

# Transport and fate of polybrominated diphenyl ethers in the Baltic and Arctic regions

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# Preface

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A project entitled "Predicting the future environmental fate of some brominated flame retardants (polybrominated diphenylethers) in the Nordic countries and the Arctic" has been financed by the Nordic Council of Ministers (NMR). The project is a co-operation between the three working groups under the environmental sector of the NMR: the Nordic Chemicals Group, the Nordic Group on Sea and Air Pollution and the Nordic Group on Monitoring and Data.

The aim of this project was to understand the historical behaviour as well as to predict the impact of various control measures regarding use and emissions on environmental levels of polybrominated diphenylethers (PBDEs) in the Nordic environment.

The project has been carried out by the Swedish Environmental Research Institute (IVL) together with the Norwegian Institute for Air Research (NILU). The participants of the project were:

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The reference group consisted of:

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The Nordic Chemicals Group: Magnus Nyström, Finnish environmental institute (SYKE)

The Nordic Group on Monitoring and Data: Britta Hedlund, Swedish Environmental protection agency (NV)

The project group wants to thank the Nordic Council of Ministers for funding the project. We also want to express our gratitude to the Nordic Risk Assessment Project group and the reference group for their support during the project work and valuable comments on the report. Special thanks to Kevin Jones at Lancaster University for providing unpublished monitoring data for model evaluation.

# Sammanfattning

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I föreliggande projekt har en dynamisk, fugacitets-baserad, regional multimediamodell (POPCYCLING-Baltic) använts i syfte att uppnå en ökad förståelse för historiska koncentrationsmönster, såväl som den troliga framtida utvecklingen av koncentrationer i olika media av polybromerade difenyletrar (PBDE) i Östersjöregionen, som resultat av olika åtgärder för att begränsa användningen och spridningen av dessa kemikalier. Resultaten exemplifieras med tre huvudsakliga kongener, PBDE 47, 99 samt 209. Historiska utsläpp för den europeiska regionen uppskattades med hjälp av en BNP-baserad metod, utgående ifrån globala uppskattningar om konsumtion, vilka anses vara tillförlitliga. Emissionsuppskattningarna för Europa är dock ytterst osäkra, vilket har sin huvudsakliga grund i bristen på information om Europas andel av den globala PBDE-konsumtionen i ett historiskt perspektiv. Luft antogs vara den primära utsläppsrecipienten, ett antagande som kan ifrågasättas, med tanke på de nya studier som påvisat förekomst av PBDE i både lak- och grundvatten. De koncentrationer som observeras i större akvatiska miljöer (t ex Östersjön), är dock troligen starkt påverkade av atmosfärisk deposition. Detta antagande baseras på en nyligen utförd studie som indikerar att PBDE som släpps ut till vatten sannolikt stannar i den absoluta närheten till källan, på grund av deras starka benägenhet att fördelas till partiklar och deponeras till sediment (Sternbeck et al., 2003). En annan nyligen utförd studie påvisade höga halter i mark, vilket indikerar att atmosfären är viktig som recipient och transportmedium (Hassanin et al., 2004).

Modellen uppvisar en tillfredsställande förmåga att förutsäga relativa förändringar över tid avseende koncentrationer av PBDE i miljön, men bör i dagsläget ej användas för att bedöma absoluta halter. De största osäkerheterna härvidlag tros vara kopplade till nedbrytningshastigheter i mark och sediment samt, framförallt på lokal nivå, kvantitativ kunskap om emissioner till vatten och andra media.

Trots de uppenbara osäkerheterna som är kopplade till modellens förmåga att förutsäga absoluta halter, kan man dra slutsatsen att den globala användningen av PBDEer nu har nått en nivå som är jämförbar med konsumtionen av PCB då den var som störst på 1970-talet. Detta kan vara en förklaring till att man idag återfinner halter av PBDE i mark som är i samma storleksordning som PCBer (Hassanin et al. 2004). Med tanke på att den totala kumulativa konsumtionen av PBDE sannolikt är mindre än motsvarande för PCB, är detta extra anmärkningsvärt. Man kan också dra slutsatsen att det föreslagna EU-förbudet av penta och oktaBDE sannolikt kommer att resultera i minskande koncentrationer av lågbromerade kongener i den baltiska miljön, och inom ca 10 år bör dessa ha nått till en nivå motsvarande ca 50 % av koncentrationerna år 2000, för sediment något senare. Detta förutsatt att användningen verkligen upphör samt att nedbrytning av BDE 209 till lägre bromerade kongener ej förkommer, en hypotes som föreslagits. Förbudet av penta och oktaBDE kommer sannolikt också att begränsa Europas bidrag till PBDE-förorening av den arktiska miljön. Dock bör nämnas att fortsatt användning av decaBDE sannolikt leder till ständigt ökande halter av BDE 209 i samtliga media, medan ett förbud även för denna substans skulle resultera i en nedgång, om än något långsammare än vad som uppskattats för de lägre bromerade kongenerna.





# Summary

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A dynamic, fugacity-based, regional multimedia fate and transport model (POPCYCLING-Baltic) has been used to assess the historical behaviour and the potential future fate of polybrominated diphenyl ethers (PBDEs) in the Baltic region, following the introduction of various measures to restrict the use and release of these chemicals to the environment. The results are exemplified using three congeners commonly occurring in technical products and the environment; PBDEs 47, 99 and 209. Historical emissions for the European area were estimated using a GDP-based approach, starting from global consumption estimates, which are believed to be fairly reliable. The emission estimates for the European region are, however, highly uncertain due to the lack of historical information on the European share of global PBDE consumption as well as the limited knowledge about consecutive emission processes. Air was assumed to be the primary emission medium, an assumption subject to significant uncertainties, since recent monitoring data indicate the presence of PBDEs in landfill leachate and groundwater. Still, concentrations observed in larger water bodies such as the Baltic Sea are assumed to be strongly affected by atmospheric deposition, as recent studies indicate that PBDEs released to water are likely to remain close to the source. This is probably due to their strong tendency to partition to particles and deposit (Sternbeck et al., 2003). Secondly, a very recent study showed elevated levels in soils, indicating that the atmosphere is an important pathway for these compounds to enter the environment within the study region (Hassanin et al., 2004).

The model used has a satisfactory ability to predict relative changes of environmental concentrations over time, however, at present date it should not be used to predict actual concentration levels. The main uncertainties coupled with this inability to predict quantitative estimates of concentrations are believed to be the uncertainty in degradation rates mainly for soils and sediment and, particularly on a local scale, quantitative knowledge on emission rates to water and other media.

Despite the uncertainties mentioned, it can be concluded that the global consumption of PBDEs has now reached a level similar in size to that of PCBs at their consumption peak in the 1970's. This may explain the fact that PBDE levels in soil have recently shown to be of similar order of magnitude as PCBs (Hassanin et al. 2004). It can also be concluded that the proposed EU ban of penta and octa commercial PBDE products is likely to result in decreasing concentrations in the Baltic drainage basin of lower brominated congeners with a 50% - level of the 2000 concentrations being reached around 2010 – 2011. This providing that the use actually stops and that no degradation to lower brominated compounds occurs for BDE 209. The ban of penta and octa is likely also to significantly reduce the European contribution to PBDE contamination in the Arctic. However, continued use of decaBDE is predicted to lead to ever increasing concentrations of BDE 209 in all environmental media, whereas a ban also of deca would result in a concentration decline, to a somewhat slower rate than predicted for the lower brominated compounds.



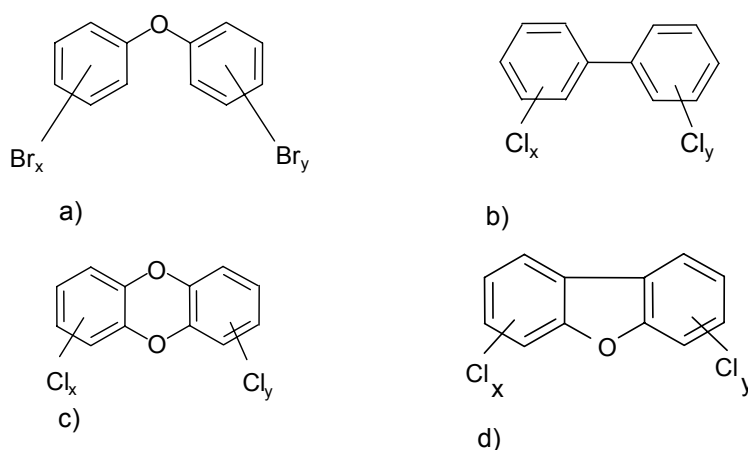
# 1 Introduction

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## 1.1 Background

Polybrominated diphenyl ethers (PBDEs) are organic chemical compounds, which are extensively used as flame retardants in products such as electronic equipment, plastic housings and textiles. The production of flame retarding chemical mixtures started as a result of the replacement of traditional materials such as wood and metal with more flammable alternatives, e.g. plastics and polyurethane foams, in the manufacture of furniture and electronic appliances. This change in manufacture started to grow in the late seventies and the use of flame retardants has increased dramatically from that time until today, when the global demand is estimated to be around 205 000 tonnes (1999 figures, BSEF, 2000). The benefits of using flame retardants are that they reduce the propensity for materials to catch fire and mitigate the combustion process, thus providing people with longer escape time. The UK Department of Trade and Industry (2000) estimated that the introduction of fire protected furniture had resulted in 710 saved lives between the years 1988 to 1997.

In recent years, concern has been raised regarding the possible environmental impact of PBDEs. Long-term monitoring of organic contaminants in human breast milk and fresh water sediments and biota in Sweden revealed increasing levels of certain PBDE substances (Merionyté et al., 1999; Nylund et al. 1992; Sellström et al, 1999). These findings initiated extensive monitoring mainly in biota and sediments but also in the atmosphere all around the world. Some PBDE compounds are now found globally. The main environmental concern about these compounds has arisen from the fact that they show structural similarities to well-known pollutants such as PCBs and dioxins/furans (Figure 1.1), and that they therefore might cause similar effects on nature and wildlife.



**Figure 1.1** General structures of a) polybrominated diphenyl ethers (PBDEs), b) polychlorinated biphenyls (PCBs), c) polychlorinated dibenzodioxins (PCDDs) and d) polychlorinated dibenzofurans (PCDFs).

It has been suggested that the PBDEs may share some of the toxic properties of PCDD/Fs and PCBs (Hooper and McDonald, 2000). Still, most toxicological evaluations have focused on the toxicity of technical PBDE products. These have been compiled within the EU risk assessments for the three commercial PBDE (ECB 200; 2002a,b). Due to the concerns about potential harmful effects, the European commission has now decided to ban two of the commercial PBDE products within the EU; the pentaBDE and the octaBDE, starting in August 2004. The risk assessment for the decaBDE is still on-going, but a ban has been suggested for 2006 unless the risk assessment proves that there are no significant risks associated with this compound (European Parliament, 2002).

The Nordic/Arctic environment may be particularly sensitive to environmental threats by persistent chemicals. Substances that are released elsewhere, that are volatile or semi-volatile and which do not degrade rapidly may be transported to the Arctic regions and ultimately be deposited and stored there, in part due to a potential prolonged persistence in cold environments. Thus, emissions occurring outside the Nordic countries may influence environmental levels within the Nordic environment - even if measures are taken within the region. It is therefore necessary for the Nordic countries to act jointly when it comes to such environmental issues, in order to influence the environmental regulation within the Nordic countries, EU and globally.

## 1.2 Objective

The aim of this project is to understand the historical behaviour as well as to predict the impact of various control measures regarding use and emissions on environmental levels of PBDEs in the Nordic environment. An existing multimedia fate model (POPCYCLING-Baltic) will be used to describe the historical, present and the future fate of the compounds in response to different (future) emission scenarios. The outcome of the study is intended to serve as a basis for further policy making and regulation concerning the use of PBDEs in the Nordic and European countries.

## 2 The POPCYCLING-Baltic Model

The modelling tool selected for this study, is the so-called POPCYCLING-Baltic model (Wania et al. 2000), which is a dynamic, fugacity-based, regional multimedia fate and transport model. The model region is shown in Figure 2.1.

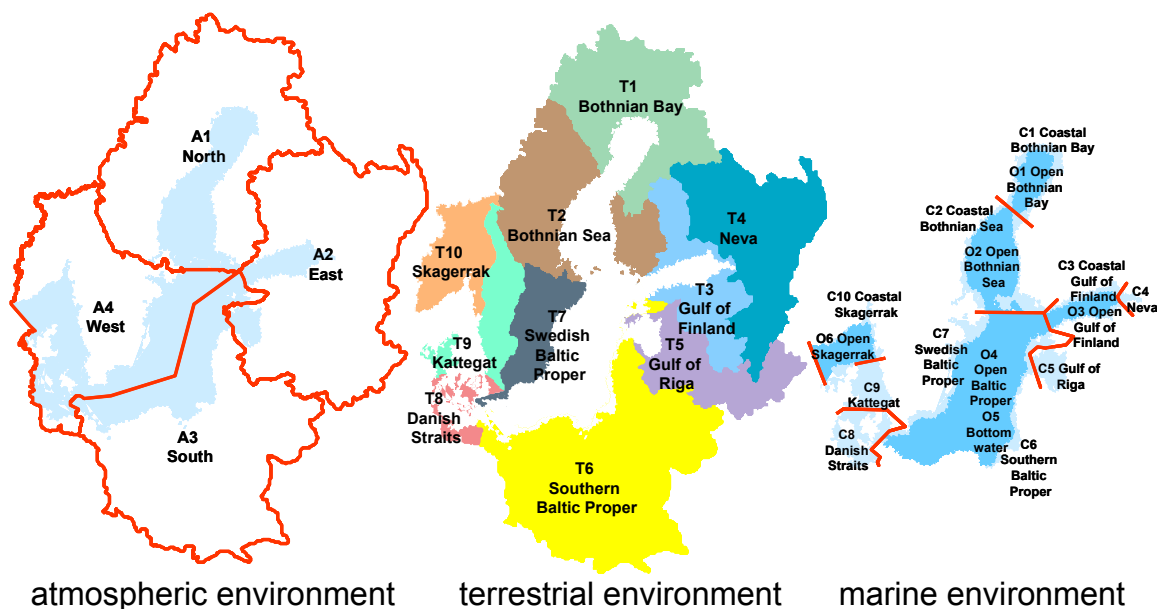


Figure 2.1. Maps showing the atmospheric, terrestrial and marine environment of the POPCYCLING-Baltic model, as divided into different "boxes" or compartments. Each of the ten terrestrial units includes five compartments (agricultural soil, forest soil, forest canopy, fresh water and fresh water sediment), whereas the marine environment is described by various coastal and open sea water compartments with underlying sediment compartments (Wania et al. 2000).

