacted for information and cooperation in this study. The manufacturers declined however to supply realistic and representative data on currently used production processes and emission factors.

With respect to the process and emission data used in this study, it must be mentioned that most recent information on production processes and emission factors originate from 1992. In this respect, recent EU risk assessments on polybrominated diphenyls did not produce any new insights or data. Further to ongoing technological process developments and recent production extension at Broomchemie, it remains questionable whether the information of 1992 is still valid.

Table 4.5
Overall emissions to the environment
(year 2000; tonnes/year)

	Industrial Amounts	Source emissions		Waste water treatment			Direct to atmosphere		
		Waste water	Process Air	Effluent	Sludge	Vapour	Vapour	Dust	Solid waste
The Netherlands									
Production									
Tetrabromobisphenol A	30000	795	285	14.67	24.03	6.3	-	2.10	750
Hexabromocyclododecane	5000	133	48	0.82	6.66	0.02	-	0.35	125
Compounding, processing and service life									
Tetrabromobisphenol A	1700	0.850	16.49	0.277	0.454	0.119	-	1.70	14.8
Hexabromocyclododecane	420	0.210	4.074	0.023	0.186	0.001	10.9	0.42	3.7
Decabromodiphenylether	611	0.306	5.930	0.024	0.281	< 0.001	0.002	0.61	5.3
Nonabromodiphenylether	33	0.017	0.324	0.001	0.015	< 0.001	0.0006	0.03	0.29
Octabromodiphenylether	45	0.023	0.440	0.002	0.021	< 0.001	0.007	0.05	0.39
Heptabromodiphenylether	53	0.026	0.513	0.002	0.024	< 0.001	0.048	0.05	0.46
Hexabromodiphenylether	7	0.004	0.068	0.000	0.003	< 0.001	0.040	0.01	0.06
Decabromobiphenyl	40	0.020	0.388	0.002	0.018	< 0.001	0.020	0.04	0.35
European Union									
Production									
Tetrabromobisphenol A	30000	795	285	14.67	24.0	6.3	-	2.10	750
Hexabromocyclododecane	5000	133	48	0.82	6.7	0.02	-	0.35	125
Decabromodiphenylether	3650	97	35	0.44	5.0	< 0.001	-	0.26	91
Nonabromodiphenylether	100	2.7	1.0	0.012	0.14	< 0.001	-	0.01	2.5
Decabromobiphenyl	1000	27	9.5	0.122	1.38	< 0.001	-	0.07	25
Compounding, processing and service life									
Tetrabromobisphenol A	40000	20.0	388	6.520	10.68	2.8	-	40	348
Hexabromocyclododecane	10000	5.0	97	0.545	4.44	0.02	260	10	87
Decabromodiphenylether	8070	4.0	78	0.323	3.71	0.000	0.021	8.07	70
Nonabromodiphenylether	441	0.22	4.3	0.018	0.20	< 0.001	0.009	0.44	3.83
Octabromodiphenylether	599	0.30	5.8	0.024	0.28	< 0.001	0.086	0.60	5.21
Heptabromodiphenylether	698	0.35	6.8	0.029	0.32	< 0.001	0.633	0.70	6.07
Hexabromodiphenylether	221	0.037	0.037	0.003	0.034	< 0.001	1.30	< 0.001	-
Pentabromodiphenylether	601	0.33	0.33	0.032	0.30	0.001	14.7	< 0.001	-
Tetrabromodiphenylether	371	2.1	2.1	0.260	1.85	0.021	101	< 0.001	-
Decabromobiphenyl	1000	0.50	9.7	0.041	0.46	< 0.001	0.495	1.00	8.70

Air (v): as vapour Air (d): as dust particles

4.5.2 Reliability of emission factors

The emission factors used in this study were derived from process and emission data in earlier risk assessments (EU, 1996; EU, 1999a,b,c and RIVM, 1993). Factual information that supports or justifies the assumed or extrapolated values could not be retrieved in these studies. In none of the reports data were given on the actual wastewater amounts e.g. the nominal wastewater production/tonne product. With respect to the magnitude of the emission factors in this study can be mentioned that the emission factors to wastewater (0.5 kg/tonne) are a factor 40 times slower than the default value used in EUSES (20 kg/tonne; EU, 1998).

Furthermore it should be mentioned that models such as EUSES do not account for concentrations that exceed the water solubility. Because the solubility of most compounds is extremely low, in many cases the emission loads will be released in levels >> water solubility. On the other hand, the wastewater can contain solvent traces or solubilisation agents which can increase the actual solubility to a great extent. Non-soluble brominated compounds can further be present in the form of a stable colloid. In latter case the whole issue of water solubility limits will be of secondary importance. Therefore, the results of the emission estimation and emission distribution calculations need to be used carefully, and where possible verified/amended by actual data.

4.6 Conclusions and recommendations

From emission computations and emission distribution results the following conclusions can be made with respect to the release of brominated flame-retardants in the Netherlands and the EU:

1. For emissions of TBBPA in The Netherlands, the production site is by far the major emission source. At Broomchemie approximately 90% of the national emission load is released. Major emission path is the discharge of effluent (15 tonnes/y). Emission to the atmosphere consists of 6.3 tonnes/y as vapour and 2.1 tonnes/y as dust. To what extent latter emissions are subject to dry/wet deposition is not known and needs further assessment because these emissions account for 35% of the total emissions to the environment.

2. Emissions of HBCD are for >90% caused by diffuse evaporation of HBCD from flame-retarded materials during service life (10.9 tonnes/y). Emission at Broomchemie is predominantly to the surface water (0.82 tonne/y); the remainder consists of dust release to the atmosphere (0.35 tonne/y).

3. TBBPA and HBCD cause also the major emissions in compounding and polymer processing. Total TBBPA emission was estimated as 2.1 tonnes/y, largely consisting of dust release to the atmosphere (80%). Total emission of HBCD amounts to 0.6 tonne/y with > 65% in the form of dust release to the atmosphere. Emissions of polybrominated biphenyls and diphenylethers to surface water and atmosphere are negligible compared to the emissions of TBBPA and HBCD.

4. On EU level, TBBPA and HBCD emissions to surface water, due to compounding and polymer processing, increase to 6.5 and 0.5 tonnes/y. Emissions to atmosphere amount to 43 tonnes TBBPA/y, mainly in the form of dust particles (> 90%). HBCD emissions to atmosphere consist of 10 tonnes/y as dust, released during compounding and 260 tonnes/y caused by evaporation losses during service life.

5. Emissions of polybrominated diphenylethers in the EU consist mainly of 0.75 tonne/y decabromodiphenylether to surface water and 8.3 tonnes/y of this compound to atmosphere as dust. For decabromobiphenyl the corresponding emissions are 0.16 tonne/y to surface water and 1.1 tonnes/y as dust.

6. The major emissions of polybrominated diphenylethers are however caused by evaporation losses of ca. 100 tonnes/y tetrabromo- and 15 tonnes/y pentabromodiphenylether during service life.

7. Besides the direct emissions to water and atmosphere, large quantities of brominated waste are produced. For quantification of direct substance release into the environment, possible releases during handling, storage and treatment of these waste, have not been evaluated e.g. included in the overall emissions.

With respect to the representativity of the computed emissions, uncertainty exists about the actual magnitude of the used emission factors and the form in which selected compounds are present in raw and treated wastewater. Practical information e.g. further research is required to verify these matters.

Furthermore, due to large vapour and dust emissions of some compounds, additional research is recommended to quantify to what extent these emissions are subject to dry/wet deposition e.g. will end up in surface water.

4.7 References

European Union (1996) Techno-economic study on the reduction of industrial emissions to air, discharges to water and the generation of wastes from the production, processing and destruction (by memeriation) of brominated flame-retardants.

European Union (1998). Technical Guidance Document on development of Risk Reduction Strategies. European Communities 1998.

European Union (1999a) Risk assessment of diphenylether, pentabromo derivate Final Draft of August 1999

European Union (1999b) Risk assessment of diphenylether, octabromo derivate Final Draft of August 1999

European Union (1999c) Risk assessment of bis(pentabromophenyl) ether

Final Draft of August 1999

PGFR (1999) Project Group Flame-retardants, the Netherlands, Personal communication Mr Fröhlich, October 1999

RIVM (1993) (in Dutch) Broomchemie, RIVM report No. 773006160

UCD (1994). Use Category Document Plastic Additives. A. M. Jolly, B. Willoughby, G. C. Karas and S. J. Hobbs. Produced under contract to UK Department of the Environment, Building Research Establishment, March 1994.

5. Behaviour in the aquatic environment

5.1 Introduction

The behaviour of organic micropollutants in the aquatic environment is determined by the properties of the compound (solubility, hydrophobicity, volatility,) and by the characteristics of the water system of concern (residence time of the water, sedimentation area, organic matter content, etcetera). These compound and system specific properties determine to what extent a compound will accumulate in organisms.

5.2 Solubility and volatilisation

The water solubility of a compound is a good indication of the extent to which this compound can be transported with water. In general poorly soluble compounds have a high affinity for silt particles in a water system. This is the reason that the compound will settle together with the sediment and suspended particles and thereby the transport along with the water stream will be slowed down. Poorly soluble compounds can also accumulate in organisms more easily. Solubility and vapour pressure further determine together whether a compound will evaporate out of water. The volatility of a compound is characterised by its Henry constant.

5.2.1 Polybrominated biphenyls (PBB)

The solubility of compounds present in commercial PBBs is very low and decreases from 10 µg/l for hexaBB to 20-30 µg/l for decaBB. Typical vapour pressures for PBBs range from $7*10^{-6}$ Pa for hexaBB to $0.6*10^{-6}$ Pa for decaBB (WHO, 1994a).

5.2.2 Polybrominated diphenylethers (PBDE)

Values for water solubility of tetrabromodiphenylether and pentabromodiphenylether were measured at 10.9 and 2.4 µg/l (WHO, 1994b). The value for commercial octabromo-diphenylether was around 0.5 µg/l at 25°C determined in a generator column method in a GLP study (Stenzel and Markley, 1997), where a mixture sample of octabromodiphenylether from three producers (5.5% hexa-, 42.3% hepta-, 36.1% octa, 13.9% nona- and 2.1% decabromodiphenylether) was used.

For decabromodiphenylether the water solubility of the commercial product was recently determined using a generator column method carried out to GLP. In this study a mixture sample of decabromodiphenylether from three producers was used (97.4% decabromo-diphenylether, 2.5% nonabromodiphenylether and 0.04% octabromodiphenylether) and the water solubility was found to be very low at <0.1 µg/l at 25°C (Stenzel and Markley, 1997).

Watanabe and Tatsukawa (1990) determined the vapour pressures for a range of brominated diphenylethers at 25°C using a GC technique. As shown in table 5.1, brominated diphenylethers have very low vapour pressures, which tend to decrease with increasing bromination.

For a commercial pentabromodiphenylether mixture (34% tetra-, 55% penta- and 11% hexabromodiphenylether) a vapour pressure of 4.69×10^{-5} Pa at 21°C was determined, using a spinning rotor gauge (Stenzel and Nixon, 1997).

The vapour pressure of the commercial octabromodiphenylether was determined as 6.59×10^{-6} Pa, using a composite sample from three manufacturers (Stenzel and Markley, 1997). This values is 30 times higher than the value measured by Watanabe et al (1990)(see table 5.1). Observed value reflects probably the most volatile components in the product.

Table 5.1 Vapour pressures of polybrominated diphenylethers (Watanabe and Tatsukawa, 1990).

Polybrominated diphenylether	Vapour pressure at 25°C (Pa)
Dibromodiphenylether	0.013-0.019
Tribromodiphenylether	$1.6\text{-}2.7 * 10^{-3}$
Tetrabromodiphenylether	$2.5\text{-}3.3 * 10^{-4}$
Pentabromodiphenylether	$2.9\text{-}7.3 * 10^{-5}$
Hexabromodiphenylether	$4.3\text{-}9.5 * 10^{-6}$
Octabromodiphenylether	$1.2\text{-}2.3 * 10^{-7}$

The vapour pressure of commercial decabromodiphenylether has been determined as $4.63 * 10^{-6}$ Pa at 21°C using a spinning rotor method. The substance tested was a composite sample from three manufacturers and had the following composition: octabromodiphenylether 0.04%; nonabromodiphenylether 2.5%; decabromodiphenylether 97.4%. Since decabromodiphenylether is a mixture, this value is likely to represent that of the most volatile components of the mixture (Stenzel and Nixon, 1997).

5.2.3 Tetrabromobispenol A and derivates

The water solubility of tetrabromobisphenol in water is low and ranges between 720 µg/l at 20°C and 1,770 µg/l at 35°C. Vapour pressure is $39000 * 10^{-6}$Pa at 20°C. For the other TBBPA derivates no values were available for water solubility and vapour pressure. From their molecular weight, it is estimated that they will have significantly lower water solubility and vapour pressure than TBBPA (WHO, 1995).

5.2.4 Hexabromocyclododecane

The water solubility and vapour pressure of this compound are very low: 3.4 – 8 µg/l and $63 * 10^{-6}$ Pa at 20°C (Hardy, 1997).

5.2.5 Comparison of compounds

In table 5.2 values for the water solubility and vapour pressure are summarised for the selected compounds. A graphical representation of the solubility and vapour pressure as function of the octanol/water partition coefficient is given in figures 5.1 and 5.2. From the values in figures 5.1 and 5.2 can be concluded that most flame-retardants have very low solubility in water and are non-volatile ($S < 10^{-4}$ mol/m^3 and $P < 10^{-4}$ Pa). Comparison of various chemical groups in figure 5.1 demonstrates that the solubility of polybrominated diphenylethers, HBCD and TBBPA show more or less the same dependency on the log K_{ow} value. The solubility of polybrominated biphenyls is significantly higher at equal log K_{ow} values.

From figure 5.2 can be seen that for most compounds the log P value strongly correlates with the log K_{ow} value, enabling interpolation/extrapolation of log P values for compounds with lacking experimental data. Representation of theoretical Henry coefficients as function of log K_{ow} shows that the volatility of a brominated compound sharply decreases with the K_{ow} (see figure 5.3).

Furthermore it can be seen that PBBs have a significantly lower volatility than other selected compounds, which can be attributed to the higher solubility of PBBs in water.

Table 5.2
Solubility and volatility parameters of selected brominated flame-retardants (Watanabe et al, 1990; Stenzel et al, 1997; WHO 1994 a,b; WHO 1995)

	Mole weight (g/mole)	Solubility (µg/l)	Solubility (mol/m^3)	Pv (10^{-6} Pa)	Henry coeffient^{a} (atm.m^3/mol)
Hexabromobiphenyl	627	10-50	$8.0*10^{-5}$	7	$8.7*10^{-7}$
Octabromobiphenyl	785	30-40	$4.5*10^{-5}$	1.6^{B}	$3.5*10^{-7}$
Nonabromobiphenyl	864	32.5^{B}	$3.8*10^{-5}$	1.0^{B}	$2.6*10^{-7}$
Decabromobiphenyl	943	20-30	$3.2*10^{-5}$	< 0.6	$1.9*10^{-7}$
Tetrabromodiphenylether	486	11	$2.1*10^{-5}$	250-330	$1.6*10^{-4}$
Pentabromodiphenylether	565	2.4	$5.8*10^{-6}$	29-73	$4.9*10^{-5}$
Hexabromodiphenylether	644	1.9^{B}	$2.9*10^{-6}$	6.9^{B}	$2.3*10^{-5}$
Heptabromodiphenylether	723	1.0^{B}	$1.4*10^{-6\,B}$	1.1^{B}	$8.0*10^{-6}$
Octabromodiphenylether	801	0.5	$6.2*10^{-7}$	0.175	$2.8*10^{-6}$
Nonabromodiphenylether	880	0.2^{B}	$2.6*10^{-7\,B}$	0.024^{B}	$9.1*10^{-7}$
Decabromodiphenylether	959	< 0.1	$1.0*10^{-7}$	0.003^{B}	$3.0*10^{-7}$
Tetrabromobisphenol A	544	720-1770	$1.3*10^{-3}$	39000	$2.9*10^{-4}$
Hexabromocyclododecane	642	3.4-8	$1.2*10^{-5}$	63	$5.0*10^{-5}$

^{a} : Quotient of vapour pressure and aquous solubility

^{B} : interpolated value

5.3 Sorption

The extent of sorption of a compound strongly depends on the compound's hydrophobicity and the availability of organic matter in soil, sediment or suspended particles. The hydrophobicity of a compound is characterised by its octanol water partition coefficient (K_{ow}). To what extent the compound will adsorb onto soil, sediment or suspended solids further depends on the organic matter e.g. organic carbon content of these media. The specific affinity of a compound can be directly related to organic carbon content by means of the K_{oc} value. For various media, the organic carbon content is known. Furthermore, detailed measurements have been performed on adsorption of organic compounds onto these media. According to the TGD for risk assessment, partition coefficients of hydrophobic chemicals in organic carbon / water systems (K_{oc}) can be derived from the following equation:

$$\log K_{oc} = 0.81 * \log K_{ow} + 0.10 \quad \text{for } 1.0 < \log K_{ow} < 7.5$$

With a standard fractional organic carbon content of soil, sediment and suspended sediment taken as 2, 5 and 10% respectively, specific adsorption constants (Kp) for soil, sediment and suspended sediment can be calculated directly from the K_{oc} or K_{ow} value.

Figure 5.1
Solubility of selected compounds

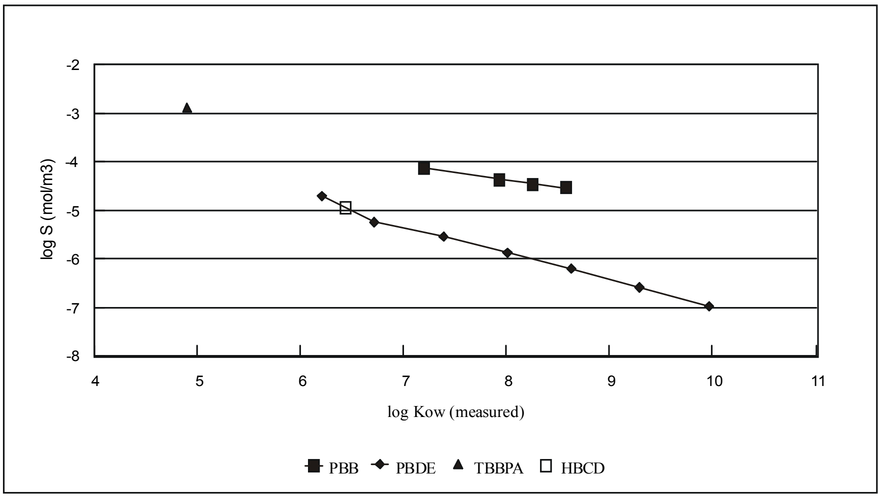


Figure 5.2
Solubility of selected compounds
(*: interpolated value)

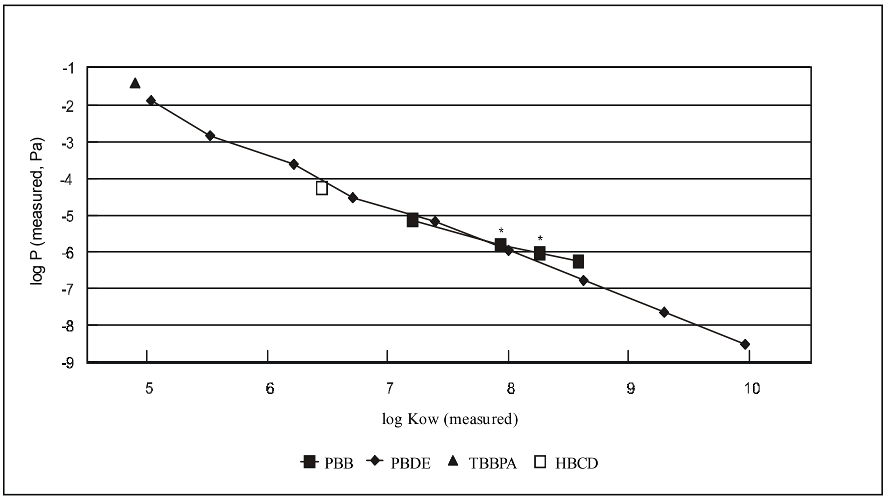


Figure 5.3
Volatility of selected compounds
(H: Henry coefficient = P/S-ratio)

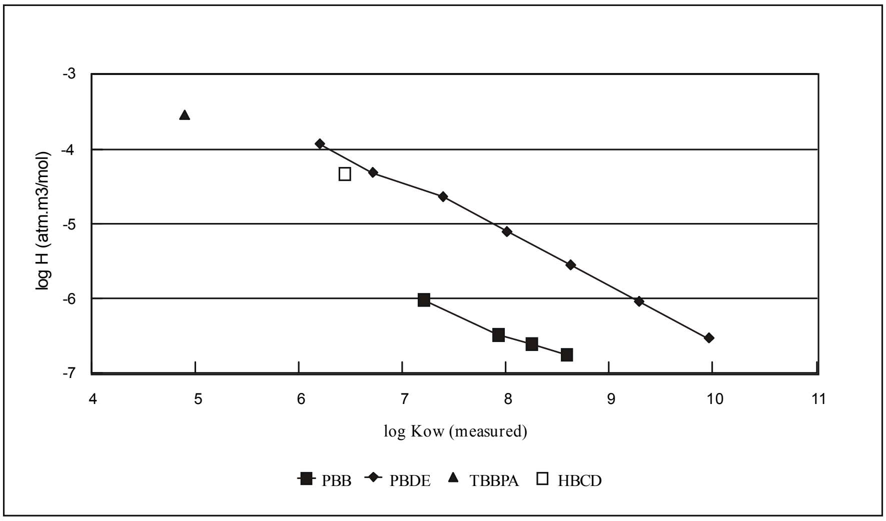
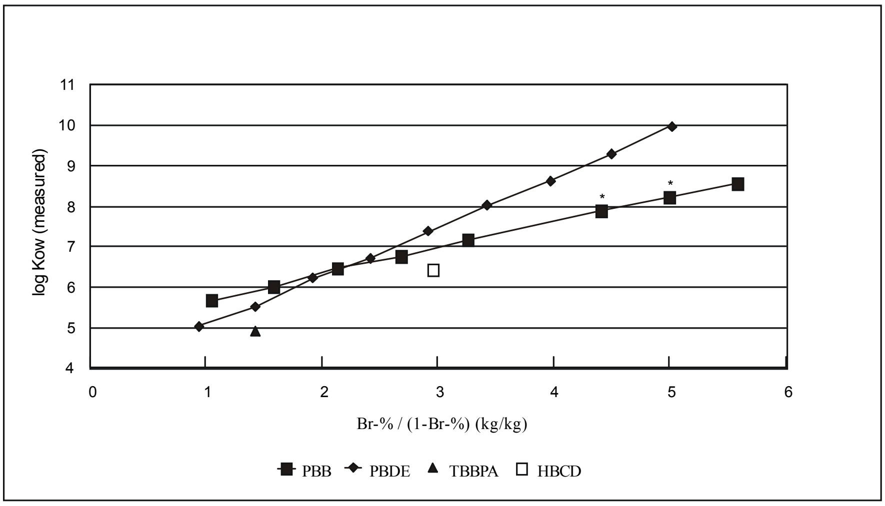


Figure 5.2
log Kow values of selcted compounds
(*: interpolated value; Br-%= bromine content (%-wt)



5.3.1 Polybrominated biphenyls (PBB)

A broad range of values for octanol-water partition coefficient was measured for the various PBB congeners, with log K_{ow} = 5.72 for dibromobiphenyl to log K_{ow} = 7.20 for hexabromodiphenyl. Experimental data for the higher brominated compounds were not available. For decabromobiphenyl only a calculated value of 8.58 is available (WHO, 1994a). The K_{ow} values of octa- and nonabromodiphenyl were estimated on basis of graphical interpolation between the K_{ow} values of hexa- and decabromobiphenyl in figure 5.4. On basis of these log K_{ow} values, the calculated log K_{oc} value will range from 5.93 to 7.05 (see table 5.3). Specific partition coefficients for soil, sediment and suspended sediment indicate that the PBB congeners will be adsorbed moderately to strong to solid media.