The aim of the model is to describe the long-term, large-scale fate of persistent organic pollutants in the drainage basin and water body of the Baltic Sea. A full description of the model is given in Wania et al. (2000). Its 85 well-mixed compartments represent the atmosphere (4 boxes), the aquatic (26 water and 25 sediment boxes) and terrestrial environment (10 forest canopy, 10 forest soil and 10 agricultural soil boxes). Chemical fate processes considered include: equilibrium phase partitioning between sub-compartments, advective and diffusive transport between compartments, first order degradation in each compartment (second order in atmosphere between vapour phase chemical and OH radical), and sediment burial. Description of these processes follows standard practice in fugacity-based multimedia fate and transport models, but the impact of temperature on partitioning and degradation is accounted for through the use of activation energies and internal energies of phase transfer. Long-term averaged monthly atmospheric advection rates between the four atmospheric compartments were derived from an atmospheric transport model. The POPCYCLING-Baltic model has previously been shown to be capable of reproducing the observed behaviour and fate of certain pesticides within the region over the last three decades (Breivik and Wania, 2002a,b).



## 3 Environmental occurrence

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This section is intended to give an overview of the general availability of empirical monitoring data for PBDEs in different environmental media, in order to provide evaluation data for the modelling results, and on the general occurrence of these compounds in the environment. The aim is not to give a full description of all monitoring data available.

Compared to e.g. the HCHs (Hexachlorocyclohexanes), long-term monitoring data on PBDEs are generally lacking for most environmental media and regions, because of the more recent interest in this group of compounds. De Wit (2002) published an extensive review on the environmental occurrence of PBDEs. From that review, it can be concluded that measurements have predominantly been performed in biota and in sediments.

A few measurements exist of PBDEs in background air. Jaward et al. (2004) recently performed a sampling campaign monitoring atmospheric concentrations of some organic pollutants, including PBDEs at ambient sites all across Europe, of which 8 were situated within the model region (Baltic sea drainage basin). Their results indicated that the UK is a major source area of PBDEs to the rest of Europe, whereas inflowing air from across the Atlantic contains only small amounts of PBDE. The UK is known for having been an important producer and user of PBDE flame retardants, and may thus have influenced European PBDE concentrations also in a historical perspective. The UK is not included in the POPCYCLING-Baltic Model but has to be treated as a source area for the background inflow of PBDEs to the region. On-going monitoring at the Swedish West Coast include PBDEs since 2001, and preliminary unpublished data show concentrations of 0.3-2.1 pg/m<sup>3</sup> for the sum of the three congeners BDE 47, 99 and 100 (Brorström-Lundén, unpublished data). Bergander et al. (1995) measured atmospheric levels of PBDEs in the north and the south of Sweden, observing levels of 8.3 pg/m<sup>3</sup> in the north and 1.1 pg/m<sup>3</sup> in the south for the sum of BDEs 47, 99 and 100. Other existing measurements of PBDEs in air mainly concern in-door air, or air close to point sources such as electronic dismantling plants.

Soil has recently been analysed for PBDEs by Hassanin et al. (2004), using surface soil samples collected in 1998 along a UK-Norway transect. Observed concentrations ranged from 0.28 – 4.6 ng/g dw in Norwegian forest soil. Data on PBDE occurrence in marine and freshwater are rare. Recently, measurements have been performed in rivers in the UK and in Finland (ECB, 2002b). Trace amounts of decabromodiphenyl ether and other PBDEs were found in one sample from Demons Beck in the UK, close to a former PBDE production plant, and in Finland 0.4 µg/L of decaBDE was detected in a creek near an urban area (ECB, 2002b). Measurements of decaBDE in over 200 Japanese freshwater samples in the 70's and 80's all showed levels below the detection limits (<0.06 - <2.5 µg/L; ECB 2002b). A recently published study indicates the presence of PBDEs in landfill leachate (Schlabach et al. 2002), which is a sign of the potential of PBDEs to be transported to the water compartment.

Temporal trends of PBDE congeners have been studied in sediments from the Baltic Sea (Nylund et al. 1992), and various other European locations (Zegers et al. 2003). Trends have also been investigated in pike from Lake Bolmen in Sweden, roach from Lake Krankesjön in Sweden (Kierkegaard et al. 1999) and in Swedish human breast milk (Merionytée et al. 1999). All of these studies indicate an increasing trend of individual congeners in the environmental samples, and in particular sediment core data suggest that PBDEs first entered the environment in the late 60s – early 70s (Nylund et al. 1992, Zegers et al. 2003). There are, however, also a few studies, which indicate decreasing trends, mainly in biotic samples (see de Wit, 2002).

More complete compilations of monitoring data have previously been published in de Wit (2002), and in the complete and draft versions of the EU risk assessments (ECB, 2000; 2002a,b).



# 4 Physical-chemical properties of PBDEs

## 4.1 Composition of technical mixtures

Theoretically, there are 10 different homologues of PBDEs and 209 possible PBDE congeners, following the same numbering system as the PCBs. A homologue refers to a subset of the mixture having the same number of bromines, whereas a congener is further identified by the exact location of bromine(s) on the PBDE molecule. The production of PBDEs is similar to the production of PCBs, involving the bromination of diphenyl ethers in the presence of a catalyst. The bromination of diphenyl ether is reported as a fairly specific process, and substitution of bromine is likely to occur first in the 4- positions, next in the 2-positions (Rahman et al. 2001 and references therein). For this reason, all technical mixtures include a number of PBDE congeners of various degree of bromination, but the PBDE mixtures generally contain fewer congeners as compared to commercial PCB mixtures (Hooper and McDonald, 2000). The commercial mixtures that are produced today are pentaBDE, octaBDE and decaBDE. These commercial mixtures mainly contain various congeners with four or more bromines, i.e. tetra- to deca-substituted congeners, but also trace amounts of tri-substituted diphenyl ethers. Previously, unknown amounts of a lighter mixture were also produced, called tetraBDE (WHO, 1994). The composition of the commercial penta product Bromkal 70-5DE has been analysed by Sjödin et al. (1998). Additional studies of octa- and deca-mixtures have been performed by e.g. Sondack et al. (1994) and Gesellschaft für Arbeitsplatz und Umweltanalytik mbH in Germany (see references within ECB, 2002a). The composition of technical PBDE mixtures with respect to their homologue content is given in Table 4.1.

**Table 4.1 Homologue composition of technical PBDE mixtures, given in % (source: ECB 2002a)**

<i>Commercial product (CAS no)</i>	<i>Tri</i>	<i>Tetra</i>	<i>Penta</i>	<i>Hexa</i>	<i>Hepta</i>	<i>Octa</i>	<i>Nona</i>	<i>Deca</i>
PentaBDE (32534-81-9)	0.23	36.0	55.1	8.58				
OctaBDE (32536-52-0)				5.5	42.3	36.1	13.9	2.1
DecaBDE (1163-19-5)						0.04	2.5	97.4

For the purpose of estimating congener production and consecutive emissions, the contents given in Table 4.1 need to be more specified, as emissions have to be derived on a congener basis because of differences in environmental behaviour and fate within

specific homologue groups. Based on the study by Sjödin et al. (1998), and references given within ECB (2002a), congener-specific compositions of each of the three technical mixtures were estimated. The study by Sjödin et al. (1998) does not fully agree with the composition given in Table 4.1, but was used due to the precision in congener content. For octaBDE, each homologue was assumed to be represented by equal amounts of the specific congeners detected in the analysis by Sondack et al. 1994 (see reference within ECB, 2002a). For example, the given content of octabrominated compounds is 36.1 %. Sondack et al. detected three different octabrominated compounds, thus each compound was assumed to represent a third (=12 %) of the total content of octabrominated compounds. For decaBDE, the congener composition was taken directly from ECB (2002a, appendix G). If only homologue content was given, the relative congener composition was estimated according to the distribution identified or estimated for the other technical mixtures, i.e. pentaBDE and octaBDE. Table 4.2 shows the composition assumed for the emission estimates (see also section 6).

**Table 4.2 Congener-specific composition of technical PBDE mixtures, given in %**

<i>Congener</i>	<i>PentaBDE</i>	<i>OctaBDE*</i>	<i>DecaBDE**</i>
BDE 17	0.022		$1.7 \times 10^{-6}$
BDE 28	0.11		$8.5 \times 10^{-6}$
BDE 47	37		$2.45 \times 10^{-5}$
BDE 66	0.22		
BDE 85	1.6		
BDE 99	35		$2.23 \times 10^{-3}$
BDE 100	6.8		
BDE 138	0.41		
BDE 153	3.9	5.5	$1.17 \times 10^{-3}$
BDE 154	2.5		
BDE 183	n.d.	42.3	$3.35 \times 10^{-3}$
BDE 196		12.0	0.013
BDE 197		12.0	0.013
BDE 203		12.0	0.013
BDE 206		6.95	1.25
BDE 207		6.95	1.25
BDE 209		2.1	97
Total	87.6	99.8	99.5
Reference	Sjödin et al. (1998)	ECB 2002a, (p 294-297) and references therein	ECB 2002a, (p 296-297) and references therein

\* Each homologue was assumed to be represented by equal amounts of the specific congeners detected in the analysis by Sondack et al. 1994 (see reference in ECB, 2002a).

\*\*When only homologue content was given, the relative congener composition was estimated according to the distribution identified or estimated for the other technical mixtures, i.e. pentaBDE and octaBDE.

## 4.2 Properties of individual congeners

Physical-chemical property data, such as water solubility, vapour pressure, partition coefficients and degradation rates are crucial input data to any multimedia mass balance model. As commercially available PBDE mixtures contain a range of congeners with different properties, and thus different environmental behaviour it is important that property data be used, which represent all the congeners of interest. In the current project, a large part of the work was focussed on obtaining reliable and internally consistent physical-chemical property data for the whole range of PBDE congeners present in the commercial mixtures. Detailed information about how this was done can be found in Appendix 1. Table 4.3, the physical-chemical properties assigned to PBDEs of varying degree for modelling purposes.

**Table 4.3. Physical-chemical properties assigned to congeners of varying degree of bromination.**

Congener	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
Le Bas MV (cm <sup>3</sup> /mol)	264.4	287.7	311	334.3	357.6	380.9	404.2	427.5
MW (g/mol)	406.9	485.8	564.7	643.6	722.5	801.4	880.3	959.2
log K <sub>OW</sub> <sup>a</sup>	5.8	6.3	6.7	7.1	7.7	8.1	8.6	9.0
log K <sub>AW</sub> <sup>a</sup>	-2.8	-3.2	-3.5	-3.9	-4.2	-4.6	-4.9	-5.3
Δ H <sub>OA</sub> (J/mol) <sup>b</sup>	80100	93900	101400	99800	89500	89500	89500	89500
Δ H <sub>OW</sub> (J/mol) <sup>c</sup>	15000	20000	20000	20000	25000	25000	25000	25000
<b>Half-lives (h)<sup>d</sup></b>								
Forest canopy	1440	3600	3600	3600	3600	3600	3600	3600
Soil	1440	3600	3600	3600	3600	3600	3600	3600
Water	1440	3600	3600	3600	3600	3600	3600	3600
Sediment	5760	14400	14400	14400	14400	14400	14400	14400
OH reaction rate in air (cm <sup>3</sup> /molecules s) <sup>d</sup>	2.45×10 <sup>-12</sup>	1.0×10 <sup>-12</sup>	5.5×10 <sup>-13</sup>	2.32×10 <sup>-13</sup>	2.41×10 <sup>-13</sup>	1.18×10 <sup>-13</sup>	7.56×10 <sup>-14</sup>	3.37×10 <sup>-14</sup>
<b>Activation Energy (J/mol)<sup>e</sup></b>								
Air	10000	10000	10000	10000	10000	10000	10000	10000
Forest canopy	30000	30000	30000	30000	30000	30000	30000	30000
Soil	30000	30000	30000	30000	30000	30000	30000	30000
Water	30000	30000	30000	30000	30000	30000	30000	30000
Sediment	30000	30000	30000	30000	30000	30000	30000	30000

<sup>a</sup>Calculated from eq A4-A6 (see Appendices

) <sup>b</sup>Average value from two studies, see Figure A 3 <sup>c</sup>Estimated values <sup>d</sup>Estimated from EPIWIN (Meylan, 1999) <sup>e</sup>Wania and Dugani (2003).



## 5 Production and use

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One of the key factors controlling emissions of intentionally produced chemicals is their production and consumption pattern (Breivik et al. 2002a). Together with the properties of the chemical of interest, the consumption pattern may act as the basis for determining emissions to the environment (Breivik et al. 2002b). Ideally, emission information should be collected on a historical basis, as the current environmental concentrations of persistent chemicals reflect the environmental lifetime of the compound considered. In order to achieve such information, national experts and industry representatives were contacted by e-mail or phone and asked to provide information on the known use in the region of interest. The outcome of this questioning was very poor, and the only information obtained was from Sweden and from the Nordic countries in the last few years, concerning the import as pure chemical or chemical product, thus not including the occurrence in consumer products or semi-produced goods. Evidently, as exemplified from this questioning exercise, it is difficult to get hold of statistical information on production and consumption for individual countries with a time perspective. Therefore, a simplified and transparent approach was deemed necessary in order to obtain estimates of global and regional consumption of these chemicals. This approach is outlined in the following.

### 5.1 Global production and consumption of PBDEs

The production and use of brominated flame retardants (BFR) is closely linked to the production of bromine. US Geological Survey has estimated the world production of bromine (Br) in the 20<sup>th</sup> century (USGS, 2002). According to these estimates, the global Br production increased from about 210,000 tonnes in 1970 to 540,000 tonnes in 2001. Bromine Science and Environmental Forum (BSEF) reported a total bromine production of 470,000 tonnes/year for the year 1999 (BSEF, 2000), which corresponds to the USGS estimates for 1996. The four countries accounting for the majority of the world's bromine production in the year 2000 were the United States (39 %), Israel (38 %), the United Kingdom (9 %) and China (7 %) (Lyday, 2001).