Table 5.3
Summary of partition coefficients
(Watanabe et al., 1990; WHO, 1994a,b;
WHO, 1995; Hardy 1997)

	log K_{ow} -	log K_{oc} -	Kp-soil l/kg ^{b}	Kp-sediment l/kg ^{b}	Kp-susp. sed. l/kg ^{b}
Hexabromobiphenyl	7.20	5.93	17101	42753	85507
Octabromobiphenyl	8.03 ^{A}	6.60	80414	201034	402068
Nonabromobiphenyl	8.31 ^{A}	6.83	134301	335753	671506
Decabromobiphenyl	8.58	7.05	224300	560751	1121502
Tetrabromodiphenylether	5.9-6.2	4.97	1876	4689	9379
Pentabromodiphenylether	6.5-7.0	5.54	6921	17303	34606
Hexabromodiphenylether	6.9-7.9	6.09	24374	60935	121871
Heptabromodiphenylether	8.0 ^{A}	6.59	77109	192772	385545
Octabromodiphenylether	8.4-8.9	7.09	243938	609846	1219692
Nonabromodiphenylether	9.3 ^{A}	7.63	855077	2137691	4275383
Decabromodiphenylether	6.27-9.97	8.18	2997298	7493246	14986492
Tetrabromobisphenol A	4.5-5.3	4.07	234	586	1172
Hexabromocyclododecane	5.8-7.1	5.30	3974	9934	19869

^{A} : interpolated value ^{b}: estimated from average log K_{ow} value

5.3.2 Polybrominated diphenylethers (PBDE)

High octanol-water partition coefficients (K_{ow}) were determined for commercial poly-brominated diphenylethers using a HPLC technique (Watanabe et al, 1990). No data were given on the actual composition of the products tested (see table 5.3).

Pentabromodiphenylether

Recently, the log K_{ow} value for pentabromodiphenylether has been determined as 6.57 using a generator column method (MacGregor and Nixon, 1997), which agrees well with the values reported in Table 5.3. For pentabromodiphenylether, K_{oc} values of 215,000-560,000 l/kg can be estimated using the values from table 5.3.
A K_{oc} value of 260,000 l/kg is estimated if the latter log K_{ow} value of 6.57 is used. With a standard fractional organic carbon content for sediment of 5% and K_{oc} values of 215,000-560,000, Kp values for sediment are estimated at 10,700 – 27,800 l/kg. The upper end of predicted values for sediment agrees reasonably well with the measured values for sediment of 49,000 l/kg by Watanabe (1988).

Since commercial pentabromodiphenylether is a mixture of several congeners, the behaviour of some of the other components should also be considered. From Table 5.3, it is clear that tetrabromodiphenylether will have slightly lower

Kp values and hexabromodiphenylether slightly higher Kp values than pentabromodiphenylether. Thus it can be concluded that all three major components are likely to adsorb strongly onto soils and sediments, but the lower brominated components are likely to be slightly more mobile in soil/sediment systems than the more highly brominated components.

Octabromodiphenylether

The octanol-water partition coefficient for commercial octabromodiphenylether has been determined as log K_{ow} = 6.29 using a composite sample from three manufacturers. This is considered as a minimum value for the commercial substance and will probably correspond with the K_{ow} of lower brominated components. High octanol-water partition coefficients (K_{ow}) have been determined for polybrominated diphenylethers using a HPLC technique (Watanabe and Tatsukawa, 1990). No information was given as to the actual composition of the substances tested. The results indicate that all components of commercial octabromodiphenylether are expected to adsorb strongly onto soil and sediment since they have high octanol-water partition coefficients, this tendency increasing with increasing bromination (EU, 1999b).

No measured K_{oc} value is available for octabromodiphenylether but values can be estimated from the K_{ow} value. According to the Technical Guidance Document a K_{oc} value of $12.3*10^6$ l/kg can be estimated from the average log K_{ow} values. Measured values for adsorption coefficients of commercial deca- and pentabromodiphenylether indicate a K_{oc} value of around 1,360,000 l/kg for commercial octabromodiphenylether. This latter value corresponds with an average log K_{ow} value of 7.45, which is still lower than the range in table 5.3. Due to this lower K_{ow} value, it is possible that some of the lower brominated components of commercial octabromodiphenylether may be more mobile in soil than octabromodiphenylether itself. For instance, an average K_{oc} value of 360,000 l/kg is estimated for pentabromodiphenylether. This K_{oc} value and corresponding Kp values are still very high. Accordingly, the other less brominated components of octabromodiphenylether are likely to be immobile in soil.

Decabromodiphenylether

Decabromodiphenylether is expected to adsorb strongly onto soil and sediment since it has a high octanol-water partition coefficient (log K_{ow} = 9.97). Recently a value of 6.27 was determined by MacGregor and Nixon (1997), which probably will reflect the value of the lower brominated compounds in the commercial product.

According to the EU TGD, estimated soil organic carbon / water partition coefficient (K_{oc}) values will vary from 150,000 to $150*10^6$ l/kg. A soil organic carbon / water partition coefficient Kp (soil) value of 693,000 l/kg can be estimated for decabromodiphenylether based on a water solubility of 0.1 g/l, using the relationship log K_{oc} = -0.55 log S + 3.64, where S = solubility in mg/l (Lyman et al, 1982). Watanabe (1988) determined a sediment / water partition coefficient for decabromodiphenylether by adding sediment, on which decabromodiphenylether already was adsorbed, to clean water. A Kp(sed) value of 79,433 l/kg was obtained. No information on the organic carbon content of the sediment was reported.

5.3.3 Tetrabromobisphenol A and derivates

Measured values for the octanol-water partition coefficient of tetrabromobisphenol A range from 4.5 to 5.3. Experimental values for K_{oc} were not available. Using the TGD formula for log K_{oc} as a function of log K_{ow}, the a value of 4.07 can be computed for log K_{oc} (see table 5.3). Comparison of the Kp-values for soil, sediment and suspended solids with those for the other compounds demonstrates that TBBPA will have the least tendency to adsorb onto solid media, and will be expected to be the most mobile compound of all.

5.3.4 Hexabromocyclododecane

Experimental values for log K_{oc} were not available, but according the TGD a value of 5.30 can be derived from log K_{ow}. Corresponding values for partition coefficients for soil, sediment and suspended solids indicate that hexabromocyclododecane will have a moderate to high affinity for solid media.

5.4 Transformations in freshwater and marine environments

5.4.1 Hydrolysis

For none of the compounds studied, data could be retrieved on possible hydrolysis. On basis of their chemical stability it is expected that none of the compounds will be influenced by primary hydrolysis reactions. Tetrabromobisphenol A has two acidic hydroxyl groups (pKa = 7.5 and 8.5), due to which compound will be ionised above pH > 7.5 (WHO, 1995).

5.4.2 Photolysis

Polybrominated biphenyls (PBB)

Under laboratory conditions, PBBs are easily degraded by UV. The photoreactivity of PBBs has been used to confirm PBB residues. The predominant photochemical reaction of PBBs in organic solvents is reductive debromination. Irradiation of 4-monobromodiphenyl at 33 nm in various polar and nonpolar solvents led to quantitative formation of biphenyl. Studies using lower brominated PBB congeners (i.e. tetra and lower) reported a preferential loss of ortho bromines. Irradiation of higher brominated congeners yielded a series of photoproducts (see Annex 4), but a stepwise cleavage of orthobromines did not appear to be preferred above meta or para debromination (WHO, 1994a).

The photoreactivity of 2,2',4,4',5,5'-hexabromobiphenyl, the main component of commercial hexaBB, was found to be relatively high. Degradation occurred more rapid than with the hexachloro analogue. Consistent with the dehalogenation pathway, photodegradation of the commercial FireMaster mixture led to reduced concentrations of the more highly substituted PBB congeners. Technical octabromobiphenyl has been reported to photodegrade in xylene by reductive debromination with a half-life of 40 h (WHO, 1994a).

Furthermore, there were investigations to enhance the photochemical process aiming at a potential technique for the breakdown and removal of PBBs from the environment. In laboratory testing, photodegradation of PBBs was accelerated in the presence of ethylenediamine and tertbutylamine. On the contrary, rates and extent of photolytic reactions of PBBs in the environment have not been determined in detail. Few field observations indicate a high persistence of the original PBBs e.g. only partial degradation to less brominated (and often more toxic) photoproducts. Measurements in soil, amended with manure from FireMaster contaminated cattle 2-3 years earlier, did not detect any significant changes in the concentrations of the major PBB peaks (Br_5, Br_6, Br_7) compared with the FireMaster composition. Soil samples obtained from the former FireMaster manufacturing site in Michigan and analysed approximately 10 years after contamination, contained enhanced concentrations of possible photodegradation products including 2,3′,4,4′,5-pentabromobiphenyl, 2,2′,4,4′,5-pentabromobiphenyl, and two unidentified tetrabromobiphenyls. Due to the diversity of micro-environments, both laboratory and field data on photo alteration of PBBs are considered to be incomplete; there is a lack of studies on the photochemistry of PBBs in water, vapour or solid states (WHO, 1994a).

Pentabromodiphenylether

No information is currently available on the abiotic degradation of pentabromodiphenylether in aqueous solution. It is thought that pentabromodiphenylether will be hydrolytically stable under conditions found in the environment. By comparison with decabromodiphenylether, it is likely that pentabromodiphenylether may photodegrade in water, although it is not currently possible to comment on the extent and rate of this reaction. For the reaction of 2,2′,4,4′,5-pentabromodiphenylether with atmospheric hydroxyl radicals, a rate constant has been estimated as $1.27 * 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} using the Syracuse Research Corporation AOP estimation program. Assuming an atmospheric concentration of hydroxyl radicals of $5 * 10^5$ molecules/ cm^3, an atmospheric half-life of around 6.4 days can be estimated for this reaction (EU, 1999a).

Octabromodiphenylether

No information appears to be available about the abiotic degradation of octabromodiphenylether. It would, however, be expected to behave similarly to decabromodiphenylether. The degradation of decabromodiphenylether is discussed in more detail below. A possible concern is the formation of lower brominated diphenylethers from the photochemical degradation of octabromodiphenylether in the environment, since these compounds, particularly tetra- and pentabrominated diphenylethers, have been found extensively in the environment and are potentially bioaccumulative (EU, 1999b). For the atmospheric reaction of octabromodiphenylether with hydroxyl radicals, a rate constant of $2.1 * 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} has been estimated. The value was obtained using the Syracuse Research Corporation AOP program which is based on the estimation method of Atkinson given in Chapter 4 of the Technical Guidance Document. Using this value an atmospheric half-life of around 36 days can be estimated for octabromodiphenylether based on an atmospheric hydroxyl radical concentration of $5 * 10^5$ molecule/cm^3 (EU, 1999b).

Decabromodiphenylether

The possibility of reductive debromination of polybrominated diphenylethers under environmental conditions has been evaluated by the EU risk assessment team. It was concluded that under anaerobic conditions, debromination is not likely to occur. Conclusive data that fully exclude the formation of lower brominated congeners. (e.g. penta- and tetrabromodiphenylether) upon direct photolysis in water, are lacking however. This issue is currently being investigated further (EU, 1999c).

Watanabe and Tatsukawa (1987) carried out photolysis experiments with decabromodiphenylether (97% deca and 3% nona congener) in a mixture of hexane, benzene and acetone (8:1:1). The decabromodiphenylether was irradiated by UV (254 nm) or natural sunlight and analysed for diphenylether (by GC-ECD) and brominated furans (by GC-MS using 2,3,7,8-tetrabromo dibenzofuran as reference). After 16 hours UV irradiation, decabromodiphenylether was found to debrominate mainly to tri- to octabromodiphenylethers. Formation of brominated furans with between 1 and 6 bromine atoms was also noted, but mass spectrum was different from that of the 2,3,7,8-tetrabromodibenzofuran reference. No brominated dioxins were detected. The total yield of brominated dibenzofurans was around 20% after 16 hours (EU, 1999c).

Recently, degradation of decabromodiphenylether has been studied using a variety of media (in toluene, and as a thin layer on silica gel, sand, soil and sediment (Sellström et al, 1998a,b)). The sediment samples were reconstituted with water before irradiation. The experiments carried out in toluene using artificial sunlight, showed a consecutive build up and decrease of nona-, octa-, hepta- and finally hexabromodiphenylether. The half-life for decabromodiphenylether was estimated to be < 15 minutes under the conditions used (EU, 1999c).

Other experiments using solid matrices in water also indicated that reductive debromination was occurring, although the increase in the amounts of nona-, octa- and hepta- bromodiphenylethers present was not nearly so pronounced as in the toluene experiments. This indicates that either the stepwise reductive debromination pathway is less significant in environmental media or that lower brominated products degrade faster in these media. Furthermore, no 2,2',4,4'-tetrabromodiphenylether was seen in this study. The half-life for decabromodiphenylether in the sand experiments was around 37 hours using natural sunlight (Sellström et al, 1998c).

Although these experiments have demonstrated the potential for decabromodiphenylether to undergo photolytic debromination and possibly form lower brominated diphenylethers (more toxic and bioaccumulative than the parent compound), the actual extent of this reaction in the environment is likely to be small. The results also indicate that, beside reductive debromination to lower brominated diphenylethers, other degradation pathways must be occurring. The photodegradation pattern seen for decabromodiphenylether is similar to that seen for other halogenated aromatic compounds. Further photodegradation testing of decabromodiphenylether under environmentally relevant conditions is recommended in order to assess the significance of the products formed in such reactions (EU, 1999c).

A second order rate constant for the reaction of decabromodiphenylether with atmospheric hydroxyl radicals has been calculated as 1.7×10^{-13} cm^3 $molecule^{-1}$ s^{-1} from the chemical structure using the Syracuse Research Corporation AOP program. Assuming a hydroxyl radical concentration of 5×10^5 $molecule/cm^3$, an atmospheric half-life of 117 days can be estimated (EU, 1999c).

Tetrabromobisphenol A and derivates

The calculated half-life of decomposition of TBBPA in water by UV was 10.2 days in spring, 6.6 in summer, 25.9 in autumn, and 80.7 days in winter. The water depth influenced the direct photodegradation more as UV-absorption of the given water system increased. Photodegradation of TBBPA absorbed onto silica gel with UV (254 nm) resulted in eight metabolites. The half-life value for TBBPA obtained in this test was 0.12 days. It is however difficult to derive environmental conclusions from the results of these experiments (WHO, 1995). For the reaction of decabromodiphenylether with atmospheric hydroxyl radicals a second order rate constant has been calculated as 1.7×10^{-13} cm^3 $molecule^{-1}$ s^{-1} from the chemical structure using the Syracuse Research Corporation AOP program. Assuming a hydroxyl radical concentration of 5×10^5 $molecule/cm^3$, an atmospheric half-life of 36 days is estimated.

Hexabromocyclododecane
Experimental data for prediction of photolysis of HBCD in water were not available in the literature. From the chemical structure a second order rate constant for the reaction with atmospheric hydroxyl radicals has been calculated using the Syracuse Research Corporation AOP program. With a hydroxyl radical concentration of 5×10^5 $molecule/cm^3$, an atmospheric half-life of 1.8 days is estimated for hexabromocyclododecane.

5.4.3 Biodegradation and mineralisation

Polybrominated biphenyls (PBB)
In laboratory investigations, mixtures of PBBs appear to be fairly resistant to microbial degradation. Soil incubation studies using FireMaster BP-6 and ^{14}C-PBB showed only little degradation of the major hexa- and heptabromobiphenyl congeners after 6-12 months. Only pentabromobiphenyl was shown to degrade slightly, based on recovery rates of PBBs from soil, $^{14}CO_2$ production, and the lack of ^{14}C-PBB intermediates (WHO, 1994a).

Soils incubated with photodecomposition products of ^{14}C-hexa and heptabromobiphenyl caused enhanced, but still minor, degradation (ca. 3%) as measured by $^{14}CO_2$ production. These findings are consistent with observations that degradation of PCBs by bacteria decreases with increasing chlorination (WHO, 1994a).

In other incubation experiments with FireMaster BP-6 with sterilized and nonsterilized soil, from the penta-, hexa-, and heptabromobiphenyl recovery was evaluated that all PBBs persisted for 6 months with no significant microbial degradation. They observed the same kind of persistence over a period of 4 weeks in PBB incubations with mixed cultures of microorganisms (predominantly Alkaligenes odorans, A. denitrificans, and an unidentified bacterium). This culture was known to degrade water-soluble PCBs. However, no PBB metabolites were found in the PBB- saturated mineral solution after 4 weeks of incubation (WHO, 1994a).

Pentabromodiphenylether
No degradation (as CO_2 evolution) was seen in 29 days in an OECD 301B ready biodegradation test carried out to GLP (Schaefer and Haberlein, 1997). The substance tested was a composite sample from two producers and had the following composition: 33.7% tetra-bromodiphenylether, 54.6% pentabromodiphenylether and 11.7% hexabromodiphenylether. The substance was tested at a concentration of 10 mg C/l and was added to the test medium by direct weight addition. An activated sludge inoculum was used. The theoretical carbon content of the test material was estimated to be 26.2%. The test was extended to 93 days to allow sufficient opportunity for adaptation to occur and at the end of 93 days, 2.4% of the theoretical amount of CO_2 had been evolved. A positive control (sodium benzoate) showed 97.8% CO_2 evolution degradation (with >60% evolution within 5 days), indicating the viability of the test organisms used. It can be concluded that pentabromodiphenylether is not readily biodegradable (EU, 1999a).

No information is available on the anaerobic biodegradability of pentabromodiphenylether. From the data generated for other halogenated aromatic substances, there is a possibility for reductive dehalogenation of polybrominated diphenylethers to occur under some conditions. If this occurs for pentabromodiphenylether then this could provide a removal mechanism from the environment. Studies are currently recommended on the higher brominated diphenylethers in order to assess the environmental significance of such reactions (EU, 1999a).

Octabromodiphenylether
Biodegradation of octabromodiphenylether has been determined in a closed bottle test (GLP, OECD 301D) using a composite sample of three commercial octabromodiphenylether products. As inoculum and activated waste water treatment sludge was used. The octabromodiphenylether was tested as a suspension at a concentration of 15 mg/l over a period of 28 days. Lack of oxygen uptake revealed that octabromodiphenylether is not readily biodegradable, whereas sodium benzoate was degraded by more than 60% at day 7 of the test (Schaefer and Haberlien, 1996). Data on anaerobic biodegradation of octabromodiphenylether are not available. Experimental data for halogenated aromatic substances suggest that reductive dehalogenation would be possible. Data to confirm the probability of such a process for octabromodiphenylether are not available (EU 1999b).

Decabromodiphenylether
The biodegradability of decabromodiphenylether was studied under aerobic conditions over a 2 week period at a concentration of 100 mg/l, using activated sludge as inoculum. No degradation (as measured by BOD) was seen, therefore decabromodiphenylether is not readily biodegradable (CITI, 1992). KEMI (1994) reported that no degradation/ transformation of decabromodiphenylether was seen after 4 months incubation in sediment samples. The results indicate that decabromodiphenylether is unlikely to biodegrade rapidly in the environment under aerobic conditions. No data are available on biodegradation of decabromodiphenylether under anaerobic conditions. Analogous to the behaviour of other halogenated aromatic substances, reductive dehalogenation would be probable. However, there is insufficient information to assess the significance of this process for the behaviour and fate of decabromodiphenylether in the environment (EU, 1999c).

Tetrabromobisphenol A and derivates
The biodegradability of ^{14}C-TBBPA was tested under aerobic conditions in three soil types, i.e. Massachusetts sandy loam, a California clay loam, and Arkansas silty loam. Thin layer chromatography (TLC) confirmed biodegradation of TBBPA in all soil types. Only 6% or less of the applied radioactive TBBPA was recovered in the volatile traps, indicating only partial degradation. After 64 days, the amount of TBBPA remaining in the soils ranged from 82 to 36% with highest levels in sandy loam soil and lowest in silty loam soil (WHO, 1995). The results are presented in table 5.4.

The biodegradability test under anaerobic conditions in the same soil types showed that 0.5% of the applied radioactive TBBPA was recovered in the volatile traps, indicating only partial degradation. The recovered radioactivity in the traps was almost exclusively CO_2. Radioactivity recovered from the water was < 2.5%. TLC analysis results indicated variable degradation rates of TBBPA (see table 5.4) In another study, the biodegradability of ^{14}C-TBBPA was tested under aerobic conditions in a sediment/water microbial test system using natural river sediment and water. The test conditions were pH 5.5, 24-26°C and the composition of the soil (6.8% carbon) was 92% sand, 6% silt, and 2% clay. Oxygen was bubbled through the system to maintain aerobic conditions. The 64-day aerobic test showed biodegradation of TBBPA in all tested concentrations, e.g. 10,100 and 1,000 µg/l. Half-lives calculated for TBBPA ranged between 55 and 100 days. Half-life correlated with both TBBPA concentration and microbial population. The half-life in sterile soil could be extrapolated to 1,300 days, clearly indicating that the degradation was due to microbial degradation rather than physical processes. Less than 8% of the radioactive carbon from TBBPA was recovered as CO_2 (See table 5.4). A biodegradation study of 2 weeks on TBBPA (100 mg/litre), using activated sludge under sewage treatment conditions showed no degradation of BOD (WHO, 1995).

Table 5.4
TBBPA removal in soil and sediment after 56- 64 days (WHO,1995)

Environmental system	Composition (%)			Aerobic conditions (%)			Anaerobic conditions (%)			
	Sand	Clay	Silt	Total	Air	DT_{50}	Total	Air	Water	DT_{50}
Mass. sandy loam	83	13	4	18	< 6	500	43-56	< 0.5	<2.5	65
Arkansas silty loam	43	24	33	64	< 6	43	35-47	< 0.5	< 2.5	85
California clay loam	16	58	26	*	< 6	*	9-11	< 0.5	< 2.5	420
Inoculated sediment	92	2	6							
TBBPA (µg/l)										
10	-	-	-	55	< 8	55	-	-	-	-
100	-	-	-	35	< 8	100	-	-	-	-
1000	-	-	-	40	< 8	80	-	-	-	-
Sterile soil	-	-	-	-	-	1300				

*: Unknown DT_{50}: half-life in days

Hexabromocyclododecane

In the literature there were no experimental data available which could be used to evaluate the biodegradation and mineralisation of this compound. Using the Syracuse Research Corporation AOP Program, indicative values were computed for biodegradation rates in aquatic systems. These values indicate that hydrolysis/hydroxylation will occur within several weeks and that it will take several months before complete mineralisation is achieved.

5.5 Bioconcentration

Bioconcentration is the process in which micro contaminants are taken up by organisms. The contaminant is concentrated to higher internal concentrations in case it is not metabolised by the organism as compared to the case that it is metabolised. Bioconcentration is considered to be a partition process between water and organisms and comparable with for example sorption and octanol-water partitioning. Bioconcentration of compounds in aquatic organisms can occur through uptake of compounds directly from the water (bioaccumulation) or through food (biomagnification). Bioaccumulation can be measured in different ways. Organisms can be exposed to water with contaminants until equilibrium is attained (internal contents do not increase anymore). The bioconcentration factor (BCF) can be calculated from the ratio between the content in organisms and water: BCF = Corganism / C water. The BCF can be expressed on lipid basis as well as on fresh weight basis.

5.5.1 Polybrominated biphenyls (PBB)

Gobas et al. (1989) reported BCF and K_{ow} values of polybrominated benzenes and biphenyls in *Poecilia reticulata* but could only detect a correlation between these values when K_{ow} was < 6. The log K_{ow} values and bioconcentration factors (log BCF) of some PBBs are given in table 5.5. Possible reasons for an incorrect determination of BCF values are the elimination via faeces or lower bioavailability due to absorption of the compounds to other molecules or to dissolved organic matter (Pijnenburg, 1995).

Table 5.5
Log K_{ow} and log BCF (*Poecilia reticulata*) values for some PBBs (Gobas, 1989)

Compound	Log K_{ow}	Log BCF
4,4'-di-B	5.72	5.43
2,4,6-tri-BB	6.03	5.06
2,2',5,5'-tetra-BB	6.50	6.16
2,2',4,4', 6,6'-hexa-BB	7.20	5.85

Zitko (1977) and Zitko and Hutzinger (1976) studied the bioaccumulation of PBBs in young Atlantic salmon (*Salmo salar*). The PBB was supplied through the water and food. To establish bioconcentration factors, a mixture of 388 μg PBB consisting of equal amounts of three di-bromo, one tri-bromo, and two tetra-bromobiphenyls was supplied to 3 L water to which the fish were exposed for 96 hours. Biomagnification factors were measured in an experiment where fish were fed with a PBB-spiked diet with the same PBB compounds. The bromine content of the food was 7.75 $\mu g/g^{-1}$. The reported bioconcentration and biomagnification factors are given in Table 5.6 (Pijnenburg, 1995).

Table 5.6
Bioconcentration and biomagnification factors of PBBs on a wet weight basis in Salmon (*Salmo salar*) (Zitko and Hutzinger 1976; Zitko 1977)

Compound	Congener	Bioconcentration	Biomagnification
di-BB	10	1.2×10^6	0.179
di-BB	8	1.3×10^6	0.318
di-BB	12	63×10^3	0
tri-BB	31	425×10^3	0.449
tetra-BB	49	314×10^3	0.589
tetra-BB	70	110×10^3	0.571
C_6H_6	-	0	0

For all PBBs, bioconcentration factors are several orders of magnitude higher than biomagnification factors. Di-BB (congener 12) was not accumulated via food and only moderately from water. Corresponding dichlorinated biphenyls showed the same effect (Zitko, 1977). Compounds with a low bromine content bioconcentrated more strongly from water than compounds with a high bromine content. PBBs with more than six bromine atoms were hardly bioconcentrated at all (Zitko, 1977). However, compounds with one to four bromine atoms were taken up more from food when the bromine content was higher. PBBs with six to eight bromine atoms were only accumulated to a slight degree from food. Zitko (1977) found only hexa-BBs in fish tissue after exposure to a diet spiked with octa-BBs. This dehalogenation e.g. enrichment of lower halogenated congeners in tissue is not known for corresponding chlorinated biphenyls. The accumulation of Firemaster from food appeared to be higher than the accumulation of other PBBs. The half-life for excretion from fish was determined for two PBB congeners, Firemaster and octa-BB-product (see Table 5.7).

Table 5.7
Excretion half-lives of PBBs in fish, after uptake from food or water (Zitko 1977)

Compound	From water	From food
2,2', 4,5' tetra-BB	21 d	28 d
2,4', 5 tri-BB	13 d	26 d
Firemaster	n.a.	93 d
OctaBB	n.a.	93 d

5.5.2 Polybrominated diphenylethers

Pentabromodiphenylether

Bioaccumulation of a commercial pentabromodiphenylether has been studied in *Cyprinus carpio* (CITI, 1982). The material used contained tetra- to hexabrominated congeners, with the major components being a pentabromodiphenylether (47.4%) and a tetrabromodiphenylether (37.6%). The bioaccumulation study was carried out under continuous flow conditions. The fish used had an average body weight of 23.7 g, average length of 9.8 cm and a lipid content of 4.8%. Two concentrations of the commercial pentabromodiphenylether were tested, 10 and 100 µg/l. Since no actual pure analytical standards were available for each component, calibration curves for each component (chromatographic peak) were determined on basis of the total nominal concentration of pentabromodiphenylether added. The BCFs values are shown in table 5.8.

Table 5.8
Bioconcentration factors for the components of a pentabromodiphenylether (*Cyprinus carpio;* CITI, 1982)

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

Using the data in table 5.8 it is possible to estimate a BCF for the commercial product by weighing the BCF for the individual components to their percentage composition in the formulation.

component A: 37.7% BCF = 35,100 l/kg
component B: 7.9% BCF = 11,700 l/kg
component C: 47.4% BCF = 73 l/kg
component D: 2.5% BCF = 5,620 l/kg
component E: 2.6% BCF = 1,080 l/kg

On basis of these specifications an overall BCF of 14,350 l/kg was estimated (EU, 1999a).

The uptake of pentabromodiphenylether by fish from food has been studied as part of a reproduction study (Holm et al, 1993). In the experiment, female three-spined stickleback (*Gasterosteus aculeatus*) (20 per group; initial weight 0.9g) were fed freeze-dried chironomids (at 20 mg/day) contaminated with pentabromodiphenylether (Bromkal 70-5DE) for 100 days. In this period a total amount of 6.29 and 10.39 mg substance was fed to fish, equivalent to doses of 3.5-5.8 mg/kg food/day. After 3.5 months, levels of pentabromodiphenylether in the exposed fish were 72 mg/kg wet weight in the low dose group and 94 mg/kg wet weight in the high dose group. Bioaccumulation factors, (concentration in fish/ concentration in food, on basis of wet weight) of around 20 and 16 were obtained for the low and high dose groups, respectively. Pentabromodiphenylether was not detected in non-exposed control fish.

Burreau et al (1997) investigated the uptake of pentabromodiphenylether in Pike (*Esox lucius*), fed rainbow trout containing a mixture 2,2',4,4'-tetrabromodiphenylether, 2,2',4,4',5-pentabromodiphenylether and 2,2',4,4',5,5'-hexabromodiphenylether, along with 5 polychlorinated biphenyls and 3 polychlorinated naphthalenes. Around 9 days after feeding the amounts of brominated diphenylethers in the pike were determined after removal of the gastrointestinal tract. The uptake efficiency (amount of substance in pike/amount fed) was estimated as 90% for the tetrabromodiphenylether isomer, 60% for the pentabromodiphenylether isomer and 40% for the hexabromodiphenylether isomer (EU, 1999a).

The half-life of commercial pentabromodiphenylether (Bromkal 70) consisting of tetrabromodiphenylether (36%) and pentabromodiphenylethers (64%). Male and female rats were given a single oral dose of 300 mg/kg body weight in peanut oil. During the 10 week experiment, adipose tissues were periodically analysed for brominated diphenylethers using a HPLC method with dibromodiphenylether as an internal standard. This method produced 5 major peaks for the commercial product corresponding with a tetrabromodiphenylether (peak 1), two pentabromodiphenylethers (peaks 2 and 3), a mixture of a penta- and hexabromodiphenylether (peak 4) and a mixture of 3 hexabromodiphenylethers (peak 5). The half-lives in adipose tissue of both male and female rats are presented in table 5.9.

Table 5.9
Half-lives of the components of a commercial pentabromodiphenylether in rat adipose tissue. (von Meyerinck et al, 1990)

Component	Peak	female rats (days)	male rats (days)
Tetrabromodiphenylether	1	29.9*	19.1*
Pentabromodiphenylether	2	47.4	36.8
Pentabromodiphenylether	3	25.4	24.9
Penta/hexabromodiphenylether	4	44.6	55.1
Hexabromodiphenylethers (3 isomers)	5	90.9	119.1

* significant difference between male and female rats

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

Recently, Örn and Klasson-Wehler (1998) investigated the uptake and metabolism of ^{14}C-labelled 2,2',4,4'-tetrabromodiphenylether in rats and mice. The animals were given a single oral dose of 15 mg/kg body weight dissolved in corn oil, after which faeces and urine were collected for 5 days. The substance was found to be well adsorbed in both rat (95%) and mice (~93% adsorbed). In rat, around 86% of the dose remained in tissues, mainly as the parent compound. Around 14% of the dose was found in faeces, with <0.5% excreted in urine. The substance was found to be poorly metabolised in the rat, with around 3% of the dose being excreted as metabolites after 5 days. In the mouse, around 47% of the dose remained in tissues. Around 20% was excreted via faeces and 33% excreted via urine. At least 39% was excreted as metabolites (EU, 1999a).

Octabromodiphenylether
Based on its octanol-water partition coefficients, octabromodiphenylether would be expected to be bioaccumulative. However, experimental results reveal that the octabromodiphenylether does not bioconcentrate, probably because its large size prevents crossing of cell walls in organisms. A study on mixed commercial octabromodiphenylethers indicated essentially no bio-accumulation in *Cyprinus carpio* (CBC, 1982). The material tested was a mixture of brominated diphenylethers with 6 to 9 bromine atoms. The product was identified as 47% heptabromodiphenylether, 17% octabromodiphenylether (isomer 1), 11% octabromodiphenylether (isomer 2) and 7% nonabromodiphenylether. The octabromodiphenylether was tested at two concentrations, 10 µg/l and 100 µg/l using a flow-through system. A dispersing agent (polyoxyethylene hydrogenated castor oil) was present at 400 and 4,000 µg/l respectively. The test fish had an average body weight of 23.7 g, and average body length of 9.8 cm and a lipid content of 4.8%. The BCF was <4 for all main components after 8 weeks exposure. The concentrations used in the test are above the reported water solubility of octabromodiphenyl-ether (around 0.5 µ/l). If it is assumed that the octabromodiphenylether isomers were present at around 0.5 µg/l, then the lower limit for the BCF would be around 9.5 l/kg for this component. The corrected BCFs would be in the order of 10-36 l/kg. The results indicate that no significant bioconcentration of compounds in octabromodiphenylether is expected, unless the commercial product contains significant amounts of lower (≤6 bromines) brominated diphenylether components (EU, 1999b).

Decabromodiphenylether
The bioconcentration of ^{14}C decabromodiphenylether (Dow FR-300-BA; 77.4% deca-, 21.8% nona- and 0.8% octabromodiphenylether) has been studied using rainbow trout under static conditions over a 48 hour period. A bioaccumulative substance, 2,2',4,4'-tetrachlorobiphenyl (TCBP; 16 µg/l) was used as positive control. Little change occurred in the initial concentration of the brominated diphenylether (20 µg/l), indicating minimal uptake by fish and insignificant losses by volatilisation or adsorption onto surfaces etc. Lack of bioconcentration of decabromodiphenylether was confirmed by analysis results of periodical flesh samples which showed little or no uptake. The positive control, TCBP, was found to bioconcentrate at least 50 times over the initial exposure levels within 4 hours (Norris et al, 1973 and 1974).

The bioconcentration of decabromodiphenylether has also been studied in carp over 6 weeks. Bioconcentration factors (BCFs) measured at the end of the experiment were <5 at an initial concentration of 60 µg/l and <50 at 6 µg/l. Concentrations used in the study were greater than the solubility of decabromodiphenylether (<0.1 µg/l). It is possible that the actual dissolved concentration present was less than indicated. If it is assumed that the substance was present at <0.1 µg/l, then the upper limit for the BCF would be 3,000 l/kg (CITI, 1992).

A recent study has investigated the uptake of commercial decabromodiphenylether (Dow FR-300-BA; 77.4% deca-, 21.8% nona- and 0.8% octa components) by rainbow trout from food. The substance was purified on a charcoal column prior to use to remove planar compounds. Test fish were juvenile rainbow trout, which were kept in a continuous flow at temperatures corresponding to those found outdoors in Sweden over the months June to September. A gelatine mixture of Barents Sea cod (*Gadus morhua*), excluding gonads, gall bladder and liver, was used as food. The decabromodiphenylether dissolved/suspended in corn oil and was mixed with the cod/gelatine solution and used in the experiment between 7.5 and 10 mg/kg bodyweight/day. The fish were sampled after 16, 49 and 120 days. Another group was exposed for 49 days, followed by a 120 day depuration period (Kierkegaard et al, 1997 and 1999).

Uptake in the fish was measured on a fresh weight basis in order to compensate for lipid loss during the test (initial 3.9%, final 1.3%). After 16 days exposure, the mean concentration of decabromodiphenylether in muscle was 10 µg/kg increasing to 38 µg/kg after 120 days. Concentrations found in livers exceeded those in muscle (560 and 870 µg/kg after 16 and 120 days). In the depuration phase the levels of decabromodiphenylether decreased by a factor of 2 on a fresh weight basis after 71 days, but no decrease was observed on a lipid weight basis. In the control fish, only 4 out of the 34 muscle samples analysed showed traces of decabromodiphenylether at levels <8% in exposed fish. Lower brominated diphenylethers such as 2,2',4,4'-tetrabromodiphenylether, 2,2',4,4',5-pentabromodiphenylether, and 2,2',4,4',6-pentabromodiphenylether, were identified in both liver and muscle but were also present at similar concentrations in control fish. Concentrations of some hexa-, hepta-, octa- and nonabromodiphenylether congeners increased with exposure period in both muscle and liver. These congeners were initially not detected in the commercial decabromodiphenylether. It is thought that their presence was a result of either a metabolic process or an efficient enrichment of trace amounts present in the food/commercial product used (Kierkegaard et al, 1999). Uptake in muscles was 0.02-0.13% based on total hexa- to decabromodiphenylethers but only ~0.005% based on the decabromo component.

The low bioaccumulation potential for decabromodiphenylether was further confirmed from metabolism studies in rats. Male and female rats were dosed with 1.0 mg of ^{14}C-labelled decabromodiphenylether as a suspension in corn oil. The composition of the commercial decabromodiphenylether was 77.4% deca-, 21.8% nona- and 0.8% octabromodiphenylether. The principle route of excretion of the dose was via the faeces. Around 90.6% of the administered radioactivity was excreted in the faeces within 24 hours and >99% at 48 hours. Other tissue accumulation studies in rats revealed that the bromine contents of liver, kidney, skeletal muscle, serum and testes were not significantly different from the levels found in unexposed controls (Norris et al 1973 and 1974).

Above stated results indicate that decabromodiphenylether is not taken up into animal tissues to any great extent and is rapidly excreted from the animal. Therefore, it can be concluded that decabromodiphenylether has a low bioaccumulation potential, which is supported by the fact that there are very few occurrences of decabromodiphenylether in environmental biota samples. This contrasts markedly with the situation with pentabromodiphenylether, which has been shown to be bioaccumulative in laboratory studies and is widely found in measurable amounts in biota samples (EU, 1999c).

5.5.3 Tetrabromobisphenol A and derivates

TBBPA labelled with ^{14}C in the aromatic ring was used for exposure of blue gill sunfish (*Lepomis macrochirus*; 0.5-2.0 g) in a flow-through system for a period of 28 days at concentrations of 8-11 µg/l. Average ^{14}C tissue concentrations were 0.196 mg/kg in edible tissue and 1.69 mg/kg in non-edible tissue, corresponding with bioconcentration factors (BCF) of 20 and 170 respectively. In depuration, the whole body half-life was < 24 h. Fathead minnows (*Pimephalus promelas*; 39 ± 4 mm, 0.57 ± 0.2 g) were exposed to a concentration of 4.7 µg/litre, in a flow-through system, throughout a 24-day exposure period. The concentration of ^{14}C-residue in the tissue of fish reached a steady-state level of 5.8 mg/kg giving a bioconcentration factor (BCF) of 1200. Following 6 days of depuration, 98% of the accumulated ^{14}C residues were eliminated from the tissues. The whole-body half-life was less than 1 day (WHO, 1995).

Table 5.10
Bioconcentration of TBBPA in various aquatic species (WHO,1995)

Species	System	E (d)	D (d)	TBBPA (µg/l)	BCF (l/kg)	DT_{50} (hr)
Lepomis macrochiros	flow through	28	14	8-11	20 – 170	< 24
Pimephalus promelas	flow through	24	6	4.7	1200	< 24
Carp	flow through	56	-	8	50 – 490	-
Carp	flow through	56	-	80	30 – 340	-
Crassotrea virginica (oyster)	flow through	20	14	1.0	780	< 120
Chirinomous tentans (larvae)	batch	14	-	low	650 – 3200	-
(measured in contaminated	batch	14	-	medium	490 – 1100	-
sediment)	batch	14	-	high	240 – 510	-

*: Unknown E: exposure period D: depuration period DT_{50} : depuration half-life

Eastern oysters (*Crassostrea virginica*) were continuously exposed to a concentration of 1.0 TBBPA µg/l in seawater for a 20-day exposure period. The concentration of ^{14}C residues reached a steady state level on the fifth day of exposure, with bioconcentration factor (BCF) of 780. The half-life of the ^{14}C residues in the oysters was between 3 and 5 days. Another bioaccumulation study on TBBPA (80 µg/litre, 8 µg/litre) using carp for 8 weeks showed 30-340 and 50-490 times bioaccumulation, respectively (WHO, 1995).

5.5.4 Hexabromocyclododecane

In a 32 days flow-through experiment the BCF of hexabromocyclododecane was determined in Pimephalus promelas at a steady concentration of 6.2 µg/l. The BCF value amounted to 18,100, which means that hexabromocyclododecane will accumulate significantly (Veith et al, 1979).

5.6 Distribution in water systems

The behaviour of a substance and its distribution in the environment is primarily governed by properties such as solubility in water, volatility and biodegradability. To what extent these properties are favoured or hindered, depends further on the environmental conditions. The influence of environmental circumstances on the substance's behaviour, can be simulated through modelling of the relevant mass transfer processes. Two modelling programmes, EPIWIN from the Syracuse Research Corporation and EUSES from the EU, have been used to compute the volatilisation from surface water and the substance distribution over air, water and sewage sludge during wastewater treatment..

With the EPIWIN estimation program it is possible to estimate environmental properties from the compound's chemical structure (chemical bond estimation method). Computed values are subsequently used to calculate basic emission distributions between water, air and soil, or the (a)biotic degradation in water and atmosphere. For compounds without experimental data for relevant environmental properties, this estimation method can provide a first indication of the required properties and behaviour in the environment. However, calibrations computations for compounds with reliable data show that sometimes computed values for K_{ow}, K_{oc} and Henry's Law coefficient significantly differ from experimental values and that accordingly, emission distributions will deviate substantially from results obtained with experimental data. EUSES (EU System for Estimation of Substances; developed by RIVM and extensively used in EU Risk Assessments) is a multi-functional, modelling programme for estimation of emission factors and emission distributions from industrial pollution sources. It contains various emissions scenarios and large databases with relevant technical data about emission sources, operating characteristics of wastewater treatment plants, meteorological data, etc.

For the selected compounds, the environmental behaviour in lakes, rivers and wastewater treatment plants was quantified. Furthermore, a theoretical half-life value was computed for atmospheric photolysis in order to obtain an indication of the persistence of compound after it is released into the atmosphere. Basic conditions for volatilisation from river and lake are given in table 5.11.

Table 5.11
Basic parameters for volatilisation (EPIWIN)

	River	Lake
Water depth (m)	1	1
Wind velocity (m/s)	3	0.5
Water current velocity (m/s)	1	0.05

For computation of the emission distribution during wastewater treatment, an activated sludge plant was chosen with a regular set-up consisting of primary sedimentation, aeration and secondary sedimentation. Under these conditions, the biodegradability of the selected compounds was assumed to be negligible. The modelling results are summarised in table 5.12. From the volatilisation results for river and lake, it shows that compounds, with high Henry's Law coefficients such as tetrabromobisphenol A and hexabromocyclododecane are rapidly removed from surface waters. For PBDE compounds can be seen that with extending bromination, log K_{ow} e.g. K_{oc} values increase and Henry's Law coefficients decrease, resulting in steady increase of the volatilisation half-life.

At the same time, emission distributions in wastewater treatment shift to the water compartment, with a slight increase of the adsorption onto sludge. Half-live values for reaction with atmospheric hydroxyl radicals further indicate that with increasing bromination (molecular weight), the compounds become resistant to photolytic degradation.

5.7 Conclusions and recommendations

With respect to the environmental properties and behaviour in the aquatic systems the following conclusions can be drawn for the selected compounds:

1. For all compounds measured values for water solubility, vapour pressure and Henry coefficient were found to correlate with measured log K_{ow} values. For PBB and PBDE it was shown that the log K_{ow} value correlates with the bromine content.

2. On basis of the log K_{ow} value, it is assessed that higher brominated compounds will bind stronger to solid media than lower brominated congeners. DecaBB levels in river sediment, which are generally 50-500 times higher than pentaBDE levels, confirm this. Similarly, compounds with high log K_{ow} value are expected to have low vapour pressure e.g. low volatility.

3. In various photolytic degradation experiments of PBB and PBDE, dissolved in organic solvent, rapid reductive debromination was established. Field observations for PBB demonstrate however that under environmental conditions the original composition of PBB was unchanged after a period of 10 years. Photolysis experiments with decabromodiphenylether in water indicate that reductive debromination to nona-, octa- and heptabromodiphenylethers may be possible. However, latter compounds are not identified in environmental samples of decabromodiphenylether.

4. Biodegradation experiments for TBBPA in various sediment and soil types resulted in half-lives of 50 – 100 days. Further, only for pentabromobiphenyl slight degradation (3%) is observed. The other brominated compounds are found to be fairly resistant to microbial degradation, both under laboratory as field conditions.

5. For PBB and PBDE it was found that compounds with more than 6 bromine atoms are hardly bioconcentrated. Compounds with low bromine content showed stronger bioconcentration than higher brominated compounds. BCF values in carp range from 35,000 for tetrabromodiphenylether to < 50 for decabromodiphenylether. TBBPA has been shown to be bioaccumulative in various fish with a BCF range of 300-1,200 l/kg. BCF value of HBCD was measured at 18,100 l/kg in fish. The observed variation of bioaccumulation factors for lower brominated compounds corresponds well with the range of log K_{ow} values.

6. Uptake through food in pike was significantly higher for tetrabromodiphenylether (90%) than for hexabromodiphenylether (40%). Comparable results were observed for uptake of 2,2′,4,4′-tetrabromodiphenylether (95%) and decabromodiphenylether (< 1%) in rat. From food uptake of decabromodiphenylether it was shown that hexa-, hepta-, octa- and nonabromodiphenylether levels increased with exposure time. This can either be the result of metabolic processes or an efficient enrichment of the most bioaccumulative compounds. Similar enhanced bioaccumulation of 2,2′,4,4′-tetrabromodiphenylether is frequently observed in environmental samples of technical pentaBDE.

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Table 5.12
Results of EPIWIN and EUSES estimation programmes for environmental distribution of selected brominated compounds

Property	**Decabromo Biphenyl**	**Tetrabromo-diphenylether**	**Pentabromo-diphenylether**	**Hexabromo-diphenylether**	**Heptabromo-diphenylether**	**Octabromo diphenylether**	**Nonabromo-diphenylether**
Log Kow (measured)	8.58	6.0	6.7	7.4	8.0	8.65	9.3
Log Koc (TGD)	7.05	4.97	5.54	6.09	6.59	7.09	7.63
H (measured) (atm m^3/mole)	$1.9*10^{-7}$	$1.6*10^{-4}$	$4.9*10^{-5}$	$2.3*10^{-5}$	$8.0*10^{-6}$	$2.8*10^{-6}$	$9.1*10^{-7}$
Volatilisation half-life from river	604 days	0.94 days	2.1 days	4.3 days	12.9 days	37.8 days	107 days
Volatilisation half-life from lake	4400 days	13.6 days	22.3 days	39.3 days	102 days	284 days	786 days
Half-life for reaction with hydroxyl radicals [c]	852 days	6.4 days	10.4 days	13.2 days	25.8 days	35.6 days	52 days
Removal in WWTP To effluent To sludge To air	 8.1 % 91.9 % < 0.01%	 12.2 % 86.8 % 1.0 %	 9.8 % 90.0 % 0.18 %	 8.5 % 91.4 % 0.03 %	 8.2 % 91.8 % 0.01 %	 8.0 % 91.9 % < 0.01%	 8.0 % 92.0 % < 0.01%

H: Henry's law constant. WWTP: Wastewater Treatment Plant TGD: Technical Guidance Document

[c] : Calculated from OH reaction rate constant estimated by the method of Atkinson and assuming a OH radical concentration of 1.5´10^6 molecules/cm^3 and 12 hours sunlight/day

7. Compounds with low log K_{ow} and high log H values, such as TBBPA, HBCD, tetra BDE and pentaBDE, readily evaporate from surface water and have also short half lives in atmosphere. The other compounds, with moderate to high low K_{ow} values are more or less non-volatile and hardly degradable in atmosphere.

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6. Occurrence in the aquatic environment

6.1 Analytical techniques

6.1.1 PBBs

Analytical methods for determination of PBBs were adapted from established methods for chlorinated hydrocarbon insecticides (like DDT) and PCBs (WHO, 1994a). Usually hexane or iso-octane are used as solvents in the analysis of PBB mixtures and individual congeners. Gas chromatography (GC) is used for the final analysis. Griffin and Chou (1981) found that for the extraction of PBBs from soils and sediments the use of a polar organic solvent was important. The best results were obtained with hexane/acetone (9:1). Extraction was followed by further sample-clean up with Florisil.