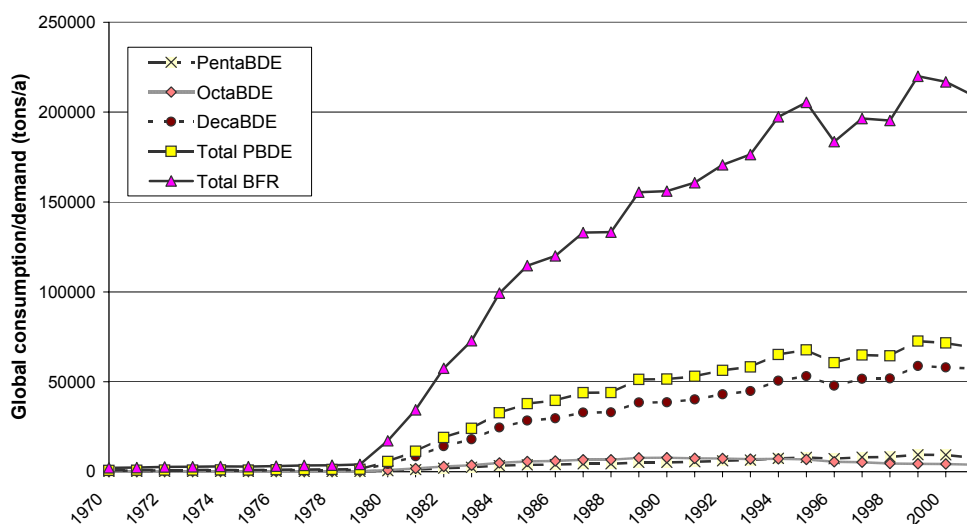
The reported percentage of bromine used to produce brominated flame retardants varies between different sources. However, there seems to be a general agreement that the demand for BFR production was low before the early eighties. This is also the current understanding at the US Geological Survey (USGS) (P Lyday, personal communication). We have thus assumed the BFR demand to be 1 % of the total bromine production between 1970-1979. The demand increased significantly over the following decades, as a result of the increased use of flammable materials. Today, about 40 % of the total bromine production is assumed used in the BFR production (Lyday, 2001). Exact figures for the BFR/bromine ratio over time are not available, thus we have assumed a step-wise increase from 1 % in the seventies to 45 % in 1993. From 1994 and onwards we have used the estimated BFR percentages from USGS, valid for the US (Lyday, 2001), assuming that the relative use of bromine as flame retardants is similar in a global perspective. This approach results in a reasonably even curve from 1970-

1993, after which the production curve makes a little “jump” and varies somewhat over the past ten years.

PBDEs account for about 33 % of the global BFR demand (1999 figures; BSEF, 2000). This percentage is likely to have varied over the years, as the production, use and consumption pattern has varied, but the historical trend is unknown. We assume here that it has been constant during the last two decades, resulting in an estimated current PBDE production of **69,000 tonnes** (2001).

Previously reported estimates of global BFR demand (150,000 tonnes in 1992; WHO 1997), are in the same order of magnitude as our estimates of 170,000 tonnes (Appendix). So are earlier estimates of global PBDE production of 40,000 tonnes in 1990 (WHO, 1997 and references therein), compared to our estimates of 51,500 tonnes (Appendix).

The consumption pattern of various commercial PBDE mixtures varies between different parts of the world. For example, pentaBDE is not used at all in Asia (BSEF, 2000), and will be banned together with octaBDE within the EU starting in August 2004 (Directive 76/769 EEC, 24<sup>th</sup> amendment), whereas the product is still used in large quantities in America (BSEF, 2000). However, decaBDE is by far the most commonly used PBDE mixture globally and accounted for 81 % and 83 % of the global PBDE demand in 1999 and 2001 respectively, followed by commercial penta (13 %, 11 %) and octa (6 % both years) (BSEF, 2000; 2003). Previously reported shares for the individual products were 75 % for deca, 15 % for octa and 10 % for penta (KEMI, 1994). Assuming a constant relative use of the various PBDE mixtures in accordance with the figures from KEMI (1994) prior to 1990 and a gradual change to the 1999 and 2001 figures, gives global consumption estimates of BFRs and PBDE chemical mixtures from 1970 to 2001 as shown in Figure 5.1.



**Figure 5.1. Estimated global production/consumption of brominated flame retardants and PBDE technical mixtures from 1970 to 2001**

Interestingly, the estimated PBDE production curve mirrors the estimated production pattern of PCBs prior to 1970 (Breivik et al. 2002). As evident from Figure 5.2 the current production of PBDE, is estimated to be similar to the peak production of PCBs.

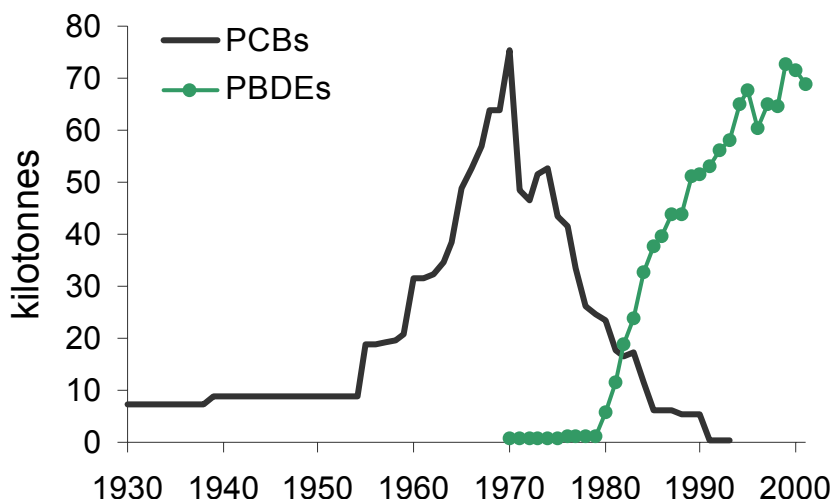
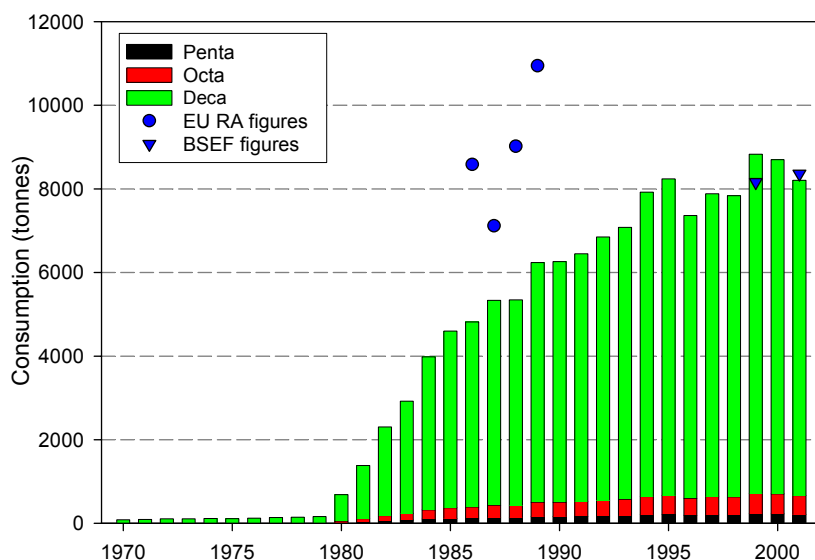


Figure 5.2. Estimated temporal trend in global production of PCBs and PBDEs – 1930 to 2001

## 5.2 European consumption of polybrominated diphenyl ethers

Due to the recently proposed ban of penta and octa within the EU, and a preceding voluntary phase-out, the consumption of these products has nearly ceased within the region. According to Bromine Science and Environmental Forum (BSEF) a limited consumption still occurs within Europe and they estimated that Europe accounted for 12 % of the total global demand for PBDEs in 1999 and 2001 (BSEF, 2000, 2003). The European share is likely to have varied over time, for example due to the above-mentioned regulation proposals. We have based this first estimate on an assumed constant European share of the world market since 1970. DecaBDE accounted for 92 % and 91 % of the European PBDE consumption in 1999 and 2001 respectively, octaBDE for 5.5 % and 7.3 % and pentaBDE for 2.5 % and 1.8 % (rounded figures, BSEF, 2000; 2003). KEMI (1994) reported a 75 % share of decaBDE, 15 % octaBDE and 10 % pentaBDE, based on global consumption patterns. In the current study the European figures from BSEF (2000) have been adopted as the European pattern is likely to be different from the global. Based on these figures and the estimated global figures presented above, the total consumption of PBDEs in Europe is estimated to have increased from around 700 tonnes in 1980 to approximately 8,400 tonnes in 2001 (see Figure 5.3). In the draft EU risk assessment of decaBDE (ECB, 2002b) figures between 7000 and 11,000 tonnes/year (total PBDE) were reported for the European Community in the years 1986-1989. This deviates somewhat from the estimates presented here (a factor of 1.3 – 1.8 higher) for the same years, which may be an indication that the European share of the global market demand previously was higher than in the latter years, and thus that European consumption was higher than estimated here. However, as a consistent time trend in PBDE consumption was desired, and as the global estimates seem to agree well with reported figures (see section 5.1), it was decided to base the emission estimates on the consumption pattern derived as described above. Especially since the historical consumption pattern of PBDEs suffers from significant uncertainties.



**Figure 5.3. Estimated European consumption of PBDE commercial products from 1970 to 2001. Figures given in the EU risk assessment (ECB, 2000) and from industry (BSEF, 2000, 2003) are indicated with blue triangles or dots.**

### 5.2.1 Consumption in European countries

It has not been possible to obtain detailed statistics on consumption or import of PBDEs for individual countries within Europe or other countries. PBDE consumption have been reported previously for some European countries; given in tonnes/year for Germany: 3000-5000, Sweden: 1400-2000, UK: 2000 and The Netherlands: 3300-3700 alternatively 2500 (WHO, 1994). These figures seem very high when compared to the estimated total European consumption of approximately 6000 tonnes/year in the mid-90s (Figure 5.3), and also in comparison to the estimated current European consumption of ca 9000 tonnes (BSEF, 2000). As previously mentioned, it is, however, possible that the relative European market share has been higher historically than in later years. In addition to the estimates mentioned above, a worst-case estimate has been presented for Denmark, resulting in a consumption of 79 tonnes/year in 1997 (Lassen et. al., 1999). A recent report from Norway estimates a Norwegian consumption of 0.1 tonnes pentaBDE and 12-25 tonnes decaBDE in 2001 (SFT 2003). Official statistics on PBDE consumption for Sweden are available from the Products Registry at the Swedish National Chemicals Inspectorate, and varied between 15-124 tonnes/year in the years 1993-2001 (almost exclusively decaBDE). Data can also be obtained for the Nordic countries from the joint Nordic consumption database SPIN (Substances in Preparations In Nordic Countries; [www.spin2000.net/spin.html](http://www.spin2000.net/spin.html)), for the years 2000-2001, and were 2.4 tonnes/year for Denmark (penta+deca) each of the years 2000 and 2001 and 1.9 tonnes/year for Finland in 2001 (only decaBDE). These statistics concern only the consumption as pure chemical or chemical product and does not take consumption of PBDEs in imported goods into account.

The Scandinavian countries account for only a small percentage of the European PBDE consumption. In order to obtain consistent estimates for the European countries assumed to affect the model region, it was decided to use a Gross Domestic Product (GDP) based approach for estimating the contribution of each European country to the



“overall” European consumption. The reported figures for the Scandinavian countries were instead used as control data.

PBDEs are mainly associated with consumer products, e.g. furniture and electronic devices such as computers and TV-sets. GDP was therefore considered to be an appropriate surrogate for the consumption of PBDEs. GDP has previously been utilised as a surrogate to estimate national emissions of both PCDD/Fs (Baker and Hites, 2000) and PCBs (Breivik et al. 2002a,b). Time series of GDP for European countries were obtained from the World Bank Group (2002). For some countries, the GDP series 1970-2001 were not complete, in which case the missing data were estimated by extrapolation. The basic assumption behind our approach is that each individual country accounts for a total market share of PBDEs (i.e. percentage of the European demand), which is equivalent to its share of the “total European GDP”. The PBDE consumption  $C$  a certain year for a country  $A$  was thus calculated according to:

$$C_A = C_E \times \frac{GDP_A}{GDP_E} \quad (1)$$

where  $C_A$  and  $C_E$  are the PBDE consumption for country  $A$  and Europe respectively,  $GDP_A$  is the GDP (US dollars, 1995 prices) for country  $A$  and  $GDP_E$  is the sum of all national GDP values for the European countries.

It should be noted that for some regions, e.g. the Eastern European countries, it has not been possible to verify that consumption of PBDEs actually has taken place. On the other hand, only a very small fraction of these countries is included in the model. As their national GDP is significantly lower than that for western European countries, the emissions assumed to origin from these areas are very limited and have a small impact on the overall emissions in the region.

The reliability of the outlined approach was checked by comparing estimated consumption values for certain countries, with data on consumption that were given in the literature. It was clear that the uncertainty is significant, in part due to uncertainties in reported national consumption data, which sometimes refer to imported amounts of pure chemical or chemical product and sometimes appear to relate to all brominated flame retardants including those contained in goods (e.g. values reported in WHO, 1994; Å Almkvist, pers. comm.).

#### *5.2.1.1 National restrictions on PBDE consumption*

As mentioned earlier, EU has decided to ban the use of two PBDE products, starting in August 2004. Although so far no international restrictions have existed concerning the use of PBDEs, certain countries have already taken independent measures to reduce the possible risk associated with these compounds. It was thus considered necessary to include a factor to take into account restrictions against consumption of PBDEs (eq. 1), from the years and for those countries where information on such measures was available.

The factor accounting for national restriction was defined on a scale ranging from total ban on import/usage via voluntary phase-out to no restrictions. Thus we get two equations, one for countries with restrictions and one for countries with no restrictions.

Consumption for country A with restrictions:

$$C_{A,R} = a \times C_E \times \frac{GDP_{A,R}}{GDP_E} \quad (2)$$

where  $a$  is a factor between 0 and 1 related to the extent of restriction, where 0 represents total ban and 1 no restrictions.  $C_E$  is again the total European PBDE consumption (tonnes),  $GDP_{A,R}$  is the GDP (US dollars, 1995 prices) for country A with restrictions and  $GDP_E$  is the sum of all national GDP values for the European countries.

Consumption for country B with **no** restrictions (NR):

$$C_{B,NR} = \left( C_E - \sum_{x=A}^N C_{x,R} \right) \times \frac{GDP_{B,NR}}{GDP_{NR,tot}} \quad (3)$$

where  $C_{x,R}$  is the consumption for a country with national restrictions on PBDE use,  $GDP_{B,NR}$  is the GDP for country B (US dollars, 1995 prices) and  $GDP_{NR,tot}$  is the sum of the GDP values for all countries with no restrictions.

It should be noted here that no distinction is made, as to which technical mixture that is being restricted. The assumption is that a country, which is generally restrictive towards the use of PBDEs, will be restrictive towards any technical mixture of PBDEs. The countries identified as being so were Denmark, Norway and Sweden, based on the survey made by Lassen et al. (1999), indicating that these countries were more active in their work towards PBDE restriction. There is also clear evidence of existing voluntary phase-out among the industry within some of these countries, e.g. within the Swedish textile industry (Remberger et al. 2003). Thus, these three countries were assigned restriction factors decreasing from 0.9 in 1991, when measures supposedly started, as the debate on PBDE phase-out flourished, to 0.1 in 1999-2001. As the measures taken within individual countries so far mainly consist of voluntary phase-out, following pressure from legislators or internal markets, there are no reliable statistics confirming this assumed downward trend in import of PBDE. Another complicating factor is that voluntary measures are likely to have impact only on the import of the pure chemical or chemical product, which is likely to account for a very small part of the total consumption within these countries. It is believed, however, that these uncertainties will have a minor impact on the total usage estimates, as the three countries included account for only a minor share of the European PBDE consumption.