Fehringer (1975) describes the use of dichloromethane for extraction of PBBs from dry animal food. Sample-clean up is performed with Florisil columns. Extraction of blood and serum follows pretreatment of the serum with methanol, and extraction is performed with a hexane/ether mixture. This method, described by Burse et al. (1980), is a standard extraction method for blood and serum, and has been used in most studies. Florisil columns are used in the sample-clean up. An analytical method was developed to quantitate PCBs and PBBs in human serum. This method includes a hexane-ethyl ether extraction of methanol-denatured serum, and an adsorption chromatography with de-activated silica gel (Needham, 1981).

PBBs can be co-extracted together with the fat from biological tissue samples but afterwards an intensive clean up procedure for PBBs is necessary. Various sample clean up methods such as adsorption chromatography with Florisil, gel permeation chromatography, Florisil cartridges and Unitrex have been proposed (WHO, 1994a). Isolation of coplanar compounds from the major compounds in the extract is achieved by using activated charcoal, since this absorbs the planar molecules more strongly than the non-planar ones. Brominated naphthalenes, dioxins and furans, will also be separated from the non-planar compounds in these steps. To aid these separations, high performance liquid chromatography (HPLC) methods are now being adopted (WHO, 1994a). Soxhlet extraction with dichloro- methane/*n*-pentane, followed by clean up over alumina columns and fractionation over silicagel columns, results in recoveries over 95 % for all PBBs. Toluene may particularly be effective for extraction of decaBB (Ranken, 1998). Saponification may be an alternative, but decomposition of some PBB congeners may occur as with PCBs (Pijnenburg, 1995).

Typical recoveries of PBBs using established methods are in the range of 80-90% (Fries, 1985). The solvent system used for sample extraction can affect recovery (WHO, 1994a). PBBs adsorb to glass more tenaciously than other halogenated hydrocarbons, and are not easy to remove by the usual cleaning methods. Using disposable glassware prevents erroneous values in the data (Willet, et al, 1978). The 209 possible PBB congeners have a wide range of volatility, which causes complex separation problems. GC oven temperatures vary between 240°C and 300°C. Although most PBBs elute after PCBs, higher chlorinated PCBs may interfere with lower brominated PBBs (De Boer, 1995). Decachlorobiphenyl caused most interference in the analytical method for quantification of PBBs in human serum (Needham, 1981). Polychlorinated terphenyls (PCTs) may also interfere with PBBs (De Boer, 1995). Therefore, mass spectrometry (MS) with electron impact (EI) or electroncapture negative ionisation (ECNI) as ionisation methods is the preferred technique for detection of peaks after separation (Pijnenburg, 1995). Quantification can be achieved by comparison with known standards (WHO, 1994a). The synthesis of pure congeners for use as standards is a prerequisite for advances in chemical analysis, as well as research into toxicological and biological effects of PBBs (WHO, 1994a). Although some individual PBB congeners are available as standards, the number of studies reporting individual PBB data is limited.

A recent method of detection is electron capture negative ionisation (ECNI) as ionization technique in combination with GC-MS analysis. This method is advantageous because it offers a high sensitivity for compounds with four or more bromine atoms (De Boer, 1995). The sensitivity of ECNI for these compounds is approximately 10 times higher than with the use of an electron capture detector (ECD) (Pijnenburg, 1995). In the analytical method which was developed to quantitate PCBs and PBBs in human serum, GC/ECD was used (Burse, 1980). Because the response, and there fore the sensitivity, of the ECD depends on the position of the halogen on the biphenyl nucleus as well as the number of halogen atoms, it is necessary to run a standard for each compound to be determined (WHO, 1994a). The use of narrow bore (0,15 mm i.d.) capillary columns is advised to obtain the required resolution (Pijnenburg, 1995).

6.1.2 PBDEs

Extraction and clean-up techniques for the analysis of PBDE residues in biological samples are similar to those developed for PBB. Table 6.1 shows several methods to determine PBDEs in various media. Most methods are based on extraction with organic solvents, purification by gel permeation or adsorption chromatography, and determination mainly by GC, either with ECD or coupled with MS, with EI or ECNI. The recovery of the different PBDEs is generally higher than 80 % (WHO, 1994b).

Other extraction methods described for PBDEs in the literature are basically batch and Soxhlet extractions. The various clean-up methods for biological, sediment, and sewage sludge samples differ, depending on other compounds of interest which are determined simultaneously. A multi-residue method has also been developed by Jansson et al. (Jansson, 1991). This method includes a multi-step separation enabling the determination of several polychlorinated an polybrominated pollutants in biological samples (WHO, 1994a). However, the recovery of 2,2',4,4'-TeBDE with this method is only 49% (Pijnenburg, 1995).

Extraction of DeBDE (and also DeBB) is more difficult than other PBDEs, but a good solvent system is hexane/acetone (3:1). Toluene may also be a good alternative (Needham, 1981). Yamamoto et al. (1998) reported the determination of DeBDE in water and sediment samples. For the extraction of DeBDE from the sediments they used ultrasonic extraction with acetone. Rapid sample preparation techniques such as C_{18} solid-phase and cartidge type Florisil extraction were used to clean up water and sediment samples. Average recoveries were 103% and detection limits were 0.12 ng/ml in water and 9.7 ng/g in sediment.

Typical GC analysis is performed using a nonpolar capillary column (15-60 m) of methyltype (SE-3O,OV-1, OV-101) or methyl + 5% phenyl groups (DB-5,SE-54,CP-Sil 8CB) (Sellström, 1996). Both GC-ECD and GC-MS with El or ECNI may be used for the final analysis of PBDEs (5). ECNI-MS is a very sensitive method for many halogenated compounds (Sellström, 1996). Using GC-MS, the type of reaction gas can influence the data.

A study of PBDE residues in guillemot eggs showed 10-35%, 25-80% and 0-20% increase in levels of 2,2',4,4',5-TeBDE an unidentified PeBDE, and 2,2',4,4',5-PeBDE respectively using ammonia as reaction gas instead of methane (Sellström, 1996).

Another variety of the GC-MS detection method is high resolution GC/high resolution MS (HRGC-HRMS). Not only human adipose tissue can be analysed with HRGC-HRMS. Loganathan et al. (1995) and Takasuga et al. (1995), described the analysis of PBDE residues in environmental samples with HRGC-HRMS. After the standard clean up an extra clean up stage with HPLC porous graphitic carbon was added. The mass spectrometer was operated in the selected ion monitoring (SIM) mode. With this method the identification of PBDEs as interferences of heptachlorinated dibenzofurans in the analysis of routine environmental samples can be quantified (Takasuga, 1995).

In most studies the technical mixture Bromkal 70 - 5 DE is used as an external standard. The percentage of PBDE congeners of Bromkal 70-5 DE is 44% 2,2',4,4'-TeBDE, 48% 2,2',4,4',5-PeBDE an 8% of an unknown PeBDE (Sellström, 1996; Pijnenburg, 1995; de Boer and Dao, 1993). Like the PBB analysis, the analysis of PBDEs requires individual PBDE congeners as analytical standards. Synthesized standards of 2,2',4,4'-TeBDE, 2,2',4,4',5-PeBDE and 2,2',4,4',5,5'-HxBDE (Sellström, 1996; de Boer and Dao, 1993) are available. Recalibration of the Bromkal mixture used with the 2,2',4,4'-TeBDE, 2,2',4,4',5-PeBDE standards showed that the percentage of the TeBDE in this mixture was 36,1 % and PeBDE 35,5 % (De Boer and Dao, 1993). Various individual PBDE,'s have recently become available (Sellström, 1996; Erikkson, 1996). Wolff and Rimkus (1985) described the synthesis of 2,2',4,4'-TeBDE for the analysis of this congener in fish. The synthesis of ^{14}C labelled 2,2',4,4'-TeBDE and 2,2',4,4',5-PeBDE was described by Örn et al. (1998).

6.2 Measurements in freshwater systems

As mentioned in 6.1 the analysis of polybrominated diphenylethers is complicated by the fact that commercial products are mixtures and that there was a lack of analytical standards for individual isomers of these mixture, particularly in the past. This has recently improved and most modern analysis use relatively pure samples of specific congeners present in commercial products for verification and quantification (Örn, 1997; Örn et al, 1998).

6.2.1 Surface water

Polybrominated biphenyls (PBB)

Surface water monitoring in the vicinity of PBB producing and processing facilities, revealed that the major PBB compounds detected in surface water were hexaBB and decaBB. Levels were generally in the range 1-20 µg/l, which is in good agreement with experimentally obtained values (WHO, 1994a).

Table 6.1
Analytical methods for PBB and PBDEs

Sample/ substance	Extraction and clean-up	Separation and detection	Limit of determination	Ref
Effluent river water/PBB	Extraction hexane/diethylether	GC/ECD	0.1 µg/l; later 0.01 µg/l	WHO (1994a)
Sediment/ PBB	Extract with hexane/acetone	GC/ECD	100 µg/kg	WHO (1994a)
Soil/PBB	Extract with hexane/acetone	GC/ECD, FID, MS	-	WHO (1994a)
Dry-animal food/PBB	Extract with dichloromethane; clean-up on Florisil	GC, TLC/ECD	8 µg/kg 30 µg/kg	Fehringer (1975); WHO (1994a)
Human serum/PBB	Pretreatment with methanol; extraction with hexane/ether mixture; clean-up with Florisil	GC/ECD	0.1 µg/l	Burse, et al (1980); WHO (1994a)
Soil/sediment/ sludge/ vegetation/ PBB	Polar organic solvent hexane/iso-octane; clean-up Florisil	GC/MS	0.2 µg/kg	Griffin & Chou (1981); WHO (1994a)
Human serum/PBB	Hexane-ethyl ether extraction of methanol denatured serum; clean-up with silica gel	ECD; MS with EI or ECNI	1 µg/l	Needham (1981) Pijnenburg (1995) WHO (1994a)
Biological tissue and fat/PBDE	Soxhlet extraction with dichloromethanol n-pentane; clean-up alumina columns and fractionation over silicagel columns	-	-	Ranken (1998)
Sewage/ PBDE	extract with chloroform; evaporate and dissolve residue in ethanol	GC/MS	0.06 mg/kg	(Kaart, 1987)
Sediment/ PBDE	extract with acetone; clean-up on Florisil	NAA; GC/EC	<5µg/kg	(Noren, 1998)
Fish/PBDE	extract with acetone-hexane + hexane-ethyl ether; treatment with sulfuric acid or clean-up on alumina; chromatography on silica gel	GC/EC; GC/MS	detection limit 0.1 mg/kg fat	(Andersson, 1981)
Animal tissues (Multi-residue method)/ PBDE	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	(Kruger, 1988)
Fish/PBDE	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	(de Boer, 1995)
Cow's milk/ PBDE	centrifuge; gel permeation chromatography; clean-up on Florisil; elute with hexane	GC/MS (NCI/SIM)	<2.5 µg/kg fat	(de Boer, 1995)
Human adipose tissue/PBDE	extract with methylene chloride; evaporate; clean-up on silica gel followed by clean-up alumina and on a carbon/silica gel column	HRGC/HRMS[a]	detection limit 0.73-120 ng/kg (different congeners)	(Cramer, 1990)
Commercial PBDE	homogenize and dissolve in tetrachloromethane for HPLC and GC/MS or *n*-hexane for TLC/UV	HPLC; GC/MS; TLC/UV	-	(Kok, 1979)

Pentabromodiphenylether

Despite numerous measurements in aquatic systems, no levels have been reported for polybromodiphenylethers in the aquous phase. In the early 1990's, extensive measurements were performed by de Boer et al (1993) in fresh water systems in the Netherlands. Traces of pentabromo- and tetrabromo compounds were found in sediments and biota, but not in water. Comparable results were established with pentabromodiphenylethers in water samples from in and around Japan in 1987 and 1988. The samples are thought to be representative for industrial, urban and rural areas of Japan. It is not known if the sampling sites were in the vicinity of polybrominated diphenylether production sites or sites of potential release. The results are reported in table 6.2.

Table 6.2
Levels of hexabromodiphenylether in water.

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

The same lack of analysis-results in the water phase applies to analysis of octa- and deca-bromodiphenylethers. Another relevant issue in the analysis of these higher brominated compounds is that only recently reliable reference standards have been developed for the individual compounds (de Boer, 1999).

Octabromodiphenylether

Measured levels of octabromodiphenylethers in water are shown in table 6.3. As shown, the levels in water are in all cases below the limit of detection (i.e. <0.07-<0.1 µg/l). The samples are thought to be representative of industrial, urban and rural areas of Japan.

Table 6.3
Levels of octabromodiphenylether in water.

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

Decabromodiphenylether

Levels of decabromodiphenylether measured in water are shown in table 6.4. As can be seen from table A, levels in water are in all cases lower than the detection limit (i.e. <0.06-<2.5 µg/l). The samples are taken from several industrial, urban and rural areas of Japan and are thought to be representative of the country as a whole.

Table 6.4
Levels of decabromodiphenylether in water

Location	Comments	Level	Reference
Japan, 1977	Detection limit 0.2-2.5 µg/l	Not detected in 15 samples	Environment Agency Japan, 1991
Japan, 1987	Detection limit 0.1 µg/l	Not detected in 75 samples	Environment Agency Japan, 1991
Kino River, Japan	Detection limit 0.1 µg/l	Not detected in 12 samples	Yamamoto et al, 1991
Japan, 1988	Detection limit 0.06 µg/l	Not detected in 141 samples	Environment Agency Japan, 1991

Tetrabromobisphenol A and derivates
Numerous measurements of TBBPA in water samples from 25 districts in Japan (1977-1987) reveal that TBBPA levels seldom exceed the detection limit (0.02-0.04 µg/l) (WHO, 1995).

Hexabromocyclododecane
Measurement data for HBCD levels in water were note available in the searched literature sources. On basis of its high K_{ow} value it is expected that conform TBBPA, levels in water will be low.

6.2.2 Sediment

Polybrominated biphenyls (PBB)
Near the former production site of the Michigan Chemical Corporation, PBB levels in sediment were measured from 1974 to 1977. During production, levels in sediment near the production site were as high as 77 mg/kg dry weight (as hexaBB) and declined to 6.2 mg/kg dry weight at half a mile downstream respectively to 0.1 mg/kg dry weight at approx. 30 miles downstream. Sediment levels upstream of the plant were typically < 30 µg/kg dry weight. Measurements after plant shut-down in 1976 demonstrated that after termination of the production, PBB levels in sediment sharply decreased. In 1977 hexaBB levels were only 100-500 µg/kg dry weight (WHO, 1994). Similar measurements at another PBB production location revealed that activated sludge treatment of PBB containing wastewater adequately prevented sediment pollution. Only 40 µg/kg dw hexaBB was found downstream the plant, whereas the sewage sludge contained several PBB congeners, varying from 0.5 mg/kg dw monobromobiphenyl to 390 mg/kg dw of decaBB (WHO, 1994).

Measurement in river sediments around the North Sea demonstrated that decaBB is the major compound in sediment, ranging from 0.33 µg/kg dw in the Mersey river to 0.40-0.80 µg/kg dw for the Rhine and the Elbe river. Parallel to decaBB, traces of hexaBB were found in levels of < 0.01-0.024 µg/kg dw (de Boer, 1999).

Pentabromodiphenylether
Several studies have measured levels of commercial pentabromodiphenylether in sediments. In most cases the commercial compound Bromkal 70 was used as reference for identification and quantification. This substance has been shown to consist mainly of 2,2',4,4'-tetrabromodiphenylether, 2,2',4,4',5-pentabromodiphenylether and an unknown pentabromodiphenylether and levels are reported for individual components or in terms of commercial formulation. The unknown pentabromodiphenylether isomer has recently been shown to be 2,2',4,4',6-pentabromodiphenylether. Furthermore, some commercial pentabromodiphenylethers contain small traces of hexabrominated compounds (Sellström et al, 1998).

Although the commercial compound Bromkal 70 is no longer supplied in the EU, the current pentabromodiphenylether compounds appear to have very similar compositions and so, although the results are expressed as Bromkal 70, they are likely to represent the total concentrations of all commercial pentabromodiphenylethers in the environment (EU, 1999a).

Furthermore it is likely that individual components of commercial products will distribute in the environment in different ways (e.g. more highly brominated components may be expected to adsorb more strongly onto sediment than components with a lower degree of bromination).

As reported earlier, measurements were performed by de Boer et al in 1992. A summary of results for fresh water sediments is given in table 6.5.

Table 6.5
Levels of commercial pentabromodiphenylether in sediments in the Netherlands (de Boer and Dao, 1993).

Location	Comments	Level (µg/kg wet weight)		
		TeBDPE (2,2',4,4')	PeBDPE (2,2',4,4',5)	Total
Haringvliet-east	River sediment from 1992	6.7	7.3	14
Nieuwe Merwede	River sediment from 1992	17	-	17
Meuse	River sediment from 1992	6.9	8.2	15.1
Waal (near Tiel)	River sediment from 1992	23	21	44

Levels of 2,2',4,4'-tetrabromodiphenylether and 2,2',4,4',5-pentabromodiphenylether have also been determined in sediments taken both upstream and downstream of a factory, of which the type was not specified, but KEMI (1999a) indicated that it was a polymer processing site which produced, amongst other things, printed circuit boards. Measurements were performed in 1988. It is not known if the factory also processed polyurethane foam at that time. Upstream of the factory sediment levels were 3.5 and 8.2 µ g/kg IG for both substances (see table 6.6).

Table 6.6
Levels of commercial pentabromodiphenylether in sediments in Sweden.

Location	Comments	Level (µg/kg IG)[a]			
		TeBDPE (2,2',4,4')	PeBDPE (2,2',4,4',5)	PeBDPE isomer	Total
Sediments from near polymer factory in southern Sweden	Upstream	3.5 (b)	8.2 (b)	-	11.7
	Downstream	840 (b)	1,200 (b)	-	2,000
Lake Marsjön	Upstream industry	<2 (c)	<1 (c)	<0.4 (c,d)	<3
Lake Öresjö	Downstream industry	7.4 (c)	3.5 (c)	1.2 (c,d,e)	12.1
River Viskan	Downstream town	12 (c)	12 (c)	3.5 (c,d,e)	27.5
River Viskan	At Moga	13 (c)	9.2 (c)	3.6 (c,d,e)	25.8
River Viskan	Upstream Skene	23 (c)	43 (c)	8.9 (c,d,e)	74.9
River Viskan	Downstream Skene	50 (c)	53 (c)	19 (c,d)	122
River Häggån	Upstream Fritsla	1.3 (c)	1.1 (c)	0.31 (c,d)	2.7
River Häggån	Downstream Fritsla	2.0 (c)	2.7 (c)	0.69 (c,d,)	5.4

Notes: a) Concentrations given on a dry weight ignition loss basis.
b) Data from Sellström et al, 1990
c) Data from Sellström et al, 1998
d) 2,2',4,4',6-pentabromodiphenylether
e) Maximum value due to interferences

Much higher levels, 840 and 1,200 µg/kg IG were found in sediments downstream of the factory (Sellström et al, 1990). Later measurements at the same locations (1996) resulted in 2.5 µg/kg dry weight upstream of polymer factory and 490 µg/kg dry weight downstream for 2,2′,4,4′-tetrabromodiphenylether, 5.9 µg/kg dry weight upstream and 770 µg/kg dry weight downstream for 2,2′,4,4′,5-pentabromodiphenylether and 1.1 µg/kg dry weight upstream and 170 µg/kg dry weight downstream for the unknown pentabromodiphenyl isomer. Sum of all three components was 9.5 µg/kg dry weight upstream and 1,400 µg/kg dry weight downstream. A background sediment sample taken from the Bornholm deep in the Baltic Sea contained around 0.52 µg/kg dry weight as the sum of all three congeners (Sellström, 1996).

More recent data on levels of 2,2′,4,4′-tetrabromodiphenylether, 2,2′,4,4′,5-pentabromo- and 2,2′4,4′,6-pentabromodiphenylether in sediments from Sweden have been determined by Sellström et al (1998). In this study, surface sediment (0-2cm) was collected at 8 locations in the River Viskan, its tributary River Häggån and nearby water systems. Samples were collected up- and downstream from industries, thought to be using flame-retardants. Levels ranged between<2-50 µg/kg IG (dry weight ignition loss basis) for 2,2′,4,4′-tetrabromodiphenylether, <1-53 µg/kg IG for 2,2′,4,4′,5-pentabromodiphenylether and <0.4-19 µg/kg IG for 2,2′,4,4′,6-pentabromodiphenylether, with the highest levels generally being found downstream from industry (see table 6.6). The industry replied that there is a possibility of commercial pentabromodiphenylether use in hydraulic mining fluids as a polychlorinated biphenyl substituent. If this use occurs, it might account for some of the reported levels in remote areas, due to many mining areas in Sweden. However, it is generally thought that pentabromodiphenylether is not used for this application in the EU. Verification work by KEMI (1999b) did not confirm this type of use in the sampled areas. Furthermore, the industry indicates that there is a possible (unconfirmed) use in completion fluids used in oil wells/drilling in the North Sea.

Recent results in the United Kingdom have shown that elevated levels of pentabromodiphenylether are found in sediments downstream from a production site and also at sites where pentabromodiphenylether may be used (Law et al, 1996; Allchin et al, 1999). The highest level reported in this study was 1,270 µg/kg dry weight. A commercial product of similar composition to Bromkal 70-5DE and a standard solution of known amounts of 2,2′,4,4′-tetra-bromodiphenylether, 2,2′,4,4′,5- and 2,2′,3,4,4′-pentabromodiphenylether were used for identification. (see table 6.7).

Table 6.7
Levels of commercial pentabromodiphenylethers measured in the United Kingdom (Law et al, 1996; Allchin et al, 1999).

Location	Comments[c]	Level (µg/kg dry weight)				
		2,2',4,4'-TetraBDE	2,2',4,4',5-PentaBDE	2,2',3,4,4'-PentaBDE	Approx. total[a]	Product basis[b]
River Tweed at Tweedmouth	Background site	0.4	<0.6	<0.4	0.4	<0.38
River Nith, upstream of wwtp	Near rubber producer	<0.3	<0.6	<0.4	nd	<0.38
River Nith, downstream of wwtp	Near rubber producer	1.7	3.5	<0.4	5.2	0.6
Avonmouth	Near flame retardant producer/user	2.4-3.6	2.9-4.7	<0.4-9.2	7.1-16.6	0.6-1.0
River Tees, upstream of confluence with River Skerne	Near a producer of pentabromodiphenylether	<0.3	<0.6	<0.4	nd	<0.38
River Tees, after confluence with River Skerne	Near a producer of pentabromodiphenylether	8.0	11	2.9	21.9	35
River Skerne at Croft-on-Tees	Near a producer of pentabromodiphenylether	51	85	3.5	139.5	34
River Skerne at Newton Aycliffe	Near a producer of pentabromodiphenylether	239	319	2.7	560.7	130
Howden Beck	Near a producer of pentabromodiphenylether	86	111	1.8	198.8	45
River Skerne, upstream of Howden Beck	Near a producer of pentabromodiphenylether	68-112	126-160	<0.4 - 0.7	194-270	51-68
Hyndburn Brook, upstream of wwtp	Near to foam manufacturer	7.6	16	<0.4	23.6	6.1
River Calder, downstream of wwtp	Near to foam manufacturer	24	46	0.5	94.1	18
Elstow landfill	Landfill receiving brominated wastes	0.8-2.4	2.9-5.7	<0.4	5.3-6.5	<0.38-1.5
Elstow Brook	Downstream of landfill site	0.4	<0.6	1.2	1.6	<0.38
River Calder at Cock Bridge	Near a foam manufacturer	2.3	0.6	4.2	7.1	
Great Ouse at Kings Lynn	Downstream of landfill site	4.2	4.6	<0.4	8.8	<0.38
Tees Estuary	Portrack wwtp	8.9	16	9.1	34	19
	Bamlett's Bight	368	898	4.8	1,271	366
	No. 23 buoy	49	99	14	162	77
	Phillips approach buoy	103	201	72	372	
River Humber at Paull		21	36	<0.4	57	6.6

Notes: TetraBDE = tetrabromodiphenylether
PentaBDE = pentabromodiphenylether
a - estimated concentration of commercial product based on the sum of the main three components
b - estimated concentration using a commercial pentabromodiphenylether product for quantitation
c – possible source of polybrominated diphenylethers in general were identified – it is not known if pentabromodiphenylether was used at all these sites

Octa- and decabromodiphenylether

Decabromodiphenylethers measurements in the Viskan River Area show that the levels in sediment correlate with industrial activities in Boras and Skene (see table 6.8). Elevated decabromodiphenylether levels downstream of these towns coincide with higher pentabromodiphenylether levels from table 6.6. However, data for further evaluation of this coincidence of elevated levels were not available (Sellström 1998).

Table 6.8
Levels of decabromodiphenylether measured in sediments from the River Viskan area (Sellström et al, 1998).

Location	Measured level (µg/kg wet wt.)	Ignition loss (% wet solids)	DecaBB (µg/kg IG)	PentaBDE[a] (µg/kg IG)
Lake Marsjön, upstream from industry	<1.1	5.5	<20	<3
Lake Öresjö, down-stream from industry	<1.1	2.7	<40	12.1
River Viskan down-stream from town of Borås	8.6	5.8	150	27.5
River Viskan at Moga	18.7	8.5	220	25.8
River Viskan upstream from Skene	49.6	1.4	3,400	74.9
River Viskan down-stream from Skene	241	2.0	12,000	122
River Häggån upstream from Fritsla	<1.7	8.4	<20	2.7
River Häggån down-stream from Fritsla	<1.2	5.9	<20	5.4
Lake Skäresjön (a parallel water system)	<1.3	4.4	<30	n.a.

a: reproduced from table 6.4

Reviews of levels of octabromo- and decabromodiphenylether in sediments in the United Kingdom are shown in table 6.9. Elevated concentrations for octabromodiphenylether (up to 1,400 and 3,000 µg/kg dry weight) were measured in areas near a manufacturing site and a storage site for decabromodiphenylether. It is not clear what the source is of the octabromodiphenylether emissions, but it could be as a result of polymer processing activity. Unfortunately no measurements were performed on decabromodiphenylether at latter site. Elevated levels of decabromodiphenylether were only noticed near a foam manufacturing site (3,200 µg/kg dry weight). Measured levels in other industrial areas are generally around 20-200 µg/kg dry weight. Background levels of octa- and decabromodiphenylether are typically <0.44 and 0.6 µg/kg dry weight respectively, indicating that these substances do not appear to be transported far from the emission source. This is consistent with the physical chemical properties of the substances that indicate that these substances will adsorb strongly onto sediment and will not be mobile in the environment (EU, 1999b,c).

Table 6.9
Levels of octa- and decabromodiphenylether in sediment in the UK (µg/kg dry wt)

Location	Comment	OctaBDE	DecaBDE	Ref.
River Tweed at Tweedmouth and at Berwick upon Tweed	Background sites.	<0.44	<0.6	A
River Nith, upstream of wwtp.	Near rubber producer.	<0.44	<0.6	A
River Nith, downstream wwtp.	Near rubber producer.	<0.44	<0.6	A
River Nith at Glencaple	Near rubber producer.	2	<0.6	A
Avonmouth	Near a possible flame retardant producer/user	<0.44	<0.6-7	A
River Tees at Croft-on-Tees	Near to a manufacturer of octabromodiphenylether	<0.44-25	<0.6	A
River Skerne at Croft-on-Tees	Near to a manufacturer of octabromodiphenylether	129	7	A
River Skerne at Newton Aycliffe	Near to a manufacturer of octabromodiphenylether	397	64	A
Howden Beck	Near to a manufacturer of octabromodiphenylether	264	23	A
River Skerne, upstream of Howden Beck	Near to a manufacturer of octabromodiphenylether	333	294	A
River Skerne, downstream of Howden Beck	Near to a manufacturer of octabromodiphenylether.	1,405	95	A
River Calder at Cock Bridge	Near foam manufacturing site	9	399	A
Hyndburn Brook, before wwtp.	Near foam manufacturing site	3	<0.6	A
River Calder, downstream wwtp	Near foam manufacturing site	17	3,190	A
Elstow landfill	Landfill with brominated wastes	<0.44-13	<0.6	A
Elstow Brook, after landfill site	Landfill with brominated wastes	1	<0.6	A
Tees estuary, Portrack wwtp.	Industrial area	29	5	A
Tees estuary, Bamlett's Bight	Industrial area	164		A
Tees estuary, No. 23 buoy	Industrial area	263	9	A
Tees estuary, Philips buoy	Industrial area	1,348	8	A
Great Ouse, The Point, King Lynn	Downstream of landfill site	7.9	<0.6	A
River Ribble, Freckleton saltings	Near foam manufacturing site	4.4	111	A
River Humber, Paull	Open surface water	29	17	A
Upstream of plastics processor.	Decabromodiphenylether used	<200	n.a.	B
Downstream of plastics processor.	Decabromodiphenylether used	<200	n.a.	B
Upstream of warehouse.	Decabromodiphenylether stored	1,480	n.a.	B
Downstream of warehouse.	Decabromodiphenylether stored	3,030	n.a.	B
Industrial area, Stockport.	Upstream of a site possibly using pentabromodiphenylether	<500	n.a.	B

References: A) Law et al, 1996; Allchin et al, 1999 B) Environment Agency, 1997.

Tetrabromobisphenol A and derivates
In the Osaka City area in Japan (1983) the average TBBPA concentrations in river sediments ranged from 10 to 20 µg/kg dry weight. Additional measurements in 1987 and 1988 demonstrated that TBBPA was identified in 25% of the sediments sampled, in concentrations ranging from 2 to 150 µg/kg dry weight (WHO, 1995). Sellström et al. (1990) analysed sediment samples taken upstream and downstream from a factory in Sweden for the presence of TBBPA and its dimethylated derivative (Me_2-TBBPA). Downstream, the level of TBBPA was 430 µg/kg (on ignition loss) and upstream 50 µg/kg. Corresponding levels of the dimethylated compound were 2,400 µg/kg and 36 µg/kg respectively.

Hexabromocyclododecane
Data on the environmental levels HBCD in fresh water levels were not available in the searched data sources.

6.2.3 Organisms

Polybrominated biphenyls (PBB)

Measurements in various fresh water fish (carp, pike, bulhead) near the former PBB production location in Michigan revealed that hexaBB was the predominant congener in fish tissue. During PBB production, levels of hexaBB near the plant ranged from 540 µg/kg wet weight (pike) to 1,330 µg/kg wet weight (carp). After shut-down of the production (1976) levels in pike roughly halved (WHO, 1994a).

Pentabromodiphenylether

Components of commercial pentabromodiphenylethers have been measured extensively in the biota in Europe. In almost all cases, 2,2',4,4'-tetrabromodiphenylether is the dominant compound of the commercial formulations found (typically >70% of the total). Since this isomer makes up around 35-40% of the commercial product, the levels found in biota indicate preferential uptake of this isomer over the pentabromodiphenylether isomers. This would be expected based on the fish bioconcentration data given earlier, where BCFs for tetrabromodiphenylethers were determined at values of around 35,000-67,000 l/kg compared with values of 12,000-18,000 l/kg for two pentabromodiphenylether isomers. Therefore, results of analyses given on a commercial product basis should be treated with caution since the distribution of isomers found in the organisms is unlikely to be the same as in the commercial formulation. Authentic standard material for analysis of individual components in commercial products, enabling more reliable quantification, is becoming available (Örn et al, 1998; Sergeant et al, 1998) and has been used in the more recent congener specific analyses.

There is a consistent pattern in the levels of commercial pentabromodiphenylethers measured in biota in Europe. The major isomer detected is 2,2′,4,4′-tetrabromodiphenylether which typically makes up >70% of the total components detected. Levels in freshwater fish are typically higher than marine fish, probably reflecting the proximity of emission sources of pentabromodiphenylether. There is evidence of bioaccumulation through the fish ⇒ fish-eating bird food chain, and also some evidence that bioaccumulation may also be occurring in marine mammals. On a lipid basis, levels of up to 88 mg/kg on a formulation basis have been measured in fish liver in Sweden. High levels have been measured in marine fish in the UK in industrialised areas near to a pentabromodiphenylether production site (EU, 1999a).

A very extensive study of the levels of 2,2',4,4'-pentabromodiphenylether and 2,2',4,4',5-pentabromodiphenylether has been carried out in the Netherlands over the years 1977-1992 (de Boer and Dao, 1993). In all, 325 samples, from 106 locations and representing 25 species were analysed. It was found that the concentration of 2,2',4,4'-tetrabromodiphenylether was generally below 100 µ g/kg wet weight in fish and shell fish and that most 2,2',4,4',5-pentabromodiphenylether concentrations were <10 µg/kg in these organisms. However, high levels of both compounds were found in organs of a cormorant (up to 25,000 µg/kg and 4,000 µg/kg wet liver weight of the tetra- and penta substance respectively). This was thought to represent bioaccumulation through the food chain. High levels of 2,2',4,4'-tetrabromodiphenylether were also detected in marine mammals (e.g. dolphin and porpoise), again indicating possible bioaccumulation. In general, historical data show a decreasing trend in the concentration with time, however, an increasing trend was noted in eels from the River Roer and this was thought to be due to possible (unconfirmed) use of polybrominated diphenylethers in mining equipment in Germany.

In a study by Sellström et al (1998), levels of 2,2′,4,4′-tetrabromodiphenyl ether, 2,2′,4,4′,5-pentabromodiphenyl ether and 2,2′4,4′,6-pentabromodiphenyl ether were determined in pike (*Esox lucius*) from the River Viskan and nearby water systems. The results are shown in Table 6.10. Comparison of historic levels in pike show that the 1987-1988 range of pentabromodiphenylether levels (sum) was significantly higher (180-8200 µg/kg lipid) than the totalised levels in 1995 (100-4600 µg/kg lipid). Comparison with earlier analysis results of total pentabromodiphenylether in Pike muscle (1981-1987) illustrates that levels have been declining with time (see table 6.11).

Table 6.10
Concentrations of commercial pentabromodiphenylethers in biota in and around Sweden (Sellström et al, 1993 and 1998; Jansson et al, 1993).

Species	Location/ Comment	Level (µg/kg lipid weight)		
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	PeBDPE[a]
Mammals				
Rabbit (*Oryctolagus cuniculus*)	Pooled muscle samples, 1.1% lipid. 1986	<1.8	<0.34	<0.21
Moose (*Alces alces*)	Pooled muscle samples, 2.0% lipid. 1985-1986.	0.82	0.64	0.24
Reindeer (*Rangifer tarandus*)	Pooled suet samples, 56% lipid. 1986	0.17	0.26	0.04
Birds				
Osprey (*Pandion haliaetus*)	Pooled muscle samples, 4% lipid. 1982-1986	1,800	140	200
Starling (*Sturnus vulgaris*)	Muscle samples, 1988.	2.7-7.8	2.3-4.2	0.62-1.1
Guillemot (*Uria aalge*) eggs	Pooled and individual samples, 1970-1989.	130-1,500	24-330	4.2-79
Freshwater fish				
Bream (*Abramis brama*)	Muscle samples, 1987.	250-750	2.3-2.4	11-37
Perch (*Perca fluviatilis*)	Muscle samples, 1987.	2,200-24,000	380-9,400	230-3,500
Trout (*Salmo trutta*)	Pooled and individual muscle samples, 1988.	120-460	64-590	33-150
Pike (*Esox lucius*) Muscle samples	1987-1988 Pooled and individual samples	94-6,500	60-1,100	25-640
	1995 Lake Marsjön, 0.46-0.56% lipid.	40-63	<52-<70	9.3-16[b]
	Lake Öresjö, 0.46-0.75% lipid.	240-2,000	68-1,600	60-1,000[b]
	River Viskan, downstream from Borås 0.49-0.57% lipid.	330-510	<48-<59	65-98[b]
	Viskan river, Moga 0.5-0.8% lipid	150-200	<37-<56	24-43[b]
	Lake Skäresjön, 0.6-1.1% lipid.	130-190	<37-58	20-49[b,c]

a) unknown pentabromodiphenylether isomer
b) identified as 2,2′,4,4′,6-pentabromodiphenylether
c) maximum value due to interference.

Table 6.11
Levels of commercial pentabromodiphenylethers in biota from the Baltic area (Jansson et al, 1987; Andersson and Blomkvist, 1981)

Species	Comment	PeBDPE[a] concentration (µg/kg lipid)
Pike (*Esox lucius*) muscle from the Viskan River system.	Mean levels, 1979-1981. Concentration on a commercial formulation basis (Bromkal 70-5-DE). 0.52-0.63% lipid.	nd-24,000
Pike (*Esox lucius*) liver from the Viskan River system	Mean levels, 1979-1981. Concentration on a commercial formulation basis (Bromkal 70-5-DE). 5.8-11% lipid.	nd-88,000
Bream (*Abramis brama*) muscle from the Viskan River system.	Mean levels, 1979-1981. Concentration on a commercial formulation basis (Bromkal 70-5-DE). 1.5% lipid.	9,700
Tench (*Tinca tinca*) muscle from the Viskan River system.	Mean levels, 1979-1981. Concentration on a commercial formulation basis (Bromkal 70-5-DE). 5.3% lipid.	950
Eel (*Anguilla anguilla*) muscle from the Viskan River system.	Mean levels, 1979-1981. Concentration on a commercial formulation basis (Bromkal 70-5-DE). 4.7-10% lipid.	900-16,000
Sea trout (*Salmo ocla*) muscle from the Viskan River system.	Mean levels, 1979-1981. Concentration on a commercial formulation basis (Bromkal 70-5-DE). 1.1% lipid.	1,400

a. 2,2',4,4'-tetrabromodiphenyl ether was found to be the major component (70-80% of total poly brominated diphenylethers present), pentabromodiphenylether isomers made up the rest.

Octa- and decabromodiphenylether
Environmental data on the occurrence of octa- and decabromodiphenylethers in fresh water biota were not available in the searched data sources.

6.2.4 Groundwater

For none of the compounds considered, measurement data were available with regard to the presence in groundwater. Computer modelling studies within the framework of current EU risk assessments of PBDEs revealed that of leaching of PBDEs from sewage sludge into soil and groundwater is negligible (WHO, 1994a,b; WHO, 1995; WHO, 1997; EU, 1999a,b,c).

6.2.5 Rainwater

For none of the considered compounds measurement data were available with respect to the presence in rainwater.

6.3 Measurements in marine systems

6.3.1 Surface water

Despite extensive measurements in marine environments, for none of the compounds, data were available on aqueous (dissolved) concentrations. Generally, investigations are focused on the detection of pollutants in the sediment.

6.3.2 Sediment

Polybrominated biphenyls (PBB)
Measurement data on the presence of PBB in marine sediments are scarce, although various investigations have been performed on the environmental occurrence of PBB. From measurement results from joint surveys on PBB and PBDE levels in Sweden and UK can be assessed that PBDE are present in significant amounts, whereas PBB are seldom found in levels above the detection limit (de Boer, 1999; Sellström, 1990).

Pentabromodiphenylether

Nylund et al (1992) carried out an investigation of the levels of polybrominated diphenylethers in a sediment core taken from the Baltic Sea. Commercial pentabromodiphenylether, Bromkal 70-5DE was used as reference. The product consisted of 41% tetrabromodiphenylether, 45% pentabromodiphenylether and 7% of an unidentified pentabromodiphenylether. Levels are shown in table 6.10. Levels of the tetra- and pentabromodiphenylethers were found to be low in the lower depths of the sediment (samples were thought to relate to 1939-1970) and were found to increase in the upper 40 mm of the core. The most rapid increase occurs in the top 20 mm, related to the early 1980s.

Table 6.12
Levels of pentabromodiphenylether in sediment of the Baltic Sea (Nyland, 1992)

Sediment core Baltic Sea	Level (µg/kg IG)[a]			
	TeBDPE (2,2',4,4')	PeBDPE (2,2',4,4',5)	PeBDPE isomer (unknown)	Total
0-5 mm depth	1.6	0.98	0.31	2.89
5-10 mm depth	0.76	0.20	0.07	1.03
10-15 mm depth	0.68	0.36	<0.04	1.04
15-20 mm depth	0.50	0.13	<0.04	1.67
80-90 mm depth	0.06	<0.04	<0.04	0.06

Recently van Zeijl (1997) reported the results of the analysis of sediments from 22 estuaries in Western Europe. The results are shown in table 6.13. In this study, the top layer (to a maximum depth of 5 cm) was sampled and the <63 µm fraction was analysed for the presence of tetrabromo-, pentabromo- and decabromo-diphenylether using a GC-MS technique (electron capture negative ionisation and monitoring formed bromide ions). Information on reference compounds used for calibration of the method was given.

Octabromodiphenylether

Measurement data on the presence of octabromodiphenylether in marine sediments are lacking. This is probably caused by the presumption that this compound will not migrate into marine environments due to its high hydrofobicity (EU, 1999b).

Decabromodiphenylether

Recently measurements have been performed on decabromodiphenyl levels in 22 sediments in the EU. The measurement results are shown in table 6.13. With respect to the levels at the individual sites can be mentioned that sediments in the Mersey and Schelde estuaries contain significantly higher levels than the other sites, where decabromodiphenylether levels range from < 0.5 to 40 µg/kg dry weight. Comparison with the tetra- and pentaBDE demonstrates that decaBDE levels are significantly higher which can be attributed to the lower water solubility of decaBDE and therefore greater preference for adsorption onto sediment (van Zeijl, 1997; EU 1999c).

Tetrabromobisphenol A and derivates

No analysis data were available on the presence of tetrabromobisphenol A in marine sediments. Reasons for the lack of these data are unknown. This lack might be the result of the fact that in earlier (not published) measurements, this compound was not found in sediments and that the need for subsequent e.g. frequent monitoring declined.

Table 6.13
Levels of tetra-, penta- and decabromodiphenylethers in sediment (< 63 µm fraction) from estuaries in the EU (van Zeijl, 1997)

Estuary/ location	% of sediment <63 µm	% organic carbon in <63 µm fraction	% organic carbon in whole sediment	Concentration in the <63 µm fraction (µg/kg dry wt.)		
				TetraBDE	PentaBDE	DecaBDE
Liffey River	23.4	2.01	0.86	0.61	0.73	40.3
Clyde	72.4	3.25	3.13	0.74	1.03	8.4
Mersey	42.1	2.44	1.09	2.20	2.27	1,700
Southampton	35.7	1.03	0.81	0.19	0.23	2.1
Thames	10.0	1.90	0.3	0.64	0.70	18.3
Humber	20.3	2.40	1.17	5.80	6.93	39
Tyne	29.2	1.89	1.01	0.70	0.99	4.3
Forth	19.8	2.41	0.78	0.39	0.36	3.3
Seine	53.3	2.77	2.92	0.69	0.83	12.2
North sea *	38.4	1.48	1.1	<0.17	<0.20	11.6
Schelde	5.8	3.53	-	0.42	0.32	200
Rijn	51.9	2.83	2.65	1.40	1.30	15.7
Noordwijk	7.4	2.91	-	0.90	1.00	11.3
Waddensee	10.2	2.27	0.33	0.19	0.42	1.1
Ems	68.9	4.13	4.53	0.38	0.44	4.9
Weser	54.7	2.73	2.46	0.17	0.20	3.4
Elbe	49.9	1.79	1.59	<0.17	<0.20	0.83
Göta	73.1	2.28	2.23	<0.17	<0.20	2.6
Glomma	71.2	2.38	2.19	<0.17	<0.20	<0.52
Skiens	70.3	3.30	3.02	<0.17	<0.20	1.0
Otria	61.2	2.68	2.64	<0.17	<0.20	0.71
100 km off Terschelling **	18.7	1.15	0.33	0.18	0.20	<0.51

*: of Belgium **:reference site

Hexabromocyclododecane
Analysis results for evaluation of HBCD in marine sediments were not available .

6.3.3 Organisms

Polybrominated biphenyls
Measurement results of PBB in marine organisms in 1987 and 1993 (Jansson, 1987 and 1993) indicate that PBB levels in seal and guillemot have significantly increased over the years (see table 6.14). Along the food chain, PBB levels in lipid increase from herring (0.16 µg/kg) to guillemot (20–90 µg/kg) and sea eagle (280 µg/kg). For seal and guillemot in remote areas (Northern Ice Sea and Spitsbergen) PBB levels have increased 3-10 times between 1987 and 1993, which might be an indication that PBB are spreading faster and more widely in the environment than previously assumed on basis of their hydrofobicity and low aquatic mobility.

A recent study has identified brominated biphenyls in various whales, dolphin and seals from around the coast of the Netherlands around 1995 (de Boer et al, 1998). The results are shown in Table 6.14. The authors concluded that the presence of the substances in sperm whales indicated that they had reached deep ocean waters, since sperm whales do not usually occur in shelf seas and usually feed in deep waters. Levels of penta- and hexaBB were found to be higher than tetraBB levels. DecaBB levels were not found above the detection limit.

Table 6.14
Total PBB concentrations calculated as technical mixture equivalents in herring, seals, and sea birds (µg/kg lipid) (Source: Jansson et al. 1987, 1993)

Organism	Area	PBB total	
		1987	1993
Herring	Baltic Sea	-	0.16
	Bothnian Gulf	-	0.09
	Skagerrak	-	0.27
Seal	Baltic Sea	20/26	90
	Kattegat	3	10
	Spitsbergen	4	40
	Northern Ice Sea	-	0.42
Guillemot	Baltic Sea	16	370
	North Sea	-	80
	Northern Ice Sea	50	130
Sea eagle	Baltic Sea	280	

Table 6.15
Levels of brominated biphenyls in marine wildlife samples (de Boer, 1998)

Species	Tissue	Fat (g/kg)	PBB concentration (µg/kg wet weight)				
			tetraBB	pentaBB	hexaBBD		decaBB
Sperm whale 1	Blubber	722	0.24-0.40	0.91	<0.1	1.9	<0.5
Sperm whale 2	Blubber	234	0.13-0.21	0.40	0.05	0.73	<0.3
Sperm whale 3	Blubber	317	020-0.36	0.70	<0.1	1.1	<0.4
Whiteb. dolphin	Blubber	990	4.1-7.5	8.3	<0.2	13	<0.9
Minke whale	Blubber	140	0.24-0.27	0.54	<0.02	0.82	<0.1
Harbour seal 1	Blubber	244	5.7-34	9.3	12	61	<1
Harbour seal 2	Blubber	963	2.3-3.1	1.4	<0.2	18	<1
Harbour seal 3	Blubber	722	0.52-3.0	1.1	<0.1	13	<1
Sperm whale 2	Liver	23	<0.01	0.63	<0.04	18	<0.3
Whiteb. dolphin	Liver	27	0.03-0.06	0.74	<0.02	19	<0.1
Harbour seal 2	Liver	35	0.05-0.10	0.62	<0.02	1.5	<0.1
Harbour seal 3	Liver	51	0.03-0.10	0.04	<0.01	0.82	<0.1
Harbour seal 4	Liver	30	0.14-0.90	0.44	<0.02	13	<0.1

Pentabromodiphenylether

Sellström et al (1993) measured the concentrations of 2,2',4,4'-tetrabromodiphenyl ether, 2,2',4,4',5-pentabromodiphenyl ether and an unidentified pentabromodiphenylether (all are components of the commercial brominated flame retardant Bromkal 70-5DE) in biota samples from in and around Sweden (see table 6.16). The concentration of the brominated diphenylethers in biota were found to be lowest in samples from the west coast and the highest in samples from the southern part of the Baltic. Concentrations (on a lipid weight basis) of brominated diphenylethers in herring were found to be higher in fish caught in the spring than fish caught in the autumn. This was thought to be due to the lower fat content of the spring fish. Levels in seal blubber were similar to those in fish, indicating that little accumulation through the food chain was occurring. In contrast to this, levels in fish-eating birds and their eggs were much higher than levels in starlings, indicating that fish may be a significant source of exposure for these species.