The POPCYCLING-Baltic model however, requires information on emissions within each country that forms a part of the Baltic Sea drainage basin (Wania et al. 2000). Figure 5.4 a) shows the estimated PBDE consumption for these countries for the time period 1970-2001, taking into account national restrictions on use. Figure 5.4 b) shows the estimated consumption (i.e. annual import) within the actual model region, which thus may contribute to the emissions herein, considering the fraction of each nation's population that lives within the model region. The Swedish annual consumption of totalBDE in the time period between 1993-2001 is estimated to have varied between 19 and 108 tonnes, which compares well with the official statistics (15-124 tonnes, see section 5.2.1)

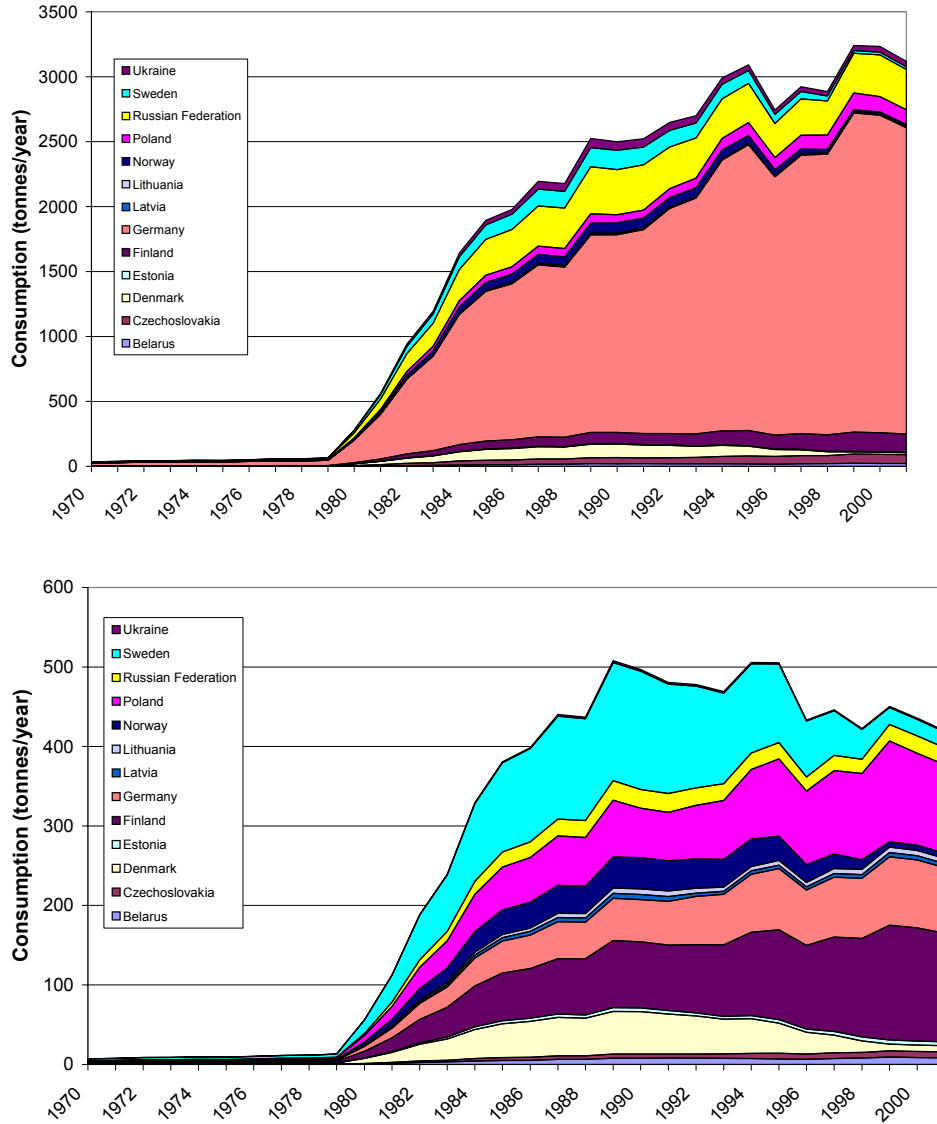


Figure 5.4. Estimated consumption (i.e. annual import) of total PBDEs in the countries included in (a) the POPCYCLING-Baltic Region and (b) within the actual model region from 1970-2001.

### 5.2.2 Consumption of individual PBDE congeners

Congener-specific consumption estimates were obtained by multiplying the consumption data for each technical mixture by the congener composition shown in Table 4.2. Thus the consumption  $U_{\#}$  of a congener # in a country a certain year was calculated according to:

$$U_{\#} = \alpha_{\#,penta} \times U_{penta} + \alpha_{\#,octa} \times U_{octa} + \alpha_{\#,deca} \times U_{deca} \quad (4)$$

where  $\alpha_{\#,penta}$ ,  $\alpha_{\#,octa}$  and  $\alpha_{\#,deca}$  are the fractions of the particular congener present in the technical mixtures pentaBDE, octaBDE and decaBDE respectively (see Table 4.2) and  $U_{penta}$ ,  $U_{octa}$  and  $U_{deca}$  are the uses of the technical mixtures pentaBDE, octaBDE and decaBDE respectively in a country a certain year.



## 6 Atmospheric emissions

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Once consumption estimates have been obtained, the next step is to estimate the consecutive emissions following PBDE consumption. The data may be used for derivation of emissions to any media desired, however, in this case we have assumed that the atmosphere is the primary recipient media. The uncertainties with this assumption will be discussed later. The fact that PBDEs are used as *additives* (not chemically bound to the material) has potentially important implications for the propensity for emissions, e.g. allowing PBDEs to “bleed” from the material to the environment over time (compare e.g. phthalates and similar compounds). Presumably, this “bleeding” of PBDEs could be expected to occur at different rates, whereby the less brominated congeners are depleted first. Although the empirical support for such a hypothesis is lacking, it has been observed for PCBs (Breivik et al. 2002b and references therein). It has also been reported that high molecular weight products were developed to prevent the material from losing the fire retarding capacity as time evolves (Rahman et al. 2001).

The emission estimates have to be done on a congener level, thus emission factors for each PBDE congener of interest have to be sought. This is a challenging task, considering the limited studies available (e.g. Breivik and Alcock, 2002). Ideally, an emission inventory should contain the collection of measured emission rates of individual substances (i.e. congeners) from various point or diffusive sources, combined with proper activity data (i.e. statistical information) for the emission sources of interest. However, information on such a detailed level is not available for PBDEs in Europe (or elsewhere) and to our knowledge, no studies have so far reported useful emission rates from point sources or diffusion rates from PBDE containing consumer products. On the initiative of the bromine industry, emissions from point sources are currently being measured, but no results are yet available (L McLaren, pers. comm.). Experiments are also currently being undertaken at Lancaster University to evaluate emissions from PBDE containing materials, but results are not yet available (R. Alcock pers. comm.). As PBDEs have found their use as fairly complex mixtures in a large variety of materials and products, it can be expected that the true emission pattern is equally complex, and difficult to predict.

Our selected approach reflects the limited empirical data available and builds upon a simplified methodology, previously elaborated for the PCBs (Breivik et al. 2002b). In order to estimate the emissions on a congener level, we first calculate the total amount of that congener that is accessible for emissions in a certain year (t). A simplified dynamic (time-dependent) mass-balance modelling approach was furthermore considered necessary as current emissions may occur as a result of import in previous years. The amount of PBDEs accessible to emissions, here denoted  $U_{\#,\text{current}}(t)$ , was estimated according to:

$$U_{\#,\text{current}}(t) = U_{\#\text{new}}(t) + U_{\#\text{rem}}(t-\text{dt}). \quad (5)$$

where  $U_{\#\text{new}}(t)$  is the annual new import (or “new” consumption) of the congener to the country of interest and  $U_{\#\text{rem}}(t-\text{dt})$  is the remaining amount in use in that country from

the previous year. Equation (5) implies that in the first year of PBDE usage in a country,  $U_{\#current}(t) = U_{\#new}(t)$ .

In addition, PBDE congeners are assumed to be “disappearing” from use by two processes, either by atmospheric emissions or by a permanent loss due to e.g. irreversible sorption and permanent burial at landfills etc. It is assumed that the amount lost will be inaccessible to further emissions to the atmosphere. This assumption is subject to uncertainties, as will be discussed later. The “loss” is assumed to occur *after* the expected average lifetime ( $k_a$ ) of general PBDE usage, which is roughly 10 years for most PBDE products (ECB, 2000, 2002a,b) and is assumed to have the same value for all congeners. Therefore, the amount that eventually “is lost” is the amount that was not emitted during the lifetime of the amount that was imported at year  $t-k_a$  and can be described as:

$$Loss_{\#}(t) = U_{\#new}(t-k_a) \times (1-EF_{\#})^{k_a} \quad (6)$$

where  $U_{\#new}(t-k_a)$  is the amount of the congener that was imported in the year  $(t-k_a)$  and  $EF_{\#}$  is the emission factor, which will be discussed later. The loss term  $Loss_{\#}(t)$  can not be higher than the supposed remaining pool of usage after emissions in that year, which may be the result of equation (6) if the import in a country ceases and the total pool of PBDE in use is depleted. If this was the case, the loss term was set equal to the remaining pool after emissions, i.e.  $Loss_{\#}(t) = [(U_{\#current}(t)) \times (1- EF_{\#})]$ . The remaining amount in use of a congener # in a country from year to year was calculated as:

$$U_{\#rem}(t) = [(U_{\#current}(t)) \times (1- EF_{\#})] - Loss_{\#}(t) \quad (7)$$

where the first term  $[(U_{\#current}(t)) \times (1- EF_{\#})]$  calculates the amount that is remaining at the end of the year after emissions, while the second term ( $Loss(t)$ ) subtracts the amount that is permanently lost (see Equation 6). The emission of a PBDE congener  $E_{\#}$  (tonnes) in a country a certain year was then calculated as:

$$E_{\#}(t) = U_{\#,current}(t) \times EF_{\#} \quad (8)$$

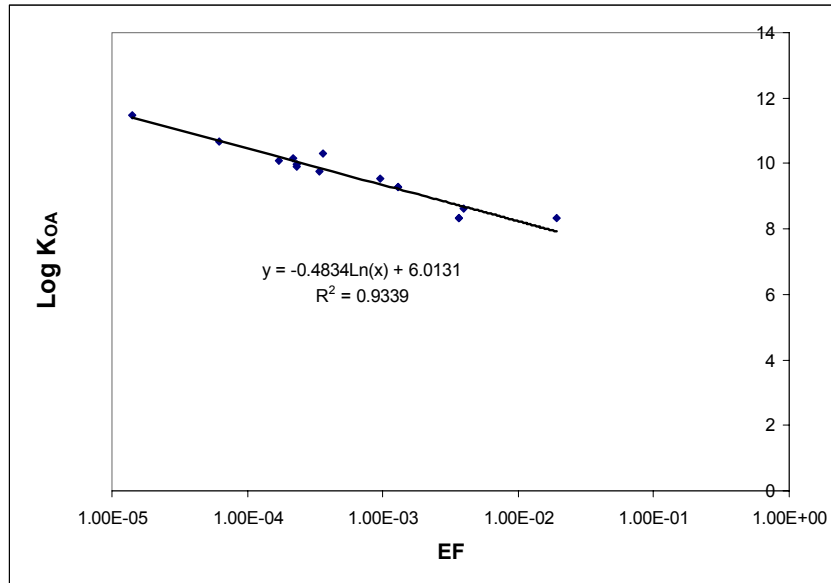
where  $U_{\#,current}(t)$  is the total amount of congener # that is present in the current pool (tonnes) in the country in the beginning of year  $t$  (see equation (5)) and  $EF_{\#}$  is the emission factor for congener #.

## 6.1 Derivation of emission factors

Breivik et al. (2002b) found a correlation between the octanol – air partition coefficient  $K_{OA}$  and the measured atmospheric losses of PCB from sealants (Persson et al. 1997). The relationship obtained is shown in Figure 6.1 and was described as (Breivik et al. 2002b):

$$\text{Log } EF = -0.839 \times \log K_{OA}(20^{\circ}\text{C}) + 4.83 \quad (9)$$

( $n = 15$ ,  $r^2=0.93$ ,  $p<0.001$ )



**Figure 6.1. Relationship between  $\text{Log}K_{\text{OA}}$  and emission rates of PCB from sealants (data from Persson et al. 1997).**

As the PBDEs have properties similar to those of PCBs, it is anticipated that an equivalent relationship exists between  $\text{Log}K_{\text{OA}}$  and the *relative* atmospheric emission rates of PBDEs. The propensity for emissions may, however, be significantly different between PCBs in sealants and PBDE usage (but still a function of  $K_{\text{OA}}$ ), thus a correction factor  $\alpha$  was introduced to get a more accurate estimate of the actual “*absolute*” emission strength. The resulting emission factor  $\text{EF}_{\#}$  was denoted as:

$$\text{EF}_{\#} = \text{EF}_{\#, \text{rel}} \times \alpha \quad (10)$$

where  $\text{EF}_{\#, \text{rel}}$  is the relative emission factor for the congener to air (calculated from the PCB correlation) and  $\alpha$  is the scaling factor. Table 6.1 shows the relative emission factors for individual PBDE congeners for emission to air as calculated from equation (10).

**Table 6.1. Calculated relative emission factors for emission to air of individual congeners.**

<b>Congener</b>	<b>Name</b>	<b>Log Koa</b>	<b><math>\text{EF}_{\#, \text{rel}}</math></b>
28	2,4,4'-TriBDE	8.6	$4.12 \times 10^{-3}$
47	2,2',4,4'-TetraBDE	9.4	$8.78 \times 10^{-4}$
99	2,2',4,4',5-PentaBDE	10.2	$1.87 \times 10^{-4}$
100	2,2',4,4',6-PentaBDE	10.2	$1.87 \times 10^{-4}$
153	2,2',4,4',5,5'-HexaBDE	11.0	$3.99 \times 10^{-5}$
183	2,2',3,4,4',5',6-HeptaBDE	11.9	$8.51 \times 10^{-6}$
197	2,2',3,3',4,4',6,6'-OctaBDE	12.6	$1.81 \times 10^{-6}$
207	2,2',3,3',4,4',5,6,6'-NonaBDE	13.5	$3.19 \times 10^{-7}$
209	DecaBDE	14.3	$6.80 \times 10^{-8}$

One crucial assumption in our selected approach is that the atmosphere is the primary recipient for PBDE emissions, from which transport of chemicals is allowed to other

compartments (e.g. soil, water etc.). Additional environmental releases could, however, also be of significance. In particular, a recent study has indicated that PBDEs also pose a local contamination problem (e.g. discharges from manufacturing plants to water, leaching from landfills to surface and groundwater; Schlabach et al. 2002). On a regional level, it is, however, assumed that the environmental concentration patterns are primarily controlled by atmospheric emissions.

## 6.2 Estimated emissions of PBDE congeners

In order to determine the size of the scaling factor  $\alpha$ , iterative test simulations were performed using the congener BDE-47, for which most monitoring data was available. Based on the limited amount of air and water data available from the borders of the model region, it is not possible to quantify in- and outflow in the various model subregions. Thus, whenever running the model, the boundary conditions were set so that any incoming air or water concentration, is assumed to equal the outgoing air and water concentrations, which corresponds to boundary condition 1 (BC1) in the model settings. Earlier model simulations, for e.g. hexachlorocyclohexane, have shown that BC1 gives satisfactory results when compared to model estimates based on "optimized" boundary conditions (Breivik and Wania, 2002a). It is, however, not certain that this is true also for PBDEs. As mentioned in section 3, recent air data by Jaward et al. (2004) indicate that the UK area may be of importance to the eastbound atmospheric inflow of PBDEs in the model domain, in which case BC1 may be an oversimplification, and would need modification through long-term measurements of PBDE concentrations in air and water along the borders of the model domain.

Test simulations were performed with different scaling factors, until predicted and measured concentrations were considered to agree reasonably well with each other, which corresponded to a scaling factor  $\alpha$  of 30. The resulting emissions in the countries included in the model region as well as in the actual model region (i.e. the fractions of the countries that influence the model region) for BDE-47 and eight other congeners, representing different degrees of bromination are shown in Figure 6.2 a-b. ECB (2000) estimated an annual emission of commercial penta to air within the EU of 43 tonnes, which is of similar order of magnitude as our estimates for the Baltic region (9 tonnes).



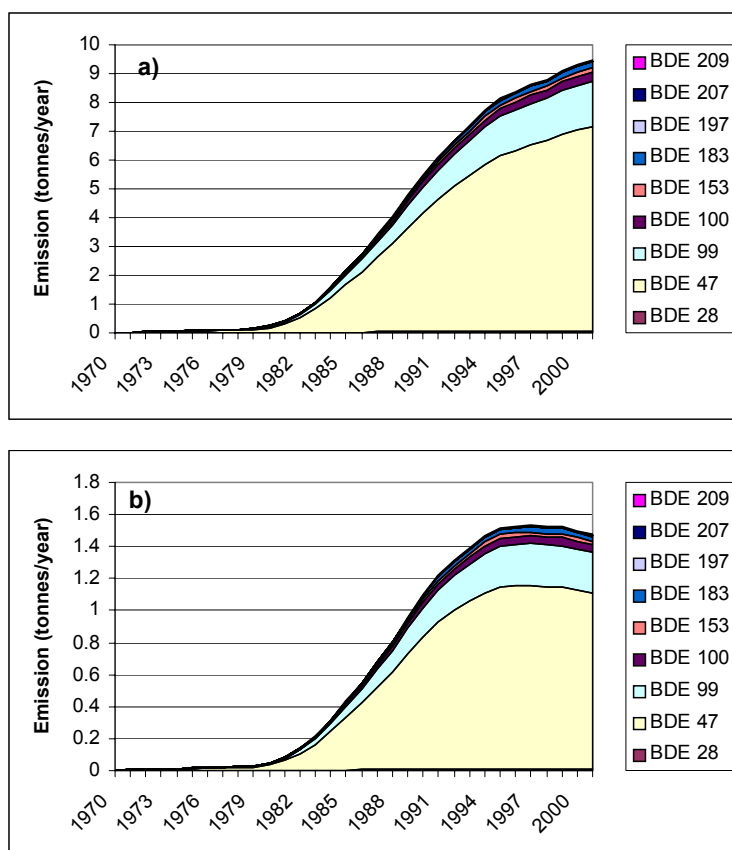


Figure 6.2. Estimated emissions of nine PBDE congeners in (a) the countries included in the POPCYCLING-Baltic region and (b) the actual model region from 1970-2001.

### 6.2.1 Seasonality of emissions

Recent monitoring data from the Swedish West Coast (Brorström-Lundén, unpubl.) indicate slightly higher atmospheric concentrations of BDEs in the summer than in the winter. Gouin et al. (2002) also observed elevated PBDE levels in springtime and suggested an "early spring-pulse" of PBDEs, due to release of accumulated chemicals during the winter. These studies indicate that PBDE emissions may be enhanced in the spring/summer, due to elevated temperatures. A similar conclusion has been drawn for other POPs such as the PCBs (Breivik et al. 2002b). Assuming a non-seasonality of PBDE emissions in the model, would instead cause elevated levels in the winter, due to a pro-longed atmospheric life-time of PBDEs in this season, as a result of the colder climate and thus reduced presence of reactive OH-radicals. To account for this seasonality, a correction factor of amplitude 4 was introduced for the month of July, indicating that the month of maximum release is July and that the total release rate is then 4 times the annual average. The size of the amplitude was selected based on test simulations.



# 7 Model evaluation

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The purpose with this chapter is to evaluate the usefulness of the model, by reconciling observed environmental concentrations in various media with estimated emission rates. In this manner, the accuracy of the emission estimates can be assessed, and knowledge gaps identified. A satisfactory reconciliation has several benefits in that it indicates that emissions are fully covered, and that the main parameters governing the environmental fate, e.g. degradation rates are in accordance with model prediction. Once a reasonable reconciliation has been achieved, the model can be confidently used to predict the change in environmental concentrations reflecting future emission changes, and with slight modifications be used for other compound groups as well. A general problem with this particular group of compounds (PBDEs), is that only a limited number of data sets include temporal trends, of which the majority have been performed in biotic matrices and in sediment. As the POPCYCLING-Baltic model is an abiotic model, data from biota may only be used for evaluation with great caution. Some temporal trends have, however, been studied in the region and BDE-47, BDE-99 and BDE-209 were considered most appropriate for the evaluation exercise. These are compounds, which are present to a large extent in the technical PBDE products, they represent different degrees of bromination, and are commonly observed in the environment. Property data were taken from Table 4.3 and emissions were adopted as calculated according to section 6. The following sections present selected model output for the years 1970-2000 in regions and media where monitoring data are available.

## 7.1 Atmosphere

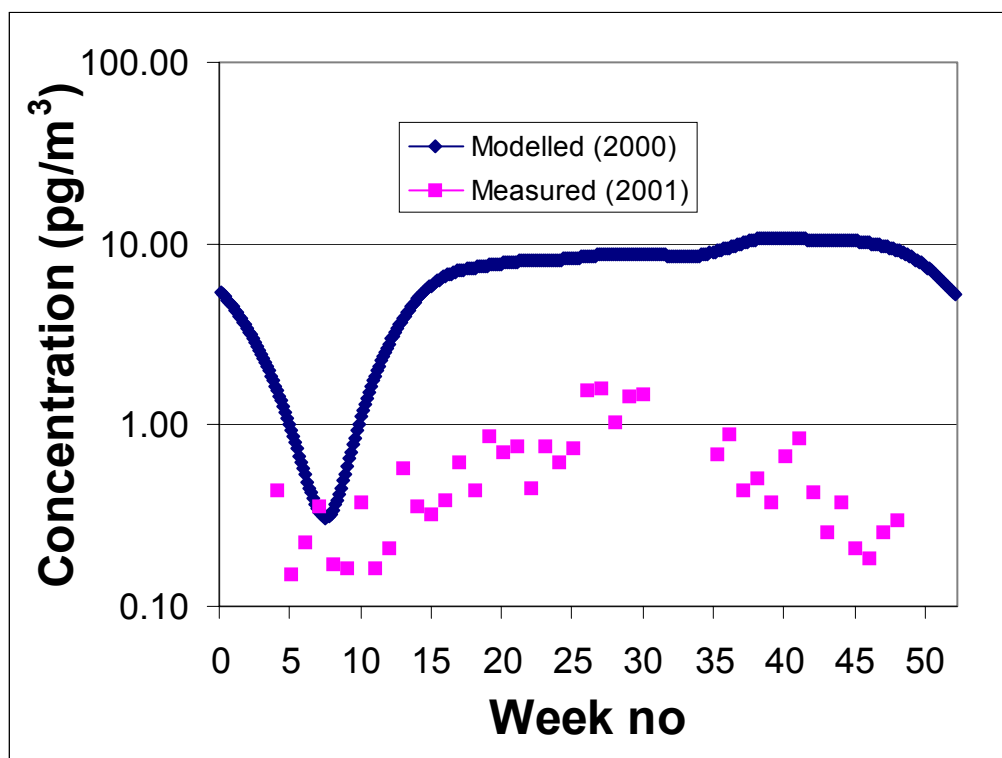
There are few empirical data of PBDE in air and no long-term time series are available for this compartment for any part of the model region. There are limited data available from model regions "North", "West" and "East" (see Figure 2.1). Modelled and observed ranges of BDE 47 for individual years are presented in Table 7.1. The latest observed data were measured after 2001, so in these cases comparison is made to predicted levels in the year 2000. As shown in the table, the modelled ranges are generally in the same order of magnitude as observed levels.

**Table 7.1. Modelled and observed levels of BDE 47 for various years and model regions**

Model region	Modelled time period	Modelled range (pg/m <sup>3</sup> )	Year sampled	Observed range (pg/m <sup>3</sup> )	Reference
North	1990-1992	<b>0-9.85</b>	1991	<b>6.3</b>	Bergander et al. 1995
North	2000	<b>1.3-11</b>	2002	<b>&lt;7 – 12</b>	Jaward et al. 2004
West	1990-1992	<b>0.02-10.8</b>	1991	<b>0.7</b>	Bergander et al. 1995
West	2000	<b>1.4-10.5</b>	2001	<b>0.2 – 1.1</b>	Brorström-Lundén, unpubl.
			2002	<b>11-14</b>	Jaward et al. 2004.
East	2000	<b>1.3-10.6</b>	2002	<b>10-12</b>	Jaward et al. 2004

### 7.1.1 Seasonal variation

Figure 7.1 shows the predicted and observed seasonal variation of BDE 47 levels for model region "West", representing the years 2000 and 2001. The observed seasonal pattern is captured by the model, but the predicted variation in concentrations between the seasons is significantly larger than what has been observed at the Swedish West Coast.



**Figure 7.1. Modelled and measured (Brorström-Lundén, unpubl.) seasonal variation in air concentration of BDE 47 in model region "West". Note the logarithmic scale on the y-axis.**

## 7.2 Forest soil

Monitoring data of PBDEs from Norwegian and UK soils have recently become available (Hassanin et al. 2004). The soil samples analysed were collected in 1998 along a UK-Norway latitudinal transect and represent the upper 5 cm of the soil crust.

The study showed that PBDE concentrations in soils were of similar orders of magnitude as measured PCB concentrations. It also showed a general pattern in the soils which was remarkably similar to the reported congener composition in technical pentaBDE (Sjödin et al. 1998). One exception was the BDE 47:99 ratio, where the relative content of BDE 47 was significantly lower in the soil samples than in the technical mixture. Hassanin et al. concluded from this that the transfer of PBDEs from source via air to soil is more or less equally efficient for all the PBDE congeners, and that there has been little change in the congener pattern during the transport, which is a sign of stability of PBDEs in the atmosphere as well as in the terrestrial environment. The samples were not analysed for decaBDE, so the study does not provide a basis for conclusions about the stability of this compound relative to that of lower brominated congeners.

Comparing the predicted soil concentrations for model region T10 in 1998 (see Figure 2.1) to measured concentrations in Norwegian soils (Hassanin et al., 2004), indicates an underestimation of soil levels by the model, by a factor of about 10 to 70. The measured concentrations (pg/g organic matter (OM)) were converted to pg/g organic carbon (OC) by assuming an OC content of 50 % in the organic matter. The predicted concentrations of BDE 47 were 73-102 pg/g OC compared to the measured 130-2200 pg/g OC (median 840), and for BDE 99 34-49 pg/g OC compared to 284-3086 pg/g OC (median 1140). This disagreement is interesting, as the model predicts concentrations in air which correlate reasonably well with measured data, or even overestimate the actual concentrations observed in the North (see section 7.1). As soil mainly receives its POP input via atmospheric deposition (with the exception of contaminated soils such as landfills etc.), it would be expected that agreement in air also would generate agreement for the soil compartment. But as shown here, this is not the case. One contributing factor to the observed disagreement may be the uncertainty in the applied degradation rates in soil. The EPIWIN software has been observed to severely underestimate degradation half-lives for persistent organic pollutants (Gouin et al. submitted). For example, EPIWIN predicts the following half-lives for PCB 101: water: 360 h, soil: 360 h, sediment: 1440 h (US EPA, default settings). More generally accepted are half-lives of the magnitude used by Wania and Daly (2002) for global PCB modelling: water: 31000 h, soil: 100000 h, sediment: 55000 h. Also, the EPIWIN half-lives in soil are extrapolated from half-lives in water, as are degradation rates in sediment. PBDEs are, however, unlikely to be readily bioavailable to micro-organisms that can degrade them, because of their strong sorption to solid phases.

### 7.3 Seawater

There are no seawater measurements available for comparison, but some studies have been made of herring. However, the measurements of PBDEs in Baltic herring cover temporal trends only from 1999 and onwards, thus a comparison of time trends with model predicted water concentrations was not considered possible.

### 7.4 Open sea and coastal sediments

Studies of PBDE concentrations in dated sediment cores in the Baltic region have been performed by Nylund et al. (1992) and Zegers et al. (2003). Both studies indicate an

increasing trend with time (Figure 7.2). The study by Zegers et al. (2003) was performed in the Norwegian Drammenfjord, which is an urban area that is under significant pressure from various anthropogenic activities in the vicinity. The concentrations in corresponding regions as predicted by the POPCYCLING-Baltic model show similar time trends, but underestimates observed concentrations by a factor of 10 for BDE 47 and 100 for BDE 209 (Figure 7.2). This discrepancy may indicate additional local emission sources to the water compartment, which have not been considered in the current approach, similar to what was hypothesised for the freshwater compartment. However, the uncertainty in estimated degradation half-lives may also contribute to the mismatch between model predictions and observations. The EPIWIN software estimates half-lives of BDE 47, 99 and 209 of 14400 h in sediment, which is about 1.6 years. If this were true, then PBDEs would be expected to be more or less fully degraded in sediments older than ten years (assuming no vertical transport of PBDEs in the sediment). Several studies have, however, as shown in Figure 7.2, detected fairly high levels of various PBDE congeners in sediment layers that are older than that. The time lag between model predictions and observed concentrations in the Bornholm example may be a result of bioturbation, which alters the distribution in the upper sediment layers.