Table 6.16
Concentrations of commercial pentabromodiphenylethers in marine biota around Sweden (Sellström et al, 1993 and 1998; Jansson et al, 1993)

Species	Location/Comment	Level (µg/kg lipid weight)		
		2,2',4,4'-TeBDPE	2,2',4,4',5-PeBDPE	PeBDPE
Whitefish (*Coregonus* sp)	Pooled muscle samples, 1986. 0.66% lipid	15	7.2	3.9
Arctic char (*Salvelinus alpinus*)	Pooled muscle samples, 1987. 5.3% lipid.	400	64	51
Herring (*Clupea harengus*)	Pooled and individual samples, 1986-1987. 3.2-5.4% lipid.	12-450	3.4-46	1.6-32
Ringed seal (*Pusa hispida*)	Pooled blubber samples, 1981. 88% lipid.	47	1.7	2.3
Grey seal (*Halichoerus grypus*)	Pooled blubber samples, 1979-1985. 74% lipid.	650	40	38

a. unknown pentabromodiphenylether isomer
b. identified as 2,2',4,4',6- pentabromodiphenylether
c. maximum value due to interferences

Table 6.17
Concentrations of brominated diphenylethers in marine wildlife samples near the Netherlands coast (de Boer, 1998)

Species	Tissue	Fat (g/kg)	PBDE concentration (µg/kg wet weight)			
			tetraPBDE[a]	pentaPBDE[b]	pentaBDE[c]	decaBDE
Sperm whale 1	Blubber	722	95	26	15	<6
Sperm whale 2	Blubber	234	58	15	8.1	<3
Sperm whale 3	Blubber	317	61	10	7.5	<5
Whiteb. dolphin	Blubber	990	5,500	1,000	1,200	<10
Minke whale	Blubber	140	88	23	11	<1
Harbour seal 1	Blubber	244	1,200	160	110	<15
Harbour seal 2	Blubber	963	1,200	40	100	<10
Harbour seal 3	Blubber	722	280	140	18	<10
Sperm whale 2	Liver	23	2.7	0.91	0.54	<3
Whiteb. dolphin	Liver	27	22	3.0	5.8	<1
Harbour seal 2	Liver	35	21	0.85	0.93	<2
Harbour seal 3	Liver	51	12	5.1	0.33	<1
Harbour seal 4	Liver	30	20	0.53	0.07	<2
Mackerel	Muscle	152	5.4	1.9	1.8	<2

a. 2,2',4,4'-congener
b. 2,2',4,4',5-congener
c. unknown structure

Measurements of pentabromo- and decabromodiphenylethers in marine wildlife species revealed that these compounds already have reached deep ocean waters, since sperm whales usually remain in deep waters (see table 6.17). From the levels in various samples, the dominant presence of the 2,2',4,4' tetrabromo-congener is confirmed again. Further it is shown that decabromodiphenylether was not observed, whereas tetra- and pentabromo congeners are present in high levels (de Boer, 1998).

A survey of levels of commercial pentabromodiphenylethers in marine species has recently been carried out in the United Kingdom (see table 6.18). The highest levels measured were in fish from the Tees estuary, downstream from a pentabromodiphenylether production site and in an area where there is a large chemical industry in general. Levels in fish liver (up to 1.3 mg/kg wet weight for 2,2',4,4'-tetrabromo diphenylether) were generally higher than in muscle (up to 22 µg/kg wet weight for 2,2',4,4'-tetrabromo diphenylether). On a lipid basis, the highest levels of the tetrabromodiphenylether isomer are up to 9.5 mg/kg in liver and 1.8 mg/kg in muscle.

Table 6.18
Levels of commercial pentabromodiphenylethers in marine species from the United Kingdom (Law et al 1996; Allchin et al, 1999).

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

a. Concentrations based on standards of each isomer

b. Concentrations based on a commercial pentabromodiphenylether standard

Octa- and decabromodiphenylether
Levels of octabromodiphenylether in biota samples in the UK are shown in table 6.19. The monitoring data indicate that commercial octabromodiphenylether is only found in biota at measurable concentrations in industrial areas, particularly where sources of octabromodiphenylether are thought to occur. The levels measured are generally of a similar order of magnitude to those predicted in fish. The detected levels probably represent the more accumulative, lower brominated congeners in commercial formulations (EU, 1999b,c).

Table 6.19
Levels of octa- and decabromodiphenylether in biota from the United Kingdom (µg/kg wet weight; Law et al, 1996; Allchin et al, 1999)

Species	Location	OctaBDE	DecaBDE
Dab (liver)	Off River Tees, UK.	325	<1.2
	Off the Wash, UK.	18	<1.2
	Bideford Bay, UK.	<1	<1.2
	Tees Bay, UK	179	<1.2
Dab (muscle)	Bideford Bay, UK.	9.7	<1.2
	Tees Bay, UK.	6	<1.2
Whiting (liver)	Bristol Channel, UK.	<1	<1.2
Flounder (liver)	Off Lune/Wyre, UK.	14	<1.2
	Off River Humber, UK.	126	<1.2
	Nith estuary, UK.	<1-16 (2 samples)	<1.2 (2 samples)
	Bideford Bay, UK.	19	<1.2
	Tees Bay, UK.	115	<1.2
Flounder (muscle)	Nith estuary, UK.	<1 (2 samples)	<1.2 (2 samples)
	Bideford Bay, UK.	<1	<1.2
	Tees Bay, UK.	7	<1.2
Plaice (muscle)	Bideford Bay, UK.	3.3	<1.2
	Tees Bay, UK.	12	<1.2
Plaice (liver)	Bideford Bay, UK.	<1	<1.2
	Tees Bay, UK.	41	<1.2
Winkles	River Tweed	<1	<1.2
Mussels	The Wash, UK.	16	<1.2

Due to the lack of analytical standards for the individual components of the mixture, the analysis of commercial octabromodiphenyl in biota samples is complicated. In many analyses, identification and quantitation is carried out by comparing the chromatographic peaks obtained from the commercial product. Since it was found in a bioaccumulation experiment that uptake by fish of the lower brominated diphenylethers is greater than for the higher brominated components, the distribution of congeners found in fish is unlikely to be the same as in commercial products used for identification and quantitation. Further, some components of commercial octabromodiphenylether (notably hexabromodiphenylether) are also constituents of both commercial octabromodiphenylether and pentabromodiphenylether. This adds extra uncertainty to the analysis of octabromodiphenylether in biota samples, so the results of the analyses should be treated with caution (EU, 1999b).

Tetrabromobisphenol A and derivates
Recent analysis data on the occurrence of tetrabromobisphenol A in marine species were not available. Earlier measurements in mussels (*Mytilus edulis*), fish and shellfish in the Osaka area (1990-1991) revealed that TBBPA was below the detection limit in mussels and between 0.8 and 4.6 µg/kg wet wt in (shell)fish, predominantly as methylated TBBPA (WHO, 1995). In other fish samples, TBBPA could not be detected above the detection limit.

Hexabromocyclododecane
Environmental data on the presence of hexabromocyclododecane in marine biota were not available.

6.4 Occurrence in human tissues

Levels of brominated diphenylether of 0.7-35 ng/g lipid have been detected in 40 blood samples randomly selected from the Swedish population. The dominant compound found was 2,2′,4,4′-tetrabromodiphenylether (Örn, 1997; Meironyté et al, 1998). Another Swedish study looked at levels of 2,2′,4,4′-tetrabromodiphenylether in human adipose tissue (77 samples between 1995 and 1997). The compound was detected in all samples and ranged from 0.6 to 98.2 µg/kg lipid. Levels were generally higher in males than females (Lindström et al, 1998).

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

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

Levels of polybrominated diphenylethers (probably tetra- and penta-congeners) of 0.6-11 µg/kg lipid have been found in human breast milk from Germany (de Boer et al, 1998a). The levels of the components of commercial pentabromodiphenylether have been measured in adipose tissue and blood of a 21 year old Israeli male, and also in cows milk and poultry fat from Israel (de Boer et al, 1998a). The levels found in adipose tissue (71.6% fat) were: 2,2′,4,4′-tetrabromodiphenyl ether 2 µg/kg wet weight; 2,2′,4,4′5-pentabromodiphenyl ether 4 µg/kg wet weight and an unknown pentabromodiphenylether 1 µg/kg wet weight. The substances were not detected in blood (0.15% fat; detection limits <0.01-<0.02 µg/kg wet weight), cows milk (1.9 % fat; detection limits <0.01-<0.02 µg/kg wet weight) or poultry fat (93% fat; detection limit <0.1-<0.8 µg/kg wet weight).

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

6.5 Conclusions

For the considered compounds the following conclusions can be made with respect to their occurrence in the environmental systems discussed:

1. For all substances it was found that their occurrence in water was below the detection limit which is in good agreement with the theoretical behaviour in aquatic systems.

2. PBBs and PBDEs were extensively identified in both fresh water and marine sediments and biota. However, only scarce information was available on the presence of the higher brominated congeners in PBDEs. No environmental data were available for evaluation of the occurrence of TBBPA and HBCD in sediments and biota.

3. All brominated compounds have a high tendency to adsorb onto solid media in water (sediment, suspended solids). Measurement data show that higher brominated congeners within the PBB and PBDE groups absorb more strongly onto sediment than the lower brominated substances, resulting in substantially higher levels in sediment.

4. For both the lower and higher PBDE, significantly elevated levels in sediment are observed near (probable) production and processing sites. Typical pentabromodiphenylether levels at such sites ranged from 1-5 µg/kg dry weight, whereas octa- and decabromodiphenylether level can increase to 1,000-3,000 µg/kg dry weight. Elevated pentabromodiphenylether levels in estuary sediments range from 1-5µg/kg dry wt, whereas octa- and deca congeners can achieve levels of 10-200 µg/kg dry wt.

5. For pentabromodiphenylether it was assessed that both in sediment and biota 2,2',4,4' tetrabromodiphenylether is generally the major compound. In highly exposed biota, pentabromodiphenylether can achieve tissue levels of 1,000-6,500 µg/kg lipid (muscle), which equals roughly a 100 fold increase of the level in, more or less, non exposed areas. Corresponding levels in marine fish range from 10 – 500 µg/kg lipid (muscle). Comparable data for octa- and decabromodiphenylethers were not available.

6. On basis of levels in various predators, for the pentabromodiphenylethers it was shown that significant bioaccumulation occurs via the food chain. Adequate data for evaluation of similar bioaccumulation of octa- en decabromodiphenylether are lacking. Measurement data in whales and harbour seal show however, that pentabromo congeners were present at significantly higher levels than decabromodiphenylether.

7. Time trends of pentabromodiphenylether levels in freshwater biota in Sweden show a tendency that pollution levels of this compound are diminishing. On the other hand, historical data for PBB in marine species indicate that PBB (and probably other compounds) are spreading to the Arctic region.

In addition to the lack of environmental relevant data on octa- and decabromodiphenylether, can be mentioned that currently an extensive EU risk assessment is being completed. In this risk assessment, the environmental aspects of the use and risks of these compounds are discussed in greater detail. It is recommended to await the final conclusions of these assessments and incorporate the findings of these studies into an overall assessment with respect to the formulation of further environmental research.
Similarly, for HBCD it was assessed that environmental assessment data were hardly available at the moment. Recent literature searches on the Internet revealed that this compound is listed for EU risk assessment in the near future. Further, various EPA research studies have been performed on this compound. It is recommended to evaluate to what extent the studies can already supply relevant data with respect to the environmental behaviour and possible hazards of this compound.

6.6 References

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7. Toxicity in the aquatic environment

7.1 Mechanism of toxicity

PBB and related halogenated compounds elicit a large number of different effects in animal species. However, the underlying mechanisms of toxicity are unknown. It is probable that several molecular mechanisms are responsible (EHC152, 1994). Most mechanisms of toxicity found for PBBs and PBDEs are similar to those of PCBs (Wells & De Boer, 1998).

Compounds with a planar structure, like the PBBs and the PBDEs have a potency to induce cytochrome P450 (Wells & de Boer, 1998). Induction of cytochrome P450 is the precursor, of a whole spectrum of possible effects at more integrated levels of biological structure: weight loss, thymus atrophy, and changes in the liver such as proliferation of the smooth endoplasmatic reticulum (location of the P450 system), increased RNA and protein content, decreased DNA content, cell necrosis, liver enlargement, and hepatic porphyria (Jensen, 1983; Koster, 1980 in De Boer, 1999).
The toxicity of PBB and PBDE congeners strongly depends on their molecular structure (WHO, 1994; WHO 1994a; Pijnenburg, 1995 in De Boer, 1999).

PBB congeners are methylacetylcholine (MC) inducers to a receptor-mediated model of toxicity. This is related to an interaction with the Ah-receptor protein, which is believed to be a member of the steroid/retinoid/thyroid hormone nuclear receptor superfamily. PBBs also have effects on membranes and membrane-mediated processes in rats, and PBBs, substituted at ortho positions, cause phenobarbital (PB)-type microsomal induction. Some toxic effects of PBBs could also be mediated through changes in the metabolism of vitamin A (retinol compounds and retinoic acid), which is important for cellular growth and differentiation (EHC152, 1994).

PBBs possibly lower the blood plasma level of T4 (thyroxine) because they compete with the binding of T4 to proteins. This leads to an effect on thyroid hormone levels in blood and indirectly to an effect on the activity of pituitary and thyroid (UBA, 1998).
There is no specific mechanism of toxicity known for aquatic organisms.

PBBs
The more toxic PBB congeners cause a decrease in thymus and/or body weight and produce pronounced histological changes in the liver and thymus. Categorisation of halogenated biphenyls has been made on a structural basis. Category 1 comprises isomers and congeners lacking ortho-substituents (coplanar PBBs). Mono-ortho-substituted derivatives constitute the second category. Other PBBs (mainly those with two or more ortho-bromine substituents) have been organised into the third category. Congeners of Category 1 tend to elicit the most severe effects, while the congeners of the second and third categories show decreasing toxicological changes. Within these categories, the degree of bromination may also influence toxicity. In all combinations tested, 3,3',4,4',5,5'-hexaBB (BB-169) was found to be the most toxic PBB (WHO152, 1994; De Boer, 1999).

PBDEs
Penta-BDEs increase cytochrome P450 to a higher extend than Octa-BDEs. 2,2',4,4'- tetraBDE alone (6 and 18 mg/kg body weight) induced several proteins (EROD (CYPIAI) and MROD (CYP 1A2)) in a minor way compared to PCBs in rats. A combination with chlorinated paraffins showed a synergistic effect on this induction. The induction of the protein PROD (CYP2B) by 2,2',4,4'-tetraBDE alone or in combination was as strong as that of the PCBs (Hallgren, 1998 in De Boer, 1999).

Metabolism
PBBs are capable of biotransformations which could yield a large number of isomeric products. The major expected end products are sulfates, glucuronides and mercapturic acids. Higher molecular weight metabolites are excreted slowly whereas the lower molecular weight metabolites are excreted quickly by the kidney (DiCarlo, 1978).
Generally, the most common metabolic route seems to be hydroxylation, whereas ether bond scission seems to be a minor route. Deca BDE is rapidly metabolised and excreted whereas 2,2',4,4'-tetraBDE is metabolised and excreted very slow by rats. On tetrabromobisphenol A there are no data available on metabolism or degradation (SEPA, 1998).
PeBDEs are persistent to biotransformation (De Boer & Wester, 1998 in WWF, 1998)

7.2 Toxic effects in the aquatic environment

General
This paragraph decribes the data on toxicity retrieved from the literature. Toxic effects for species in the aquatic environment are distinguished into acute and chronic effects. Furthermore a distinction is made between (pelagic) water organisms and ((epi) bentic) sediment organisms. It is not possible to base this distinction on the larger taxonomic groups. Within every group there are representatives of a typical bentic and a typical pelagic way of living. Even within one species there can be a shift of one compartment to the other during the development from larvae to adult. The placing of a taxonomic group under pelagic or bentic organisms is therefore arbitrar.

In this report the available toxicity data are presented per group of species. The retrieved toxicity data are not evaluated. However, when available, the test methodology used is reflected, which gives an indication about the quality of the data.
The level of toxicity of the brominated flame-retardants is classified according to the classification system in Annex 5.1.

7.2.1 Toxic effects in freshwater aquatic environment

General
In this report the Daphnids, are incorporated with the pelagic freshwater environment. The other freshwater crustaceans and insect larvae are incorporated with the bentical environment. Algae, bacteria, protozoa and fish are incorporated with the pelagic environment. Data from tests with sediment with several organisms are also incorporated with the bentical environment. The decision whether a test is acute or chronic depends on the generation time of the specific species (group) and in principal chronic tests should enclose more than 1 generation. In this report the toxicity tests on insects, crustaceans and molluscs with a testing time of 96 h and less, are regarded as acute. The other tests are regarded as chronic. For algae, bacteria and protozoa the EC_{50} values

at 96 h and less are regarded as acute and the NOEC values at 96 h as chronic. For fish the data are regarded per test. Tests on early life stages (ELS) are regarded as chronic.

In table 7.2 to 7.9 all retrieved acute and chronic toxicity data of the brominated flame-retardants for freshwater organisms are presented. Table 7.1 gives an overview of the level of toxicity. In this table the data from crustaceans of pelagic and bentic environments are combined.

Table 7.1
Overview of the toxicity data on brominated flame-retardants in the freshwater environment classified according to the classification system in Annex 5.1 0 = very slightly toxic; * = slightly toxic; ** = moderately toxic; *** = very toxic.

Chemical	CAS no	Algae		Protozoan/ Bacteria/Insects		Crustaceans		Fish	
		Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	chronic
Tetrabromodiphenylether	40088-47-9	-	-	-	-	-	-	-	-
Pentabromodiphenylether	32534-81-9	-	**	-	-	***	***	0	-
Hexabromodiphenylether	36483-60-0	-	-	-	-	-	-	-	-
Heptabromodiphenylether	68928-80-3	-	-	-	-	-	-	-	-
Octabromodiphenylether	32536-52-0	-	-	-	-	-	***	0	-
Nonabromodiphenylether	63936-56-1	-	-	-	-	-	-	-	-
Decabromodiphenylether	1163-19-5 61345-53-7	-	-	-	-	-	-	0	-
Tetrabromobisphenol A	79-94-7	***	-	*[a]	0[b]	***	*	***	*[d]
TBBPA PC oligomer	94334-64-2 71342-77-3	-	-	-	-	-	-	-	-
TBBPA epoxy oligomer	32844-27-2	-	-	-	-	-	-	-	-
Hexabromocyclododecane	25637-99-4 3194-55-6	-	-	-	-	-	-	-	-
TetraBB	40088-45-7	-	-	-	-	-	-	-	-
PentaBB	56307-79-0	-	-	-	-	-	-	-	-
HexaBB	36355-01-8	-	-	-	-	-	-	*	-
DecaBB	13654-09-6	-	-	*[c]	-	*	-	-	-

a: Protozoan
b: Insects
c: Bacteria
d: Based on a no effect concentration (mortality)

Tetrabromodiphenylether

The table 7.2 shows that there is only one the toxicity data available of tetrabromodiphenylether for water and sediment organisms. However this is not a regular toxicity test, because it involves an injection into fish eggs. Therefore substance can not be classified with the classification system of Annex 5.1. The study is regarded as chronic because the effect type is a NOEC and the test concerns a highly sensitive developmental stage of the species. There are no data on the toxicity to sediment organisms. The water solubility is 10.9 μg/l.

Table 7.2
Retrieved chronic effect concentration (NOEC) (µg/l) of tetrabromodiphenylether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (µg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Fish	2,2',4,4' TetraBDE 98%	>12 µg/g egg	Injected in eggs 24-50h after fertil.	NOEC sac-fry mortality	Oncorhynchus mykiss	Early life stage	Hornung, et al, 1996

Pentabromodiphenylether

The tables 7.3a and b show the toxicity data of pentabromodiphenylether for water and sediment organisms.

Pentabromodiphenylether is acute very toxic to crustaceans but only very slightly toxic to fish. However, the toxicity to fish is based on a less reliable study.

Pentabromodiphenylether is chronic moderately toxic to algae, but very toxic to crustaceans. It should be noted however that the tested substance is a mixture of tetra-, penta- and hexabromodiphenylether. Fish toxicity could not be classified, as the data were based on concentrations in food or egg. There are no toxicity data available on sediment organisms.

The water solubility is 2.4 µg/l. This means the effect concentrations are just above the water solubility limit.

Table 7.3.a
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (µg/l) of pentabromodiphenylether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (µg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Crustaceans	33.7% TetraBDE 54.6% PentaBDE 11.7% HexaBDE	14[a]	48 h	EC_{50} Immobility	Daphnia magna	OECD 202 GLP Flowthrough	Palmer, et al, 1997b
Crustaceans	33.7% TetraBDE 54.6% PentaBDE 11.7% HexaBDE	17[b]	96 h	EC_{50} immobility	Daphnia magna	OECD 202 21 d life-cycle flowthrough	Drottar & Krueger, 1998
Fish	33.7% TetraBDE 54.6% PentaBDE 11.7% HexaBDE	>21[a,c]	96 h	NOEC Mortality	Salmo gairdneri	OECD 203 GLP Flowthrough	Palmer, et al, 1997c
Fish	Commercial PentaBDE	$>500.10^3$	48 h	LC_{50}	Oryzias latipes	-	CITI, 1982

a. Mean measured concentrations
b. Cumulative mortality slightly higher than seen in DMSO control, significantly higher than control: effect partly due to method of administration
c. Greater than water solubility

Table 7.3.b
Retrieved chronic effect concentration (NOEC) (µg/l) of Pentabromodiphenylether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (µg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Algae	33.7% TetraBDE 54.6% PentaBDE 11.7% HexaBDE	>26[a]	96 h	NOEC Growth	Selenastrum capricornutum	OECD 201 GLP Static	Palmer, et al, 1997a
Crustaceans	33.7% TetraBDE 54.6% PentaBDE 11.7% HexaBDE	5.3[b]	21 d	NOEC mortality, reproduction	Daphnia magna	OECD 202 21 d life-cycle flowthrough	Drottar & Krueger, 1998
Fish	Bromkal 70-5DE	>5.77 mg/kg food/day (0.5 mg)	3.5 months	NOEC Mortality, Mean EROD activity	Gasterosteus Aculeatus	-	Holm, et al, 1993
Fish	2,2',3,4,4' PentaBDE 98% 2,2',4,4',5 PentaBDE 98%	>12 µg/g egg >12 µg/g egg	Injected in eggs 24-50h after fertil.	NOEC sac-fry mortality	Oncorhynchus mykiss	Early life stage	Hornung, et al, 1996
Fish	Bromkal 70	4 µg/egg	Injected In eggs 1 week before hatching	LOEC Cumulative mortality[b] Changes in liver morphology	Oncorhynchus mykiss	-	Norrgren, et al, 1993

a. measured concentration at the beginning of the test; at the end of the test concentrations were below the detection limit (<0.8 µg/l); other results at 24 h there was 11-15% inhibition of algal growth at 6.5 µg/l
b. mean measured concentrations

Hexabromodiphenylether and nonabromodiphenylether

There are no toxicity data retrieved on hexabromodiphenylether and nonabromodiphenylether for water and sediment organisms.

Heptabromodiphenylether

Table 7.4 shows the toxicity data of heptabromodiphenylether for water and sediment organisms.
There is only one toxicity data retrieved, which is not a regular toxicity test, because it involves parenteral administration, this study can not be classified with the classification system of Annex 5.1. The study is regarded as acute because it is a single dose test with an observation period of 5 days. There are no data on the toxicity to sediment organisms.
The water solubility is not available.

Table 7.4
Retrieved acute effect concentration (µg/l) of heptabromodiphenylether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (µg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Fish	2,2',3,4,4',5,5'-heptaBB (BB 180)	150mg/kg bw.day parenteral	Single dose (5 d .obs)	NOEC MFO induction	Oncorhynchus mykiss	-	Franklin, et al, 1981 (EHC152)

Octabromodiphenylether

The tables 7.5a and b show the toxicity data of octabromodiphenylether for water and sediment organisms.

There is just one data on acute toxicity available. Based on this less reliable study, octabromodiphenylether is acute very slightly toxic to fish.

There are chronic toxicity data available for just one group of species: the crustaceans. These data indicate that octabromodiphenylether is chronic very toxic to crustaceans. There are no acute or chronic toxicity data available on sediment organisms.

The water solubility is 0.5 µg/l. This means the lowest effect concentrations (NOECs) are just above the limit of water solubulity.