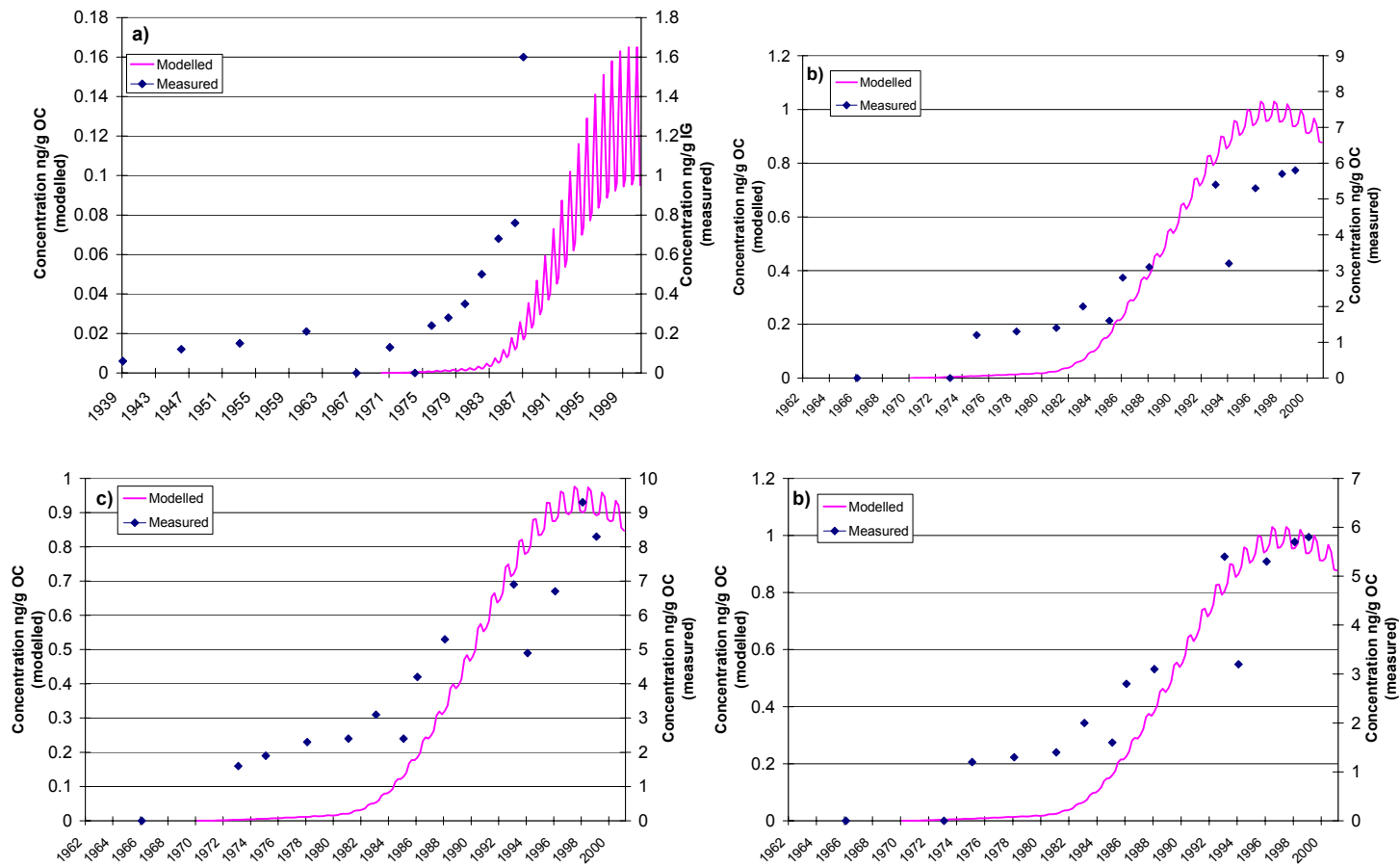
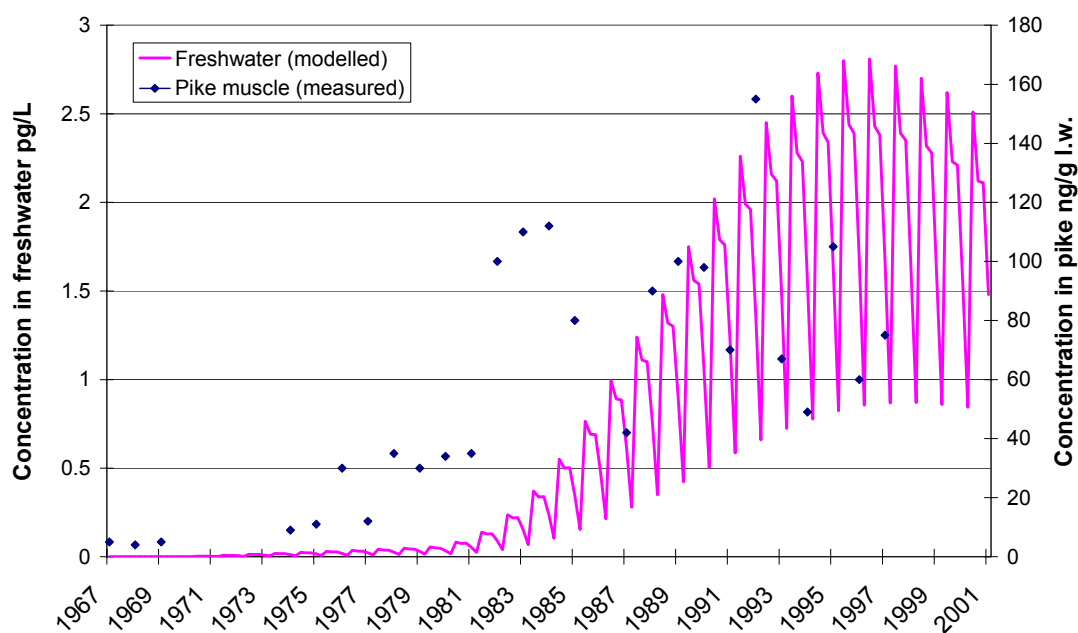


Figure 7.2. Modelled concentrations ng/g OC and measured levels ng/g IG (or ng/g OC) in dated sediment cores at (a) model region O5 and Bornholm for BDE 47 (Nylund et al., 1992), (b) model region C10 and Drammenfjord in Norway for BDE 47, (c) Drammenfjord for BDE 99, (d) Drammenfjord for BDE 209 (Zegers et al., 2003).

## 7.5 Freshwater

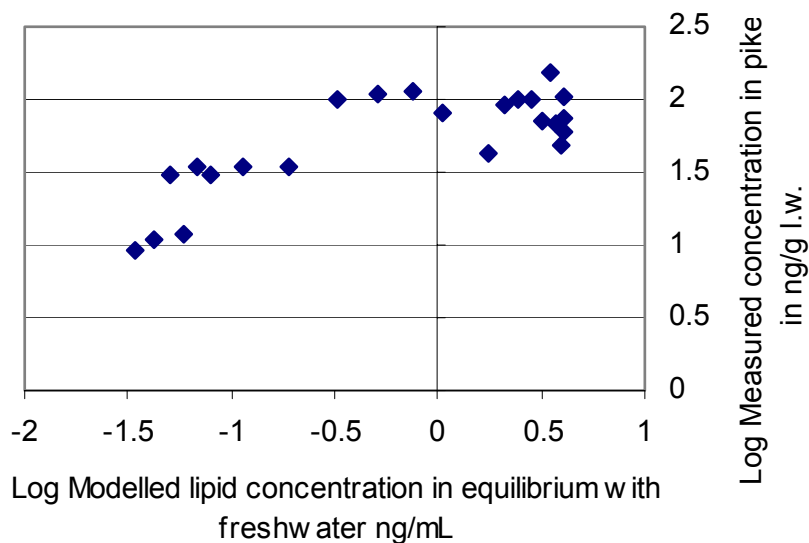
Below, model results are presented for the freshwater compartment. As no experimental freshwater data are available for the PBDEs, we have instead compared the estimated data with measured temporal trends in pike muscle from a freshwater lake (Kierkegaard et al., 1999). As shown in Figure 7.3, the time trends agree fairly well, with increasing levels from the early 70's until today. Experimental data vary considerably from year to year, however, the general increasing trend is evident from both modelled and measured data.



**Figure 7.3. Comparison of modelled time trends of BDE 47 in freshwater (model region Kattogat) and measured mean concentrations in pike from Lake Bolmen (Kierkegaard et al. 1999).**

In order to determine the agreement between model data and experimental data more specifically for the freshwater compartment, modelled water concentrations were converted to lipid concentrations in equilibrium with water, through multiplying the concentration in water by the octanol-water partition coefficient. These were then plotted against measured concentrations in pike muscle (Kierkegaard et al. 1999), see Figure 7.4 a,b. For data representing earlier years (Figure 7.4a), there is a close-to linear correlation between modelled and measured data. Model values are, however, approximately a factor of 200-300 lower than measured data. For data representing more recent years (Figure 7.4b), there is no clear correlation between modelled and measured data, and again, model data are considerably lower than measured data. This could be the result of biomagnification, meaning that concentrations in pike are higher because they take in PBDEs mainly via the food-chain and not only through water intake. A comparison with fish lower in the food-chain would be more appropriate. Long-term monitoring data from such fish are, however, not available. On the whole, comparison between model estimates for water and observed biotic concentrations is highly uncertain due to the many processes involved in biotic uptake of chemicals, but it the general temporal trend seems to be captured.





**Figure 7.4. Comparison between modelled lipid concentrations of BDE 47 in equilibrium with freshwater ( $=K_{OW} \cdot C_{water}$ ) and measured mean concentrations in pike from Lake Bolmen representing the time periods a) 1970-1983 and b) 1984-1997.**

## 7.6 Overall evaluation

With the current knowledge and empirical basis with respect to emissions, monitoring data and environmental half-lives, it is difficult to have a full confidence in model outputs. However, a model exercise like this is considered valuable as it facilitates an overview of the overall features as well as key knowledge gaps with respect to the overall sources and fate of PBDEs on a regional scale. Having these uncertainties in mind, the model is shown to be capable of reproducing the major features of the observed temporal trends for PBDEs for media, for which there is a fair amount of monitoring data available for evaluation. The predicted atmospheric concentrations are also in fair agreement with the limited monitoring data that are available from the region.

The model underestimates concentrations in the aquatic compartment, e.g. in sediments. This could possibly indicate an impact from additional emission sources to water, such as STPs and landfills close to urban areas. However, this underestimation is observed also for the soil compartment, which is mainly affected by atmospheric deposition. This again indicates that the half-lives in soils may be underestimated by EPIWIN. A recent study of substances prioritised in the EU water framework directive (including PBDEs) in sediments in central Stockholm and the adjacent coastal area showed that emissions in central Stockholm have very limited impact on the concentrations found in the coastal sediments. With the exception of a few stations very close to the city, the concentrations found in coastal sediments were in the same order of magnitude as levels observed in the open Baltic Sea (Sternbeck et al. 2003). This indicates that although PBDEs may be emitted to the water compartment, they strongly sorb to solids and quickly deposit to sediments not far from the source. Emissions to the water compartment may thus be important on a local scale, but the observed concentrations in

the aquatic compartment of the Baltic region are more likely to be influenced only by atmospheric deposition. The discrepancy between model predictions and observed levels in soils and sediment is likely due to underestimation of degradation half-lives in soils and sediments. Due to the observed discrepancy between model estimates and observed concentrations particularly for soils and sediments, the following sections will be focussed on relative concentration changes over time rather than predictions of exact environmental concentrations as this has proven difficult with the current parameterisation and empirical basis.

## 8 Future fate of PBDEs

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For future model scenarios, again BDEs 47, 99 and 209 were used, for reasons that have been explained previously (see section 7) Property data were taken from Table 4.3 and emissions were adopted as calculated according to section 6.

### 8.1 Future emission scenarios

The following scenarios were selected for simulation:

1. *No PBDEs banned, reference situation*

Adopting scenario 1 would mean that the consumption and emission would continue as previously. As consumption was estimated based on national GDP, and future GDPs are not available, we assume that for scenario 1, the GDP will continue to grow with a rate corresponding to previous trends, and that the consumption and thus emissions in each country will continue according to the assumed GDP growth.

2. *PentaBDE & octaBDE banned from August 2004 in EU and Norway but not Russia, Ukraine and Belarus*

Here we simulate the scenario that will become reality starting in 2004. We assume that the "new consumption" of congeners associated with penta and octa-mixtures will cease in all EU countries and Norway from January 2005 and onwards (thus allowing for a few months adaptation period), and that subsequently emissions will decrease. For pragmatic reasons, decaBDE is here assumed to contain only BDE 209, as this congener dominates here and is not present in the other mixtures. Thus, a ban of penta and octaBDE means a ban of all the PBDE congeners apart from BDE 209. For Russia, Ukraine and Belarus we however assume continued consumption as in scenario 1.

3. *PentaBDE & octaBDE banned from August 2004 in EU, Norway and Russia, Ukraine and Belarus*

As in scenario 2 but with a cease in consumption also in Russia, Ukraine and Belarus.

4. *PentaBDE & octaBDE banned from August 2004 and decaBDE from January 2006 in the EU and Norway but not in Russia, Ukraine and Belarus*

As in scenario 2 but adding a cease in decaBDE consumption within EU countries and Norway starting in January 2006.

5. *PentaBDE & octaBDE banned from August 2004 and decaBDE from January 2006 in the EU, Norway and Russia, Ukraine and Belarus*

As in scenario 3 but adding a cease in decaBDE consumption within EU, Norway and Russia starting in January 2006.

## 8.2 Impact on environmental concentrations

In the following section, model outcome is presented for BDEs 47, 99 and 209, for three model subregions (Bothnian Bay, Swedish Baltic Proper and Danish Straits) and for three different media (atmosphere, open seawater and deep sediments). In the model region Danish Straits, the entire water body is classified as coastal water, thus the results from this model region represent coastal water and sediments. Due to the previously stated uncertainties in the model's ability to predict exact concentrations, the model output is presented on a temporal relative scale, i.e. the time it takes for each compound to reach a concentration corresponding to a certain percentage of the concentration in the year 2000. In this way, the relative decline can be observed. Table 8.2.3 shows the predicted time it would take for the three compounds to reach 50, 10 and 1 % of the concentration in the year 2000. Results are shown for three regions and the two media seawater and sediment. For BDE 47 and 99, scenarios 2 and 3 are equivalent to scenarios 4 and 5, and for BDE 209, scenario 1 is equivalent to scenario 2 and 3.