Table 7.5.a
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (µg/l) of Octabromodiphenyl ether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (µg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Fish	Mixture with around 86% hepta-, octa- and nonaBDE	>500,000[a]	48 h	LC_{50}	Oryzias latipes	-	CITI, 1992

a. Dispersing agent used (20g/l)

Table 7.5.b
Retrieved chronic effect concentration (NOEC) (µg/l) of Octabromodiphenylether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (µg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Crustaceans	5.5% HexaBDE 42.3% HeptaBDE 36.1% OctaBDE 13.9% NonaBDE 2.1% DecaBDE	1.7[a] >1.7[a]	21 d 21 d	NOEC reprod-uction NOEC Growth, survival	Daphnia magna	OECD 202 GLP Flow-through	Graves, et al, 1997
Crustaceans	5.5% HexaBDE 42.3% HeptaBDE 36.1% OctaBDE 13.9% NonaBDE 2.1% DecaBDE	1000[b]	9 d	LOEC Survival	Daphnia magna	Range finding immobilisation test	Graves, et al, 1997

a. measured concentration (nominal 2.0 µg/l)

b. significance of test results unknown, at 1 mg/l nominal 7 of the 10 exposed animals died after 2-3 days; nominal concentration exceed water solubility; mortality may be due to physical effects by undissolved substance.

Decabromodiphenylether

The tables 7.6a and b show the toxicity data of decabromodiphenylether for water and sediment organisms.

There is only one data on acute toxicity available. Based on this less reliable study, decabromodiphenylether is acute only very slightly toxic to fish.

There is only one chronic toxicity test retrieved, which is not a regular toxicity test, because it involves a dosing test. Therefore this study can not be classified with the classification system of Annex 5.1. There are no data on the toxicity to sediment organisms.

The water solubility is 4.6 µg/l. This means the effect concentrations are above the water solubility limit.

Table 7.6.a
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of Decabromodiphenylether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Fish	DecaBDE	>500	48 h	LC_{50}	Oryzias latipes	-	CITI, 1992 (IUCLID)

Table 7.6.b
Retrieved chronic effect concentration (NOEC) (mg/l) of Decabromodiphenyl ether for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Fish	DOW FR-300-BA 77.4% DecaBDE 21.8% NonaBDE 0.8% OctaBDE	7.5-10 mg/kg bw.day	120 d	LOEC Increased liver weights and lactate levels in blood	Salmo gairdneri	-	Kierkegaard, et al, 1997 and Kierkegaard, et al, 1999
		7.5-10 mg/kg bw.day		NOEC Number of lymphocytes or blood Hb levels, EROD or ECOD activity			

Tetrabromobisphenol A

The tables 7.7a and b show the toxicity data of tetrabromobisphenol A for water and sediment organisms.

Tetrabromobisphenol A is slightly toxic to protozoans and very toxic to algae, crustaceans and fish in acute tests. However the the value for algae is a greater than value which means the actual LC_{50} may be much higher. In chronic tests tetrabromobisphenol A is slightly toxic to crustaceans and fish. To sediment organisms tetrabromobisphenol A is very slightly toxic for insects.

The water solubility is 720 µg/l. This means the lowest effect concentrations are below the limit of water solubility.

Table 7.7.a
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of Tetrabromo-bisphenol A for groups of species from the freshwater aquatic environment

Class	**Substance**	**Concentration (mg/l)**	**Testing time**	**Effect type**	**Organism**	**Method**	**Literature (source)**
Protozoan	TBBPA	82 (0.15 mmol/l)	72 h	EC_{50} inhibition of NADH oxidase, NADPH oxidase	Giardia lamblia	-	Kawamura, et al, 1986 (EHC 172)
Protozoan	TBBPA	163 (0.3 mmol/l)	72 h	EC_{50} inhibition of endogenous respiration	Giardia lamblia	-	Kawamura, et al, 1986 (EHC 172)
Algae	TBBPA	>0.0056	96 h	EC_{50} growth	Selenastrum capricornutum	-	Giddings, 1988 (EHC 172)
Crustaceans	TBBPA	0.96	48 h	LC_{50}	Daphnia magna	-	Morrissey, 1978 (EHC 172)
Crustaceans	TBBPA, 97.7%	7.9[a]	48 h	EC_{50} mortality	Daphnia magna	Renewal	Brooke, 1991 (AQUIRE)
Fish	TBBPA	0.1	96 h	NOEC mortality	Lepomis macrochirus	GLP Static	Calmbacher, 1978a (EHC 172)
Fish	TBBPA	0.18	96 h	NOEC mortality	Salmo gairdneri	GLP Static	Calmbacher, 1978b (EHC 172)
Fish	TBBPA	0.26[a]	96 h	NOEC mortality	Pimephales promelas	GLP Flowthrough	Surprenant, 1988 (EHC 172)
Fish	TBBPA	0.4	96 h	LC_{50}	Salmo gairdneri	GLP Static	Calmbacher, 1978b (EHC 172)
Fish	TBBPA	0.51	96 h	LC_{50}	Lepomis macrochirus	GLP Static	Calmbacher, 1978a (EHC 172)
Fish	TBBPA	0.54[a]	96 h	LC_{50}	Pimephales promelas	GLP Flowthrough	Surprenant, 1988 (EHC 172)
Fish	TBBPA 97.7%	0.06-0.89[a]	96 h	LC_{50}	Pimephales promelas	Static	Brooke, 1991 (AQUIRE)
Fish	TBBPA 97.7%	1.04[a]	96 h	LC_{50}	Pimephales promelas	Flowthrough	Brooke, 1991 (AQUIRE)
Fish	TBBPA	8.2	48 h	LC_{50}	Oryzias latipes	-	CITI, 1992

a. measured

Table 7.7.b
Retrieved chronic effect concentration (NOEC) (mg/l) of Tetrabromobisphenol A for groups of species from the freshwater aquatic environment

Class	**Substance**	**Concentration (mg/l)**	**Testing time**	**Effect type**	**Organism**	**Method**	**Literature (source)**
Crustaceans	TBBPA 99.15%	>0.98 [a]	21 d	NOEC survival, growth	Daphnia magna	Flowthrough	Surprenant, 1989b (EHC 172)
Fish	TBBPA	0.16 [a]	35 d	NOEC survival	Pimephales promelas	GLP	Surprenant, 1989a (EHC 172)
Sediment organisms							
Insects	TBBPA	0.13	14 d	LC_{50}	Chironomus tentans	GLP	BFRIP, 1989
Insects	TBBPA	45-46 [a]	14 d	NOEC growth survival	Chironomus tentans	Flowthrough	Breteler, 1989 (EHC 172)
Insects	TBBPA	230-340 mg/kg [a]	14 d	NOEC growth, survival	Chironomus tentans	Flowthrough	Breteler, 1989 (EHC 172)

a. measured

TBBPA PC oligomer, TBBPA epoxy oligomer, Hexabromocyclododecane, TetraBB and PentaBB

There are no toxicity data retrieved on TBBPA PC oligomer, TBBPA epoxy oligomer, hexabromocyclododecane, tetraBB and pentaBB for water and sediment organisms.

HexaBB

The table 7.8 shows the toxicity data of hexaBB for water and sediment organisms. There are acute toxicity data on hexaBB. However these data involve NOEC values of acute tests. Based on these values and the assumption that an EC50 is approximately a factor 10 higher than a NOEC, hexaBB is slightly toxic fish. There are also about seven data on dosing test with fish. These data can not be classified with the system in Annex 5.1. No data are available on other groups of species, on sediment organisms or on chronic toxicity.
The water solubility is 11-610 µg/l. This means all effect concentrations are above the water solubility limit.

Table 7.8
Retrieved acute effect concentration (NOEC) (mg/l) of HexaBB for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Fish	HexaBB	5[a]	24 h	No effect on behaviour (stress)	Petromyzon marinus	Static	Applegate, 1957 (AQUIRE)
Fish	HexaBB	> 10[a]	24 h	No mortality	Oncorhynchus kisuth	Static	MacPhee, 1969 (AQUIRE)
Fish	HexaBB	>10[a]	24 h	No mortality	Oncorhynchus tshawytscha	Static	MacPhee, 1969 (AQUIRE)
Fish	HexaBB	>10[a]	24 h	No mortality	Ptychocheilus oregonensis	Static	MacPhee, 1969 (AQUIRE)
Fish	FM FF-1	15 mg/kg bw.day ip	Single dose, 56 d. obs.	No mortality	Archosargus probatocephalus	-	James & Little, 1981 (EHC 152)
Fish	2,2',4,4',5,5'-HexaBB	20 mg/kg bw.day ip	Single or multiple doses; 17-40 d. obs.	No mortality	Archosargus probatocephalus	-	James & Little, 1981 (EHC 152)
Fish	2,2',4,4',5,5'-HexaBB	20 mg/kg bw.day ip	Single dose; 17 d. obs.	No MFO induction	Archosargus probatocephalus	-	James & Little, 1981 James & Bend, 1982 (EHC 152)
Fish	FM BP-6	66.3 mg/kg bw.day oral	3 doses in 5 days, 18 d. obs.	No mortality	Salvelinus fontinalis	-	Law & Addison, 1981 (EHC 152)
Fish	FM BP-6	150 mg/kg bw.day parenteral	Single dose, 5 d. obs.	NOEC MFO induction	Oncorhynchus mykiss	-	Franklin, et al, 1981 (EHC 152)
Fish	FM BP-6	150 mg/kg bw.day ip	Single dose, 15 d. obs.	No mortality, no effect on liver	Oncorhynchus mykiss	-	Elcombe & Lech, 1978 (EHC 152)
Fish	FM BP-6	200 mg/kg bw.day oral (total dose)	Multiple dose; 18 d.	No effect on liver	Salvelinus fontinalis	-	Law & Addison, 1981 (EHC 152)
Fish	FM BP-6	500 mg/kg bw.day parenteral	Single dose; 5 d. obs.	LOEC MFO induction	Oncorhynchus mykiss	-	Franklin, et al, 1981 (EHC 152)

a. measured

DecaBB

The table 7.9 shows the toxicity data of decaBB for water and sediment organisms.

In acute tests decaBB is slightly toxic to bacteria and crustaceans. For the other organism groups and for sediment organisms no data are available. There are no data on chronic toxicity.

The water solubility is < 30 μg/l. This means all effect concentrations are above the limit of water solubility.

Table 7.9.
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of DecaBB for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Bacteria	Tech. DecaBB Adine 0102	53	-	EC_{10} cell multiplication inhibition	Pseudomonas putida	ISO TC 147 /SC5/WG 1 /N111	Atochem, 1990 (EHC 152)
Crustaceans	Tech. DecaBB Adine 0102	<2	24 h	NOEC immobility	Daphnia magna	ISO 6341	Atochem, 1990 (EHC 152)
Crustaceans	Tech. DecaBB Adine 0102	>66	24 h	EC_{50} immobility	Daphnia magna	ISO 6341	Atochem, 1990 (EHC 152)

Overview of the toxicity data for fresh water organisms

In table 7.10 and 7.11 an overview is given of the lowest retrieved acute and chronic effect concentrations. The concentrations are reflected in mg/l.

Table 7.10
Overview of the lowest retrieved acute effect concentrations ($L(E)C_{50}$) (in mg/l) of the brominated flame-retardants in the freshwater environment.

Substances	Algae	Protozoans/ bacteria/ insects	Crustaceans	Fish
Pentabromodiphenylether	-	-	0.014	>500 (NOEC >0.021)
Octabromodiphenylether	-	-	-	>500
Decabromodiphenylether	-	-	-	>500
Tetrabromobisphenol A	>0.0056	82 protozoan	0.96	0.06-0.89
HexaBB	-	-	-	5 (NOEC) behaviour
DecaBB	-	-	>66 (NOEC <2)	-

Table 7.11
Overview of the lowest retrieved chronic effect concentrations (NOEC) (in mg/l) of the brominated flame-retardants in the freshwater environment.

Substances	Algae	Protozoans/ bacteria/ insects	Crustaceans	Fish
Pentabromodiphenylether	>0.026	-	0.0053	-
Octabromodiphenylether	-	-	0.0017	-
Tetrabromobisphenol A	-	45-46 (LC50 0.13)	>0.98	0.16

Tables 7.10 and 7.11 show that most data are available on fish and crustaceans and that ecotoxicity data on brominated flame-retardants are scarce.

Effects observed in the environment
No data on brominated flame-retardants are retrieved on effects observed in the environment.

7.2.2 Comparing exposure concentrations to environmental criteria

Until now no environmental criteria are set for brominated flame-retardants. Therefore a comparison with exposure concentrations can not be made. However, at the moment the derivation of environmental criteria has started.

7.2.3 Toxic effects in marine aquatic environment

General
In table 7.13 to 7.18 the retrieved acute and chronic toxicity data of the brominated flame-retardants for marine organisms are reproduced. In this report the toxicity tests on crustaceans and molluscs with a testing time of 96 h and less, are regarded as acute. The other tests are regarded as chronic. For algae the EC_{50} values at 96 h are regarded as acute and the NOEC values at 96 h as chronic. For fish the data are per test. Tests on early life stages (ELS) are regarded as chronic. No distinction is made between water and sediment organisms. Table 7.12 gives an overview of the level of toxicity.

Table 7.12
Overview of the toxicity data on brominated flame-retardants in the marine environment classified according to the classification system in Annex 5.1. 0 = very slightly toxic; * = slightly toxic; ** = moderately toxic; *** = very toxic.

Chemical	CAS no	Algae		Molluscs		Crustaceans		Fish	
		Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic
Tetrabromodiphenylether	40088-47-9	-	-	-	-	-	-	-	-
Pentabromodiphenylether	32534-81-9	-	-	-	-	-	-	-	-
Hexabromodiphenylether	36483-60-0	-	-	-	-	-	-	-	-
Heptabromodiphenylether	68928-80-3	-	-	-	-	-	-	-	-
Octabromodiphenylether	32536-52-0	-	-	-	-	-	-	-	-
Nonabromodiphenylether	63936-56-1	-	-	-	-	-	-	-	-
Decabromodiphenylether	1161-19-5/ 61345-53-7	-	*	-	-	-	-	-	-
Tetrabromobisphenol A	79-74-7	***	-	-	-	***	-	-	-
TBBPA PC oligomer	94334-64-2/ 71342-77-3	-	-	-	-	-	-	-	-
TBBPA epoxy oligomer	32844-27-2	-	-	-	-	-	-	-	-
Hexabromocyclododecane	25637-99-4/ 3194-55-6	***	-	-	-	-	-	-	-
TetraBB	40088-45-7	-	-	-	-	-	-	-	-
PentaBB	56307-79-0	-	-	-	-	-	-	-	-
HexaBB	36355-01-8	-	-	-	-	-	-	***	-
DecaBB	13654-09-6	-	-	-	-	-	-	-	-

No data are retrieved on Tetrabromodiphenyl ether, Pentabromodiphenyl ether, Hexabromo- diphenyl ether, Heptabromodiphenyl ether, Nonabromodiphenyl ether, TBBPA PC oligomer, TBBPA epoxy oligomer Penta PBB and Deca PBB. The data on the other substances are described in the next paragraphs.

Octabromodiphenylether
The table 7.13 shows the toxicity data of octabromodiphenylether for marine organisms.
There is only one toxicity data retrieved, which is not a regular toxicity test, because it involves a dosing test. Therefore this study can not be classified with the classification system of Annex 5.1. The study is regarded as chronic because the effect type is a NOEC and the test duration is 74 days. There are no data on acute toxicity or other chronic toxicity data on octabromodiphenylether.
The water solubility is 0.5 µg/l.

Table 7.13
Retrieved chronic effect concentration (NOEC) (µg/l) of Octabromodiphenylether for groups of species from the marine aquatic environment

Class	**Substance**	**Concentration (µg/l)**	**Testing time**	**Effect type**	**Organism**	**Method**	**Literature (source)**
Fish	OctaBB (Dow chemical)	100 mg/kg feed	74 d	No mortality	Salmo salar	-	Zitko, 1977

Decabromodiphenylether
The table 7.14 shows the toxicity data of decabromodiphenylether for marine organisms.
Decabromodiphenylether is very slightly toxic to algae. On the other organism groups no data are available. The water solubility is 4.6 µg/l.

Table 7.14
Retrieved chronic effect concentration (NOEC) (mg/l) of Decabromodiphenylether for groups of species from the marine aquatic environment

Class	**Substance**	**Concentration (mg/l)**	**Testing time**	**Effect type**	**Organism**	**Method**	**Literature (source)**
Algae	DecaBDE	1[a]	72 h	LOEC growth	Skeletonema costatum	-	Walsh, et al, 1987 (EHC 162, AQUIRE)
Algae	DecaBDE	1[a]	72 h	LOEC growth	Thalassiosira sp.	-	Walsh, et al, 1987 (EHC 162, AQUIRE)
Algae	DecaBDE	1[a]	96 h	LOEC growth	Chlorella sp.	-	Walsh, et al, 1987 (EHC 162, AQUIRE)

a. Above the limit of water solubility; measured; salinity 30 promille added as a solution in acetone.

Tetrabromobisphenol A
The table 7.15 shows the toxicity data of tetrabromobisphenol A for marine organisms. Acute tests show that tetrabromobisphenol A is very toxic to algae and crustaceans. For other organism groups no data are available. There are no data on chronic toxicity.
The water solubility is 720 µg/l. This means the lowest effect concentrations are above the water solubility limit.

Table 7.15.
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of Tetrabromobisphenol A for groups of species from the marine aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Algae	TBBPA	0.09-0.89	72 h	EC_{50} growth	Skeletonema costatum	-	Walsh, 1987 (EHC 172, AQUIRE)
Algae	TBBPA	0.11-1	72 h	EC_{50} growth	Thalassiosira sp.	-	Walsh, 1987 (EHC 172, AQUIRE)
Algae	TBBPA	>1.5	96 h	EC_{50} growth	Chlorella sp.	-	Walsh, 1987 (EHC 172, AQUIRE)
Crustaceans	TBBPA	0.0062 [a]	96 h	NOEC reduction of shell deposition	Crassostrea virginica	Acute, Flowthrough	Surprenant, 1989c (EHC 172)
Crustaceans	TBBPA	0.098 [a]	96 h	EC_{50} reduction of shell deposition	Crassostrea virginica	Acute, Flowthrough	Surprenant, 1989c (EHC 172)
Crustaceans	TBBPA	0.86	96 h	LC_{50}	Mysidopsis bahia, <1d	Flowthrough	Goodman, et al, 1988 (EHC 172, AQUIRE)
Crustaceans	TBBPA	1.1	96 h	LC_{50}	Mysidopsis bahia, <5d	Flowthrough	Goodman, et al, 1988 (EHC 172, AQUIRE)
Crustaceans	TBBPA	1.2	96 h	LC_{50}	Mysidopsis bahia, <10d	Flowthrough	Goodman, et al, 1988 (EHC 172, AQUIRE)

a. measured

Hexabromocyclododecane

The table 7.16 shows the toxicity data of hexabromocyclododecane for marine organisms.

Acute tests show that hexabromocyclododecane is very toxic to algae. For other organism groups no data are available. There are no data available on the chronic toxicity of hexabromocyclododecane for marine organisms.

The water solubility is 3.4 – 8 µg/l. This means the lowest effect concentration is around the limit of water solubility.

Table 7.16
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (µg/l) of hexabromocyclododecane for groups of species from the marine aquatic environment

Class	Concentration (µg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Algae	9.0-12.2	72 h	EC_{50} growth	Thalassiosira sp.	-	Walsh, 1987 (AQUIRE)
Algae	40-380	72 h	EC_{50} growth	Skeletonema costatum	-	Walsh, 1987 (AQUIRE)
Algae	>1500	96 h	EC_{50} growth	Chlorella sp.	-	Walsh, 1987 (AQUIRE)

TetraBB

The table 7.17 shows the toxicity data of tetraBB for marine organisms.
There is only one toxicity data retrieved, which is not a regular toxicity test, because it involves a dosing test. Therefore this substance can not be classified with the classification system of Annex 5.1. There are no data on acute toxicity or other chronic toxicity data on tetraBB.

Table 7.17.b
Retrieved chronic effect concentration (NOEC) (µg/l) of tetraBB for groups of species from the marine aquatic environment

Class	**Substance**	**Concentration (µg/l)**	**Testing time**	**Effect type**	**Organism**	**Method**	**Literature (source)**
Fish	Mixture of di-, tri- and tetraBB	7.75 mg/kg feed	In diet for 40 days	LC100	Salmo salar	-	Zitko & Hutzinger, 1976 (EHC 152)

HexaBB

The tables 7.18a and b show the toxicity data of hexaBB for marine organisms.
The acute toxicity data on hexaBB has a NOEC level.
Chronic tests show that hexaBB is very toxic to fish. It should however be noted that possibly the actual NOEC level is higher because only 1 concentration is tested.
There are no other data available.
The water solubility is 11- 610 µg/l. This means the effect concentrations are below the limit of water solubility.

Table 7.18.a
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (µg/l) of HexaBB for groups of species from the marine aquatic environment

Class	**Substance**	**Concentration (µg/l)**	**Testing time**	**Effect type**	**Organism**	**Method**	**Literature (source)**
Fish	HexaBB	8.76	48 h	No mortality	Salmo salar	BCF study	Anderson, 1975 (AQUIRE)

Table 7.18.b
Retrieved chronic effect concentration (NOEC) (µg/l) of HexaBB for groups of species from the marine aquatic environment

Class	**Substance**	**Concentration (µg/l)**	**Testing time**	**Effect type**	**Organism**	**Method**	**Literature (source)**
Fish	HexaBB	7.75	42 d	No mortality	Salmo salar	BCF study	Anderson, 1975 (AQUIRE)
Fish	FM BP-6	100 mg/kg feed	42 d	No mortality	Salmo salar	-	Zitko, 1977 (EHC 152)

Overview of toxicity data for marine organisms.
In the Tables 7.19 and 7.20 an overview is given of the lowest retrieved acute and chronic effect concentrations. The concentrations are reflected in mg/l.

Table 7.19
Overview of the lowest retrieved acute effect concentrations (L(E)C_{50}) (in mg/l) of the brominated flame-retardants in the marine environment.

Substances	**Algae**	**Protozoans/ bacteria/ insects**	**Crustaceans**	**Fish**
Tetrabromobisphenol A	0.09-0.89	-	0.86 (0.098 shell deposition)	-
Hexabromocyclododecane	0.009-0.0122	-	-	-
HexaBB	-	-	-	0.00876 NOEC

Table 7.20
Overview of the lowest retrieved chronic effect concentrations (NOEC) (in mg/l) of the brominated flame-retardants in the marine environment.

Substances	**Algae**	**Protozoans/ bacteria/ insects**	**Crustaceans**	**Fish**
Decabromodiphenylether	1	-	-	-
HexaBB	-	-	-	0.00775

From the Tables 7.19 and 7.20 it is clear that toxicity data on the brominated flame-retardants are scarce. From the available data it seems that these substances are very toxic to marine organisms.

7.3 Standards and derivation of iMTRs

In MilBoWa (1991) harmonized standards are derived for several environmental compartments for a number of chemicals. The purpose of MilBoWa (1991) is to create a system of limit- and target values for soil and surface water.
A limit value is a quality level that minimally should be achieved or maintained. A target value is a quality level at which no adverse effects are to be expected. The limit value is based upon the “maximal tolerable risk level” (MTR), the target value on the “negligible risk level” (NR).
As a starting-point it is formulated that a MTR is comparable to the concentration at which at least 95% of the species in the ecosystem will be protected (method of Van Straalen and Denneman (1989), modified to the model of Aldenberg and Slob (1991; 1993). There is also formulated that the negligible risk level is comparable to 1% of the MTR.

For the brominated flame-retardants there are no standards derived yet but at the moment work is being done to derive MTRs by the RIVM.

The 95% protection level (MTR) can be defined for an individual substance if there are NOEC values for at least four different groups of species (e.g. fish, mollusc, crustacean and algae) available. If there are not enough data to applicate the method, abitrar safety factors are used (the modified EPA-method). In table 7.21 the safety factors of the modified EPA method, dependent on the number of available toxicity data, are presented.
The calculated MTR in this report will be defined as "indicative MTR" (iMTR). In contradiction to the limit and target values the derived iMTRs have only a technical status and no political value. They are not legally set and may change as soon as more toxicity data become available.