### 8.2.1 Scenario 1

A continued increase in the use of penta, octa and decaBDE, with a consumption growth rate equivalent to past consumption would obviously lead to increasing concentrations in the environment of all congeners occurring in the technical products. In Table 8.2.1 - Table 8.2.3, this increase is denoted with a + sign. On the whole, a continued increasing use of all the technical products, is predicted to result in a 60-70 % increase in environmental concentrations in the year 2020 compared to the year 2000.

### 8.2.2 Scenarios 2 and 3

A ban of penta and octaBDE, is predicted to result in decreasing concentrations of BDE 47 and 99, with the fastest decrease in air, followed by water and sediment. For air and water, the concentrations are predicted to reach half their 2000 levels after roughly 10 years; after about 15 years the concentrations are expected to have reached 10 % of the levels in the year 2000. BDE 47 decreases with a rate slightly higher than BDE 99. For scenario 2, i.e. a ban in most countries apart from Russia, Belarus and Ukraine, the 1% level is not reached within the modelled time period for any compartment, extending the ban to include also these three countries (scenario 3) would result in the 1 % levels being reached after about 17 years for air and water, but not for the sediment compartment. On the whole, the response to reduced releases are slowest in the sediment compartment, which is understandable considering that remobilisation and degradation is generally slower here than in air and water. The response time in the atmosphere does not differ significantly between the three model subregions, however for the aquatic compartments (water and sediment), removal of the chemicals from the atmosphere and water is predicted to be fastest in the Danish Straits, followed by Swedish Baltic Proper, and Bothnian Bay. The difference in response time between the three regions is small, however, differing by a maximum time of 1 year. For the sediment compartment, the situation is the opposite, with fastest removal in the Bothnian Bay, and slowest in Danish Straits. This difference can be explained by the faster burial flux of organic carbon in the Danish Straits ( $6.0 \text{ g/m}^2 \times \text{year}$ ) compared to

the other regions (1.8 and 1.6 g/m<sup>2</sup> × year for Bothnian Bay and Swedish Baltic Proper respectively) (Wania et al. 2000).

### 8.2.3 Scenarios 4 and 5

Introducing a ban also of decaBDE, would naturally lead to decreasing environmental concentrations also of this compound. As the ban is assumed to be introduced 1.5 years later than the penta/octa ban, a corresponding time lag would be expected in the response time for this substance. As shown in the Tables, such a time lag is estimated, however this time lag is predicted to be longer than 1.5 years, reflecting the slower mobilisation/degradation of this substance compared to the lower brominated congeners. Again, removal processes from air and water are predicted to be faster in the Danish Straits than in the other two regions, whereas the response time in sediments here is slower. Excluding Russia, Belarus and Ukraine from the restrictions, is predicted to imply that the 1 % level is not reached within the modelled time period for any compartment, and for water and sediment, not even the 10 % level is reached. Including them would enhance the removal processes at least for air and water.

**Table 8.2.1. Time until the concentrations in the Bothnian Bay have reached 50, 10 and 1 % of the concentrations in the year 2000.**

Scenario	Congener	Seawater			Sediment		
		50 %	10 %	1 %	50 %	10 %	1 %
1	47	+	+	+	+	+	+
	99	+	+	+	+	+	+
	209	+	+	+	+	+	+
2	47	11.2	16	>20	11.8	17.2	>20
	99	11.4	16.4	>20	12.6	17.8	>20
	209	+	+	+	+	+	+
3	47	11	15.4	16.4	11.4	16.4	19.4
	99	11.4	15.6	17.6	12.2	17.4	>20
	209	+	+	+	+	+	+
4	47	11	15.4	16.4	11.4	16.4	19.4
	99	11.4	15.6	17.6	12.2	17.4	>20
	209	14.6	>20	>20	15.8	>20	>20
5	47	11	15.4	16.4	11.4	16.4	19.4
	99	11.4	15.6	17.6	12.2	17.4	>20
	209	13.8	19.8	>20	15.6	>20	>20

**Table 8.2.2. Time until the concentrations in the Swedish Baltic Proper have reached 50, 10 and 1 % of the concentrations in the year 2000.**

Scenario	Congener	Seawater			Sediment		
		50 %	10 %	1 %	50 %	10 %	1 %
1	47	+	+	+	+	+	+
	99	+	+	+	+	+	+
	209	+	+	+	+	+	+
2	47	10.6	15.2	>20	13	>20	>20
	99	11.4	16.4	>20	14	>20	>20
	209	+	+	+	+	+	+
3	47	10.2	15.2	16	13	18.8	>20
	99	11.4	15.2	17.2	14	19.8	>20
	209	+	+	+	+	+	+
4	47	10.2	15.2	16	13	18.8	>20
	99	11.4	15.2	17.2	14	19.8	>20
	209	13.6	18	>20	18	>20	>20
5	47	10.2	15.2	16	13	18.8	>20
	99	11.4	15.2	17.2	14	19.8	>20
	209	13.4	16.8	>20	17	>20	>20

**Table 8.2.3. Time until the concentrations in the Danish Straits have reached 50, 10 and 1 % of the concentrations in the year 2000.**

Scenario	Congener	Seawater			Sediment		
		50 %	10 %	1 %	50 %	10 %	1 %
1	47	+	+	+	+	+	+
	99	+	+	+	+	+	+
	209	+	+	+	+	+	+
2	47	10.4	15.2	>20	14.2	>20	>20
	99	11.4	15.8	>20	15.2	>20	>20
	209	+	+	+	+	+	+
3	47	10.2	14.4	16.4	13.8	19.6	>20
	99	11.4	15.2	17.6	14.8	>20	>20
	209	+	+	+	+	+	+
4	47	10.2	14.4	16.4	13.8	19.6	>20
	99	11.4	15.2	17.6	14.8	>20	>20
	209	14.2	>20	>20	18.8	>20	>20
5	47	10.2	14.4	16.4	13.8	19.6	>20
	99	11.4	15.2	17.6	14.8	>20	>20
	209	14.2	19	>20	17.8	>20	>20

#### 8.2.4 Overall impact

As mentioned, the model should not be used for prediction of absolute environmental concentrations of PBDEs with the current parameterisation, due to substantial uncertainties in current input parameters, such as emission and degradation rates and due to the scarcity of monitoring data for accurate model evaluation. Still, the model evaluation indicates a fair capability to reproduce concentration changes over time. The model output therefore provides a potential basis for assessing to what extent the current environmental concentrations of BDEs 47, 99 and 209 in the Baltic Sea Region would be influenced by introducing restrictions in different regions.

A 50 % reduction of seawater concentrations in the year 2000 is predicted to be reached after 10 to 11 years for BDE 47 and 99 following the proposed EU ban, for BDE 209 it would take 13-14 years, providing that a ban is introduced in 2006. For sediment, the response time is slower, and especially for BDE 209, it would take longer than 20 years to reach a level corresponding to 10 % of the concentrations in the year 2000.

Bearing in mind that the assumed PBDE consumption in Eastern European countries has not been verified, it may be concluded that banning PBDE usage also in Russia, Belarus and Ukraine would result in a faster reduction of the environmental levels. A 50 % reduction in concentrations is, however, reached at the same time regardless of whether usage is banned in these countries or not. On the whole, usage in these three countries is predicted to have limited impact on the concentrations in the Baltic region. The main reasons for this are likely to be i) the assumption that there is limited use and emissions of PBDEs in the countries mentioned ii) only a very small part of the Russian population lives within the actual model region, and the geographical distribution of emissions is population-based, iii) air is assumed to be the primary emission recipient and iv) the predominant wind direction in the Baltic region is eastbound.





## 9 Potential for long-range transport and possible impact on the Arctic region

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The propensity for transport of PBDEs to Arctic regions may be studied using long-range transport models. Such an analysis has recently been performed by Wania and Dugani (2003), thus it was considered unnecessary to redo the assessment. Instead, the findings by Wania and Dugani (2003) are utilised to analyse the possible implications they would have in the context of the current project. Wania and Dugani used four multimedia fate models, particularly designed for assessment of long-range transport potential of organic chemicals, to assess the potential for long range transport LRT of polybrominated diphenyl ethers. It was concluded that the four models (TaPL3-2, ELPOS-1.1.1, Chemrange-2 and GloboPOP-1.1.), which all calculate a numeric indicator of long-range transport potential, gave comparable results. The model predictions suggest that congeners of intermediate degree of bromination are more efficiently transported long distances than are low and high brominated substances. This is explained in terms of the interaction between the two processes of atmospheric partitioning and degradation. Congeners of very low bromination degree are more rapidly degraded in the atmosphere, whereas heavier compounds tend to deposit to terrestrial or marine surfaces closer to source regions. Thus, the congeners most likely to be transported to the Arctic environment, are PBDEs of low to moderate halogenation, e.g. tetra and pentaBDEs, and this LRT potential would be of the same order of magnitude as for highly chlorinated PCBs. In this assessment, that would imply LRT for BDEs 47 and 99, but not 209. The model predictions described in Wania and Dugani (2003) are supported by monitoring data in Arctic air (Alaee et al. 2000.), in marine mammals (Ikonomou et al., 2002) and in sediments from Greenland lakes (Malmquist et al., 2003). Considering the emission scenarios assessed here, measures taken to prevent the use of penta and octaBDE in Europe should contribute to reduce the PBDE levels observed in the Arctic environment. However, environmental levels in the Arctic are also likely to be controlled by emissions in other parts of the globe.



# 10 Discussion

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The overall aim with this study has been to increase the understanding of the historical behaviour and to predict the impact of various control measures regarding use and emissions on environmental concentrations of PBDEs in the Baltic region.

We are fairly confident that the global production estimates of PBDEs are of the right order of magnitude indicating a current production level of similar size as that of PCBs at their production peak in 1970. The global production and consumption estimates presented herein may thus provide useful information for other studies aiming to present environmental budgets of PBDEs on a global scale. Estimates of the current consumption should be fairly reliable as they are in close agreement with independent information from the bromine industry. For earlier years, the estimated figures show a larger discrepancy to reported consumption data, which indicates that the European share of the global PBDE consumption may have been different in the past. On the whole, the GDP-based approach to estimate national consumption seems to be the only feasible approach at present. More accurate information on national use would be required to evaluate the quality of the consumption data in this region.

Concerning the emission estimates, the adopted approach rely on the assumptions that

- i) air is the primary emission recipient
- ii) emissions predominantly occur diffusely from products in use
- iii) the diffuse emission rate is related to the octanol-air partition coefficient  $K_{OA}$

These assumptions are crucial in the adopted approach and thus govern the model output together with physical-chemical property data. Assumption i) is questionable, as recent monitoring data indicate that PBDEs may be emitted from landfills via landfill leachate and suggest that they may reach the groundwater and control environmental levels on a local scale. Thus, emissions to the water column are possible and releases to larger the Baltic Sea from e.g. sewage treatment plants cannot be ruled out. However, an extensive study in sediments in the Stockholm region and its adjacent coastal area indicates limited impact of local emissions to water on the concentrations in coastal sediments. The relatively higher PBDE concentrations in the urban area did not result in elevated concentrations along the coast. The levels observed in the coastal area were instead comparable to those observed in the open Baltic Sea (Sternbeck et al. 2003). Therefore, emissions to the water compartment are likely to have a significant impact locally, but PBDEs are unlikely to be transported over great distances by seawater in this region, presumably due to their strong tendency to partition to particles and consecutive deposition to sediments. On a regional scale, atmospheric deposition may thus be the main source for observed concentrations in the aquatic environment. This hypothesis seems to be supported by the soil data (Hassanin et al. 2004). Assumption ii) is considered reliable for current PBDE emissions, as no production occurs within the region. However, the potential for significant atmospheric emissions of PBDEs from landfills and recycling plants cannot be ruled out. Assumption iii) has not been experimentally verified for the PBDEs, but are considered plausible but due to the structural similarities between PBDEs and PCBs. However, atmospheric emissions to

air may also occur through wear and abrasion and subsequent particle or dust emissions containing PBDEs.

In terms of objective achievement, the model provides a reasonable description of observed temporal patterns. Predicted declines following various restriction measures should thus be fairly reasonable. However, it has not been possible to reproduce observed historical concentrations for PBDEs in media for which a more detailed evaluation was feasible. For the air compartment, the predicted concentrations agree fairly well with observations but the model clearly underestimates concentrations in soils and sediments. We assign this discrepancy mainly to uncertainties in estimated degradation rates (possibly too high). Further experimental studies on the degradation of PBDEs in soils and sediments would therefore be valuable. On a local scale, observed elevated concentrations in sediments may also be a result of additional, local releases to water.

# 11 Conclusions and recommendations

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These are the main conclusions that can be drawn from the project:

- At present, the knowledge about emission pathways and emission strengths is limited. This mitigates the possibility to assess the relative importance of sources as well as the confidence in current model outputs.
- Key physical-chemical properties are fairly well known for individual PBDE congeners, degradation rates are however, still highly uncertain and should benefit from experimental studies.
- The global PBDE production seems to have reached a level similar to the peak production of PCBs in 1970.
- The proposed ban of penta and octa in the EU is likely to result in declining concentrations in the Baltic region of lower brominated congeners (e.g. tetra and penta) in all media, with a 50 % decline after roughly 10 years in water and after 14-15 years in sediment.
- A ban of penta and octa is likely to significantly reduce European contributions to the environmental contamination of these compounds in the Arctic region. However, continued use in other regions of the world may also have an impact on future environmental levels in the Arctic.
- Continued use of decaBDE, corresponding to previous usage trends will most probably result in a 60 – 70 % increase in environmental concentrations in the Baltic region after 20 years.
- A ban of decaBDE introduced in January 2006, is predicted to result in a similar decline as for lower brominated congeners, however the decline is predicted to be slower, and 10 % of the concentration levels in the year 2000 is predicted not to have been reached by the year 2020.

In order to reduce the contamination of the Baltic environment, of all PBDE compounds, a ban of penta, octa *and* deca would be required. The Arctic environment may be well protected from PBDE contamination if the use of penta and octa would cease globally, but a continued or increasing use of deca would ultimately lead to increasing concentrations in the environment.