Table 7.21
Safety factors for the derivation of iMTRs in surface water (EPA method).

Available toxicity data	**Safety factor**
Lowest acute $L(E)C_{50}$ or QSAR estimation for acute toxicity	1000
Lowest acute $L(E)C_{50}$ or QSAR estimation for acute toxicity for at least algae, crustaceans and fish	100
Lowest NOEC or QSAR estimation for chronic toxicity	10*
Lowest NOEC or QSAR estimation for chronic toxicity for at least algae, crustaceans and fish	10

* this value will be compared with the value based on acute $L(E)C_{50}$ values. The lowest value will be selected.

Based on the retrieved toxicity data the iMTRs are derived using the procedure described by Slooff (1992) and Beek (1993). For the derivation of the iMTRs the fresh and salt water toxicity data are combined just as the data concerning pelagic and bentic organisms (based on the assumption that bentic organisms are exposed through the same medium as the pelagic organisms). Biomagnification is not included in this calculation. The toxicity data used for the derivation of the iMTRs are reflected in Annex 5.2. The iMTRs are in table 7.22.

The iMTRs for sediment are calculated using the equilibrium partition (EP) method (see Slooff, 1992; Beek, 1993).

MTR sed = MTR water x Kp

The equilibrium partition coefficient is calculated with the K_{oc} (see chapter 5, table 5.2) using the following formula:

$Kp = K_{oc} \times foc\ (l.kg^{-1})$

In the calculation the standard soil is assumed to contain 5% organic carbon.

Table 7.22
iMTRs for surface water (µg/l) and sediment (µg/kg dry soil).

Substance	**Surface water (µg/l)**		**Sediment (µg/kg)**	
	iMTR	Method	IMTR	Method
Tetrabromodiphenylether	-	-	-	-
Pentabromodiphenylether	0.014	EPA/1000	21	EP (log k_p = 3.18)
Hexabromodiphenylether	-	-	-	-
Heptabromodiphenylether	-	-	-	-
Octabromodiphenylether	0.17	EPA/10*	1232	EP (log k_p = 3.86)
Nonabromodiphenylether	-	-	-	-
Decabromodiphenylether	-	-	-	-
Tetrabromobisphenol A	>0.056	EPA/100	>1578	EP (log k_p = 4.45)
TBBPA PC oligomer	-	-	-	-
TBBPA epoxy oligomer	-	-	-	-
Hexabromocyclododecane	0.0090-0.0122	EPA/1000	54-74	EP (log k_p = 3.78)
TetraBB	-	-	-	-
PentaBB	-	-	-	-
HexaBB	0.775	EPA/10*	4.89 mg/kg	EP (log k_p = 3.8)
DecaBB	>66	EPA/1000	>3.3*10^6	EP (log k_p = 4.7)

As no limit values are derived for the brominated flame-retardants there is no comparation possible with the iMTRs. However a comparison with the concentrations in the environment can be made. No brominated PBBs or PBDEs are found in water in the Netherlands. It is possible that there may be data in the project LOES but these are not yet available. In table 7.23 the concentrations in the sediment from chapter 6.2.2 and 6.3.2 are summarized. Data are available on tetraBDE, pentaBDE, octaBDE and decaBDE and compared with iMTRs derived for pentaBDE and octaBDE, the iMTR of pentaBDE in sediment is 21 µg/kg. PentaBDE concentrations in sediment in the Netherlands range from 7.3 to 21 µg/kg wet weight in fresh water sediments and from <0.2 to 1.3 µg/kg dry weight in marine sediments. This means that in the Netherlands the concentrations in sediment do not exceed iMTR. However in Sweden and the UK much higher concentrations in the sediment have been found although the concentrations in Sweden are based on ignition loss weight. This means that the dry weight concentrations will be lower. The iMTR of octaBDE for sediment is 1232 µg/kg. There are no measurements on octaBDE in the Netherlands. The concentrations in sediment in the UK range from <0.44 to 3030 µg/kg dry weight. This means the iMTR is exceeded and that there is a potential risk for the environment.

Table 7.23
Concentration ranges in fresh water and marine sediments in µg/kg on several locations based on data from chapter 6.2.2. and 6.3.2.

Location	Fresh water/ Marine	TetraBDE In µg/kg	PentaBDE In µg/kg	OctaBDE In µg/kg	DecaBDE In µg/kg
Netherlands	Fresh	6.7-23 wet weight[a]	7.3-21 wet weight[a]	-	-
Netherlands	Marine	<0.17-1.4 dry weight[g]	<0.2-1.3 dry weight[g]	-	1.1-200 dry weight[g]
Sweden	Fresh	1.3-840 µg/kg IG [b]	<1-1200 µg/kg IG [b]	-	-
Baltic sea	Marine	0.06-1.6 µg/kg IG[f]	<0.04-0.98 µg/kg IG [f]	-	-
UK	Fresh	<0.3-368 dry weight[c]	<0.4-898 dry weight[c]	<0.44-3030 dry weight[d]	<0.6-399[e] dry weight
EU (except Netherlands)	Marine	<0.17-5.8 dry weight[g]	<0.2-6.93 dry weight[g]	-	<0.52-1700 dry weight[g]

a. based on table 6.5 b. based on table 6.6 c. based on table 6.7
d. based on table 6.9 e. based on table 6.9 f. based on table 6.12
g. based on table 6.13

7.4 Human toxicity

General effects
The PBBs and the PBDEs are listed as endocrine disrupters (Colborn, 1993) and also have effects on thyroid hormones. The interactions of both classes of brominated flame-retardants with the thyroid hormone system seems to follow those of all major classes of polyhalogenated aromatic hydrocarbons (PAHS) (Brouwer, 1998 in De Boer, 1999).

PBBs
HexaBB appears to have a similar acute toxicity to rats as the PCB mixtures Aroclor 1254 and Kanechlor 500 (Pijnenburg, 1993 in De Boer, 1999). The LD_{50} values of commercial mixtures show a relatively low order of acute toxicity (LD_{50} > 1 g/kg b.w.) in rats, rabbits and quails, following oral or dermal administration. The toxicity of PBBs was higher with multiple dose rather than single dose administration. The few studies performed with commercial octabrominated biphenyl mixtures and BB-209 (decaBB) did not result in mortality in rats and fish. On the basis of the limited available data, octabrominated biphenyls and BB-209 appear to be less toxic than other lower brominated PBB mixtures, probably because they are less efficiently absorbed (EHC152, 1994).
Several reports on the carcinogenicity of PBBs and PCBs have concluded that there are strong indications that these compounds are not mutagenic in itself, but do promote the carcinogenicity of mutagenic compounds, such as nitrosamine and certain polyaromatic hydrocarbons (PAHS). This is highly relevant, since in the marine environment halogenated compounds often co-occur with PAHS (De Boer, 1999).

The endocrine disrupting activity of PBBs follows from the next studies.
FM FF-1 (hexaBB) caused a longer sexual cycle in monkeys (Pijnenburg, 1995 in De Boer, 1999), and PBBs caused decreased egg production and nesting behaviour in Japanese quail (Aust, 1987 in De Boer, 1999). One recent study reported that in mice PBB (di-BBs and tetra-BBs) reduced the in vitro fertilisation rate at higher dosages. Furthermore, an increased incidence of abnormal two-cell embryos and degenerative oocytes was observed at the 1 and 10 mg/ml concentration of PBB (Kholkute, 1994 in De Boer, 1999). PBBs also affect the regulation of steroid hormones. The extent depends on the species as well as the dose and duration of exposure.

PBBs cause immuno-suppression at levels that also cause a number of the other toxic effects described (Pijnenburg, 1995 in De Boer, 1999).

PBDEs
The acute toxicity of commercial pentaBDE, decaBDE and octaBDE for laboratory animals is also low (LD_{50} > 1 g/kg body weight). BDE-209 (decaBDE) and octaBDEs were also not irritating to the skin. BDE-209 is neither irritant to the eyes of a rabbit nor had it effect on survival, body weight or food consumption in feeding studies on rats and mice. No gross or microscopic pathological effects have been found (EHC162, 1994).
However in short term toxicity studies with octaBDEs, rats administered dietary levels of 100 mg/kg had increased liver weights and showed microscopic changes of liver tissue. These liver changes were more severe at the even higher dose levels, i.e. 1000 and 10,000 mg/kg diet. octaBDEs gave also minor eye irritation to rabbits (EHC162, 1994). In addition, pentaBDEs increased liver/body weight ratio with 64 %, octaBDEs with 45 % and BDE-209 with 25 % in a study where a dose of 0.1 mM/kg/day was administered to male rats during 14 days (Carlson, 1980a in De Boer, 1999).

Exposure routes in the aquatic environment.
Contamination of the aquatic environment (surface water and sediment) can pose a threat to public health. The hazards can be caused by direct and/or indirect contact with the contaminants.
In principle, uptake of contaminants by humans can take place by ingestion (oral), dermal contact (via the skin) and inhalation (via the lungs).

Human health risk assessment evaluation with exposure to sediment
BKH (1991) has conducted a study into the human health risks of recreants potentially exposured to contaminants in sediment. Because children are seen as the most vulnerable group, recreating children are used as a starting point for the derivation of a human-toxicologic based advisory value (HTBA-value) for contaminations in sediment.
Above this value adverse health effects may be expected. In Annex 5.3 the human health assessment evaluationmethod is described. In Table 7.24 the calculated HTBA-values for brominated flame-retardants are given. The HTBA-values are based on ADI-values (Acceptable Daily Intake) from the literature and the K_{ow}-values. In EHC 152 (1994) an indicative ADI is calculated for PBBs from a 2-year rat study on carcinogenity using the NOAEL of 0.15 mg Firemaster/kg bw.day and a safety factor of 1000, since the compounds probably produce cancer by an epigenetic mechanism. For octaBDE a daily dose of 0.38 μg/kg.day is calculated using a concentration of 8000 ng/kg in human adipose tissue. Compared to the lowest NOEL of 2.5 mg/kg.day from a subchronic teratology study on rats this is a factor 10,000 lower EHC162, 1994). Using this lowest NOEL and a safety factor of 1000 (Vermeire, 1991) an indicative ADI of 2.5 μg/kg.day can be calculated. Based on a NOEL of 1 mg

decaBDE/kg bw.day of a carcinogenity studie on rats for 100-105 weeks (EHC162, 1994) an indicative ADI of 10 µg/kg can be calculated using a safety factor of 100 (Vermeire, 1991).

Because there are only indicative ADI-values available for the PBBs in general, the HTBA-value is only calculated for these chemicals. It should be noted that the Dutch RIVM is working on the derivation of TDIs (Tolerable Daily Intake) which are comparable to ADIs.

The derived HTBA-values only have an indicative value, because the risk assessment method contains uncertainties. These uncertainties concern in the exposure model, which is based on a number of assumptions, as well as the ADI-values, that contain intrinsic uncertainties. Because dissociation is not adjusted for, it is possible that the HTBA values might be underestimated. When the HTBA-values are exceeded, the actual risk must be assessed. This means that the actual exposure on the particular location must be defined so that the human health risks can be estimated.

Table 7.24
Humane toxicologic based advisory value (HTBA-value) for the brominated flame-retardants

Substance	**Log K_{ow}**	**ADI (µg/kg/day)**	**HTBA-waarde (mg/kg dw)**
OctaBDE	8.63	2.5[c]	19
DecaBDE	9.97	10[c]	79
PBB (Firemaster)	8.03[b]	0.150[a]	1.19

a. indicative total daily intake estimated from a NOEAL (no-observed effect level) of a positive carcinogenity study using a uncertainty factor of 1000, from IPCS Environmental Health Criteria 152 (EHC 152, 1994;).
b. averaged
c. calculated using Vermeire, 1991

Comparing with exposure concentrations in sediment and water
The measured concentrations in sediment are given in chapter 6 and are summarized in table 7.23. No measured concentrations in water are available. For the PBBs there are no measured concentrations in sediment. For octaBDE there are measured values in sediment for the UK. These vary between <0.44 and 3030 µg/kg. This means the indicative HTBA-value is not exceeded. For decaBDE there are measured values in marine water in the Netherlands of 1.1-200 µg/kg dry weight. This means that the indicative HTBA-value is not exceeded.
It should be noted that the used ADI values are derived from NOELs and that the used log K_{ow} are relatively high to use the model on which the derivation of the HTBA-value is based. It should also be noted that the derivation of the HTBA-value uses a worst case approach.
The derivation of HTBA-values should be done with official ADI values and measured log K_{ow} values as soon as these values are available.

7.5 Conclusions and recommendations

Mode of action
The underlying mechanism of the toxicity of brominated flame-retardants is probably due to molecular mechanisms. PBBs and PBDEs have a potency to induce cytochrome P450, which can lead to a number of effects. Furthermore these substances are expected to interact with receptors.

Toxicity in freshwater environment
On the freshwater organisms toxicity data are available on pentaBDE, octaBDE, decaBDE, TBBPA, hexaBB and decaBB. Most data are available on crustaceans and fish. Their toxicity varies from very slightly toxic to very toxic. PentaBDE, octaBDE and TBBPA are very toxic to one or more groups of species and their toxicity lies around the limit of solubility.

Toxicity in saltwater environment
Toxicity data of the selected brominated flame-retardants on marine organisms are only available for decaBDE, TBBPA, hexabromocyclododecane and hexaBB. Except for decaBDE data indicate that these substances are very toxic to marine organisms. Their toxicity lies just below or around the limit of solubility, except for decaBDE.

Limit values and indicative MTRs
There are no limit values derived for the brominated flame-retardants. The indicative MTRs for surface water vary from 0.014->66 µg/l. No brominated flame-retardants have been found in water. In sediment in the Netherlands the concentration varies from 7.3 to 21 µg/kg in fresh water and from <0.17 to 200 µg/kg in marine water. Comparing the derived iMTR and the concentration ranges in sediment, the iMTR for PeBDE is just not exceeded in the Netherlands. However, In the UK and Sweden concentrations in sediment exceed the iMTR of PeBDE and the iMTR for octaBDE is exceeded in the UK.

Humane toxicity
The acute toxicity of brominated flame-retardants is relatively low. Long term effects on the balance of endocrine systems seem to present the greatest risk of these compounds. These endocrine effects need further consideration, since the majority of animals and man are exposed to these brominated flame-retardants. The exposure range for humans through food was calculated as 0.2 - 0.7 mg per day (Darnerud, 1998 in De Boer, 1999).

Recommendations
Toxicity data on the brominated flame-retardants are scarce. More research is absolutely necessary. Furthermore also data on concentrations in the environment are hardly available. More measurements in the environment are necessary.

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8. Policy overview

8.1 National environmental policy

8.1.1 Netherlands

In the National Environmental Policy Plan (NMP, 1989) and the more recently published National Environmental Policy Plan-3 (NMP-3, 1997) the general environmental policy is described.
In the year 2010 the environmental targets and target values must be reached. Concerning the reverse of the risks caused by high concentrations of chemicals, specific policy targets have been set in the National Environmental Policy Plan of 1989. These targets imply the aim to not exceed the Maximum Permissible Concentrations (MPCs) and the Negligible Concentrations (NCs) in 2010, by means of prevention and reconstruction. In the report on integral standardisation on substances (INS, 1997) environmental quality standards have been derived.
The current water policy is reflected in the fourth note on watermanagement (1997). In this note the targets and headlines of the policy for the national water management are given.

In the Netherlands a system has been developed for the specification of environmental quality standards based on two risk levels, the Maximum Permissble Concentration (MPC) and the Negligible Concentration (NC). These values are guidelines but not legally binding. When the environmental quality standards are set, other aspects, such as political and technical feasability, are also taken into account. Target values are either set at the NC or at the background value, limit values are set between the MPC and the NC. The derivation of MPCs and NCs is explained in chapter 7.3. For the brominated flame-retardants no specific quality standards, MPCs or NCs have been set.

Brominated flame-retardants

In 1991 there has been a proposition to forbid the use of PBBs and PBDE in the Netherlands. Because this would cause commercial barrier the proposition is retracted. In 1993 there was a proposition to forbid storage and trade, to third parties, of PBBs or products and preparations containing these. The export was excluded from this. Up till now this ban is not yet enforced.

8.1.2 Other country specific policy (OECD, 1994)

In table 8.1. the other country specific policy has been described.

Table 8.1
Other country specific policy

Austria	Bann on the production, marketing, import and use of PBBs and products containing PBB
Canada	Bann on production, use, put up for sale, process, sell or import of PBBs for commercial purposes
Denmark	Implementation of the EC guideline 89/677 on the prohibition of the use of PBBs in textiles
Germany	Indirect regulation through Dioxin ordinance
Finland	PBB may not be used in textile that contacts the skin (according to EC guideline 83/264)
French	Implementation of the EC guideline on PBBs
Italy	Some voluntary measures to end the use
Japan	Industry voluntary diminishes the production and use of PBB, hexaBDE and tetraBDE.
Sweden	Bann on use of PBBs in textiles that contacts the skin by implementation of the EC guideline
Switzerland	Bann on production, delivery, import and use of PBBs and products that contain these chemicals. Delivery and import of condensors and transformators containing PBB is prohibited
USA	No production or use. Companies that want to manufacture the chemicals must inform the EPA 90 days ahead and ask permission

8.1.3 Current development

In 1999 KEMI (National Chemicals Inspectorate) has proposed to forbid the production and use of PBB and PBDE as well as products that contain these chemicals, in Sweden and furthermore proposed that Sweden must launch itself to do the same within the European Commission. A suitable period to have the bann enforced is 5 years (KEMI, 1999).

8.2 European Commission

In the EC guideline 83/264/EC, the fourth amendment of guideline 76/769/EC the marketing and use of PBBs (CAS no 59536-65-1) is forbidden in textiles that make contact with the skin when using them (EC, 1983).
In 1991 the European Commission has proposed (COM/91/7) to phase out all trade for 10 brominated flame-retardants under the guideline on marketing and use of dangerous substances (76/769/EC). The parliament has decided not to give an opinion on this proposition and it has been retracted in 1995 (Bjerregaard, 1998).
In 1991 there was proposed a guideline to prohibit the use of PBDE to 0.1%. This proposition is not honoured by the environmental comittee of the EC because there would be not alternatives. In 1994 this proposition is retrieved, because it was superannuated and because the European Commission established the fact that Germany and the Netherlands did not introduce legislation for PBDE. The international scientific committee was also less convinced that PBDE produced an unacceptable danger for human health and the environment (Hardy, 1997).

8.2.1 Current development

In the risk assessment of the EC on brominated flame-retardants, that is comes out at the end of 1999, it will probably be concluded that no measures are necessary for octaBDE and decaBDE and it will be for pentaBDE.

In the concept guideline on waste electrical and electronical equipment (WEEE) of DGXI of the EC it is porposed to forbid the use of all halogenated flame-retardants in 2004.

8.3 International policy

8.3.1 North Sea conference

The ministers of environment have decided at the NorthSea conference of 1995 (Esbjerg declaration), to start action to supersede the brominated flame-retardants by less harmfull products.

8.3.2 OSPAR

The brominated flame-retardants are on the DIFFCHEM agenda since 1990. In 1994 Sweden has recommended the OSPAR to outphase pentaBDE and decaBDE. This recommendation was not supported by the member states. In 1995 Sweden has proposed a decision on outphasing decaPBB. But this was also not supported although member states have pronounced for research into these chemicals. For DIFF 1996 Sweden has sent a questionairre to the member states that had little response. At the suggestion of Sweden the Commission decided a rest in place until the results of the research of several international phora become available. The discussion on outphasing the brominated flame-retardants will put on the DIFFCHEM agenda at the utmost in 2001 (OSPAR, 1999).

8.3.3 United Nations

In the POP (Persistent Organic Pollutants) treaty it is decided to reduce or forbid the use and production of chemicals. The POP agreement must be ready in 2000 and must be signed by the contributing parties in the spring of 2001 and must be put in action in 2003.

Admission on the POP list means that the contributing parties oblige themselves to effort reduction and elimination of emissions and losses. The goal of the convention is to disminish the spreading of POP because parties will take measures to end production and use.

HexaBB is in the POP protocol of the UN Convention on long-range transboundary air pollution (CLRTAP).

8.3.4 PIC

This UN treaty is part of the “London guidelines for the exchange of information on the chemicals in International trade” of 1987 and is added to this in 1989. The treaty will be inplemented by the FAO (for pesticides) and the UNEP (for other chemicals).

The “Rotterdam convention” is signed on 11 september 1998 by the ministers of the representants of 57 countries and the European Commission.

The goal is to protect man and environment against abuse of chemicals and damage by accidents, especially in the third world countries. By the action of the treaty chemicals on the PIC list, cannot be exported or imported in any country affiliated to the treaty, without the explicit permission of the importing country. In the treaty a list of chemicals is drawn up for which the PIC will apply. This list is drawn up by experts of the FAO and UNEP. On the list are 5 industrial chemicals and 22 pesticides. In the future this list may be extended. One condition is that a chemical is forbidden or strictly regulated in one affiliated country after 1992. If the prohibition was before 1992 then it must be in five affiliated countries. For each chemical a Decision Guidance Document (DGD) will be drawn up that will be sent to all contributing countries, so that the receiving country, together with an expert, can decide if they want to import the chemical. Until the convention is put in action an interim procedure is followed, voluntarily, for those chemicals on the list for which a DGD is drawn up. Chemicals on the list for which, at the acceptation of the convention, such document was not available, are put under the interim procedure until a DGD becomes available.

PBBs (hexaBB, octaBB, and decaBB) are on the PIC list since 1993 and There is a DGD available on them.

8.4 Policy on emissions

8.4.1 List of attention chemicals

PBB and PBDE are on the VROM list of chemicals that are considered as dangerous for the environment. Brominated flame-retardants are on the list of attention chemicals of OSPAR (OSPAR, 1997). The pursued goal is to take measures that end discharges, emissions and loss of PBBs and PBDEs in the year 2010. The interim goal (2005) is to end the most important sources of emission. Considering the bann on PBB OSPAR thinks 2003 is a better goal (OSPAR, 1999).

The OECD and the WHO (IPCS) have performed a risk analysis.

OctaBDE and DecaBDE are on the first priority list of the EC. PentaBDE is on the second list. The PBBs are also on the priority list of the US EPA.

8.4.2 Emission limits

There is no national legislation in the European Commission that inspect brominated flame-retardants in the atmospheric emissions, fluid discharges and waste (European Commission, 1996).
In the Netherlands an emission limit is prepared for a factory that produces PBDE/TBBPA: maximal 10 mg/m^3 particles in air (European Commission, 1996).

8.4.3 Agreements (international) policy makers and industry

In 1995 a voluntarily agreement with the OECD has been signed by the greatest bromide producing producers in Europe and America. This was part of the pilot risk reduction programme of the OECD in which the industry has agreed to inform and teach its customers, to use the chemicals responsively, and how to recycle and remove the product. Next to that PBB will not be produced, imported or exported with the exception of one French company that produces decaBB, which fact will be revised in 2000. The industry will also increase the purity of DBDE and OBDE flame-retardants, and diminish the emission levels at the production of a type flame-retardant (PeBDE). Regularly the industry will report on the continuation of the implementation of the agreement.
In 1996 the Japanese producers of brominated flame-retardants have decided on a similar agreement.

The (E)BFRIP ((European) Brominated Flame Retardant Industry Panel) and the OECD have set a voluntary agreement in 1998 in which the EBFRIP declares to make an extensive risk-evaluation on decaBB and also have agreed to inform the users on use, recycling and removal of PBBs. Next to that the use of some PBBs will be limited. The Voluntary industry commitment (VIC) is agreed worldwide without international regulations.

In 1989 the German chemical industry and the plastic producers have pronounced the intention to no longer produce nor use PBDE. The production is ended but the use continues, as chemical product and as in imported products.

8.4.4 Ecolables

In Germany there is a blue angel ecolable, that is attributed to a product if it does not contain halogenated flame-retardants, with the exception of products which have to resist high temperatures. There is an ecolable for copiers, PCs and printers. The White swan label (for Norway, Sweden, Iceland and Finland) is for the same ubovementioned products. They are introduced between 1994 and 1996 (Hardy, 1998).

8.5 References

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