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# 13 References

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- Alcock R.E., Sweetman A.J., Prevedouros K., Jones K.C. 2003. Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. *Environment International* 29, 691-698
- Almkvist Åsa. National Chemicals Inspectorate, Solna, Sweden. Personal Communication
- Baker J.I.; Hites, R.A. 2000. Is Combustion the Major Source of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans to the Environment? A Mass Balance Investigation. *Environ Sci Technol* 34: 2879-2996.
- Beyer A, Wania F, Gouin T, Mackay D and Matthies M (2002) Selecting Internally Consistent Physical-Chemical Properties of Organic Compounds. *Environ Toxicol Chem* 21: 941-953
- Braekevelt, E.; Tittlemier, S.A.; Tomy, G.T. 2003. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere*, 51 (7): 563-567
- Breivik, K., Alcock, R. 2002. Emission impossible? The challenge of quantifying sources and releases of POPs into the environment. *Environment International*. Vol. 28 (3): 137-138.
- Breivik, K. and F. Wania, 2002a. Evaluating a Model of the Historical Behavior of Two Hexachlorocyclohexanes in the Baltic Sea Environment. *Environmental Science and Technology*. Vol. 36 (5): 1014-1023.
- Breivik, K. and F. Wania, 2002b. Mass Budgets, Pathways, and Equilibrium States of Two Hexachlorocyclohexanes in the Baltic Sea Environment. *Environmental Science and Technology*. Vol. 36 (5): 1024-1032.
- Breivik, K.; Sweetman, A.; Pacyna, J.M.; Jones, K.C. 2002a. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. 1. Global production and consumption. *Sci. Tot. Environ.* 290, 181-198
- Breivik, K.; Sweetman, A.; Pacyna, J.M.; Jones, K.C. 2002b. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. 2. Emissions. *Sci. Tot. Environ.* 290, 199-224
- Bromine Science and Environmental Forum. 2000. An introduction to Brominated Flame Retardants. Downloadable at <http://www.bsef.com>
- Bromine Science and Environmental Forum. 2003. Major Brominated Flame Retardants Volume Estimates. Downloadable at <http://www.bsef.com>
- Chen, G., Konstantinov, A. D., Chittim, B. G., Joyce E.M., Bols, N.C., Bunce N.J. 2001. Synthesis of Polybrominated Diphenyl Ethers and Their Capacity to Induce CYP1A by the Ah Receptor Mediated Pathway. *Environ. Sci. Technol.* 35, 3749-3756

- Cole, J.G., Mackay, D., 2000. Correlating environmental partitioning properties of organic compounds: the three solubility approach, *Environ. Toxicol. Chem.* 19, 265-270.
- Cousins I., Mackay D. 2000. Correlating the physical-chemical properties of phthalate esters using the 'three solubility' approach. *Chemosphere* 41, 1389-1399
- Darnerud, P.O., G.S. Eriksen, T. Jóhannesson, P.B. Larsen and M. Viluksela, 2001. Polybrominated Diphenyl Ethers: Occurrence, Dietary Exposure, and Toxicology. *Environmental Health Perspectives*, Vol. 109, Supplement 1, March 2001: 49-68.
- De Maagd P.G-J., Ten Hulscher D. T. E. M., Van den Heuvel H., Opperhuizen A., Sijm D T.H.M. 1998. Physico-chemical properties of polycyclic aromatic hydrocarbons: aqueous solubilities, n-octanol/water partition coefficients and Henry's Law Constants. *Environ. Toxicol. Chem.* 17, 2, pp 251-257
- De Wit, C. 2002. An overview of brominated flame retardants in the environment *Chemosphere* 46, 583-624
- European Parliament. 2002. Document P5\_TAPROV (2002)04-10
- ECB (European Chemicals Bureau) 2000. European Union Risk Assessment Report. diphenyl ether, pentabromo derivative. EUR 19730 EN.
- ECB (European Chemicals Bureau) 2002a. European Union Risk Assessment Report. diphenyl ether, octabromo derivative. Updated draft report, July 2002
- ECB (European Chemicals Bureau) 2002b. European Union Risk Assessment Report. Bis(pentabromophenyl) ether Final draft, June 2002.
- Gouin T., Thomas G.O., Cousins I., Barber J., Mackay D., Jones K.C. 2002 Air-Surface Exchange of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls *Environ. Sci. Technol.*, 36,1426-1434
- Gouin T, Cousins I, Mackay D. Comparison of Methods for Obtaining Degradation Half-Lives (submitted manuscript)
- Harner T, Shoeib M. 2002. Measurements of Octanol-Air Partition Coefficients ( $K_{OA}$ ) for Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment. *J Chem Eng. Data.* 47 (2), 228-232
- Hassanin A., Breivik K., Meijer S.N., Steinnes E., Thomas G.O., Jones K.C. PBDEs in European Background Soils: Levels and factors controlling their distribution. *Environ Sci Technol.* 38: 738-745.
- Hooper, K. and T.A. McDonald, 2000. The PBDEs: An Emerging Environmental Challenge and Another Reason for Breast-Milk Monitoring Programs. *Environmental Health Perspectives*, Vol. 108, No. 5, May 2000: 387-392.
- KEMI 1994, Risk assessment of polybrominated diphenyl ethers. KEMI report No 9/94. National Chemicals Inspectorate.
- Ikonomou MG., Rayne S., Addison R. 2002. Exponential increases of brominated flame retardants, polybrominated diphenyl ethers in the Canadian Arctic from 1981-2000. *Environ Sci Technol.* 36: 1886-1892

- Jaward F.M., Farrar N.J., Harner T., Sweetman A.J., Jones K.C. 2004 Passive Air Sampling of PCBs, PBDEs and Organochlorine Pesticides Across Europe. *Environ Sci Technol.* 38: 34-41.
- Junestedt C., Solyom P., Ek M., Palm A., Öman C. *In preparation*. Karakterisering av utsläpp - jämförelse av olika utsläpp till vatten. [Characterising emissions – a comparison between different emissions to water]. *In Swedish*
- Lassen C., Løkke S., Andersen L. I. 1999. Brominated Flame Retardants - Substance Flow Analysis and Assessment of Alternatives. Danish Environmental Protection Agency. Environmental Project, 494
- Lyday P. A. Bromine. 2001. Annual statistics 1994-2001. In: Minerals Yearbook: Volume I.- Metals and Minerals. Available at <http://minerals.usgs.gov/minerals/pubs/commodity/myb/> August, 2002
- Lyday Phyllis A. US Geological Survey. Personal communication; E-mail message dated August 21, 2002
- Mackay D, Shiu WY and Ma KC (1999) Physical-Chemical Properties and Environmental Fate and Degradation Handbook. CRCnetBASE 2000, Chapman & Hall CRCnetBASE, CRC Press LLC, Boca Raton, FL (CD-ROM)
- Malmquist C., Bindler R., Renberg I., van Bavel B., Karlsson E., Anderson N.J., Tysklind M. 2003. Time Trends of Selected Persistent Organic Pollutants in Lake Sediments from Greenland. *Environ. Sci. Technol.* 37: 4319-4324
- Marsh, G., Hu, J., Jakobsson, E., Rahm, S., Bergman, Å., 1999. Synthesis and Characterization of 32 Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.* 33, 3033-3037.
- Meylan W. 1999. EPIWIN x3.04 [computer program: US EPA Version for Windows], Syracuse Research Corporation, Syracuse, NY, US. <http://esc.syrres.com/interkow/epi.htm> (June 22, 2002)
- Merionyté D., Norén K. Bergman Å. 1999. Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997. *Journal of Toxicology and Environmental Health, Part A.* 58, 329-341.
- Nylund K. Asplund L. Jansson B., Jonsson P., Litzén K., Sellström U. 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. *Chemosphere* 24, 1721-1730
- Palm A, Cousins I. T., Mackay D, Tysklind M, Metcalfe C, Alae M. 2002. Assessing the environmental fate of chemicals of emerging concern: A case study of the polybrominated diphenyl ethers. *Environmental Pollution*, Vol 117/2, pp 195-213
- Persson J., Axelman J., Zebühr Y., Ishaq R., Bandh C., Broman D. 1997. PCB från fogmassa till luft och vatten. [In Swedish]. Report for the Swedish EPA on the work and results of studies on release of PCBs from sealants. Inst Applied Environmental Research, Stockholm University, Sweden
- Platz J., Christensen J.H. 2001. Screening of brominated flame retardants in Danish Marine and freshwater sediments. Poster presentation at the second international workshop on brominated flame retardants. May 14-16, Stockholm University, Stockholm, Sweden.

- Rahman, F., K.H. Langford, M.D. Scrimshaw and J.N. Lester, 2001. Review. Polybrominated diphenyl ether (PBDE) flame retardants. *The Science of the Total Environment*, Vol. 275: 1-17.
- Reid, R.C., Prausnitz, J.M., Poling, B.E., 1987. The properties of Gases and Liquids, 4th ed.; McGraw-Hill: New York
- Remberger M., Sternbeck J., Palm A., Kaj L., Strömberg K., Brorström-Lundén E. 2003. The environmental occurrence of hexabromocyclododecane in Sweden. *Chemosphere*, *in press*.
- Renner, R. 2000. What Fate for Brominated Fire Retardants? *Environmental Science and Technology*, May 1. Feature Article. 223A-226A.
- Schlabach M., Mariussen E., Borgen A., Dye C., Enge E-K., Steinnes E., Green N., Mohn H. 2002. Kartlegging av bromerte flammehemmere og klorerte parafiner. [In Norwegian]. Rapport NILU 62/2002, Norsk Institutt for luftforskning, Norway
- Sellström U., Kierkegaard A., de Wit C., Jansson B., Bignert A., Olsson M. 1999. Temporal Trend Studies on Polybrominated Diphenyl Ethers in Guillemot Egg from the Baltic Sea. In: Sellström U. 1999. Determination of Some Polybrominated Flame Retardants in Biota, Sediment and Sewage Sludge. Doctoral Dissertation. Environmental Chemistry. Stockholm University
- SFT, 2003: Bruken av bromerte flammehemmer i produkter. [Use of brominated flame retardants in products]. SFT Report TA-1947/2003. *In Norwegian*. Available at: <http://www.sft.no/publikasjoner/kjemikalier/1947/ta1947.pdf>
- Sternbeck J., Brorström-Lundén E., Remberger M., Kaj L., Palm A., Junedahl E., Cato I. 2003. WFD Priority Substances in Sediments from Stockholm and the Svealand Coastal Region. IVL B 1538
- Stevens, G.C. Mann, A.H. 1999. Risks and Benefits in the Use of Flame Retardants in Consumer Products, Polymer Research Centre, School of Physical Sciences and School of Biological Sciences, University of Surrey, UK, January 1999
- Tittlemier, S., Halldorson, T., Stern, G., Tomy, G. 2002 Vapour Pressures, Aqueous Solubilities, and Henry's Law Constants of Some Brominated Flame Retardants *Environmental Toxicol. Chem.* Vol. 21, No. 9, pp. 1804–1810
- Tittlemier, S.A., Tomy G.T. 2001. Vapor Pressures of Six Brominated Diphenyl Ether Congeners - Short Communication. *Environmental Toxicol. Chem.* Vol. 20, No. 1, pp. 146-148.
- UK Department of Trade and Industry. 2000. Effectiveness of the Furniture & Furnishings (Fire) (Safety) Regulations 1988. Government Consumer Affairs Directorate. United Kingdom
- United States Geological Survey. 2002. Bromine Statistics. By David A. Buckingham and Phyllis A. Lyday. Will be available through the internet <http://minerals.usgs.gov/minerals/pubs/of01-006/>
- Wania F., Daly G. L. 2002. Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs. *Atmos. Environ.*, 36, 5581-5593

- Wania F., Dugani, C. B. 2003. Assessing the Long-Range Transport Potential of Polybrominated Diphenyl Ethers: A Comparison of Four Multimedia Models. *Environmental Toxicology and Chemistry*. 22, pp 1252–1261
- Wania F., Duan Lei, Y., Harner, T., 2002. Estimating Octanol-Air Partition Coefficients of Nonpolar Semivolatile Organic Compounds from Gas Chromatographic Retention Times. *Anal. Chem.* 74, 3476-3483.
- Wania, F.; Persson, J.; Di Guardo, A.; McLachlan, M.S. 2000. The POPCYCLING-Baltic Model. A Non-Steady State Multicompartment Mass Balance Model of the Fate of Persistent Organic Pollutants in the Baltic Sea Environment. Norwegian Institute for Air Research, NILU OR 10/2000, ISBN 82-425-1159-4; Kjeller, Norway, 2000, 81 pp.
- Watanabe, I., Tatsukawa, R., 1989. Anthropogenic brominated aromatics in the Japanese environment. Proceedings, Workshop on brominated aromatic flame retardants, Swedish National Chemicals Inspectorate, Solna, Sweden 24-26 October 1989, pp. 63-71.
- Wong, A., Lei, Y.D., Alae, M., and Wania F., 2001. Vapor Pressures of the Polybrominated Diphenyl Ethers. *J. Chem. Eng. Data*. 46, 239-242.
- World Bank Group. 2002. Development Indicators 2002. Database at SCBs library
- WHO (World Health Organization) 1994. Environmental Health Criteria 162: Brominated diphenyl ethers. Geneva Switzerland
- WHO (World Health Organization) 1997. Environmental Health Criteria 192 Flame Retardants: A General Introduction. Geneva Switzerland
- Zegers B.N. Lewis W.E., Booij K., Smittenberg R.H., Boer W., de Boer J., Boon J.P. 2003. Levels of Polybrominated Diphenyl Ether (PBDE) Flame Retardants in Sediment Cores from Western Europe. *Environ. Sci. Technol.* 37, 17, pp 3747-3754.
- Örn, U., Eriksson, L., Jakobsson, E., Bergman, Å., 1996. Synthesis and Characterization of Polybrominated Diphenyl Ethers - Unlabelled and Radiolabelled Tetra-, Penta- and Hexabromodiphenyl Ethers. *Acta Chem. Scand.* 50, 802-807



# 14 Appendices

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## Appendix 1 Physical-chemical properties of polybrominated diphenyl ethers

Each PBDE congener has physical-chemical characteristics unique to that particular compound and which are dependent on its structure. When released into the environment, the components of the technical mixtures become dispersed, degraded and diluted reflecting their specific individual properties and environmental half-lives. Therefore, it is currently common practice to measure physical-chemical properties of the individual compounds included in a technical mixture and estimate their environmental fate and exposure individually, rather than measuring "overall" properties of the technical mixture itself. There has been a similar trend in ecotoxicology, where the toxicity of individual congeners is now more usually measured than the toxicity of the technical mixtures.

As the environmental interest in brominated flame retardants is increasing, the number of determinations of physical-chemical properties of individual congeners is steadily rising. Watanabe and Tatsukawa (1989) performed one of the first studies of the properties of PBDEs, measuring vapour pressures and octanol-water partition coefficients ( $K_{OW}$ ) of PBDEs of various degrees of bromination. Since then, additional measurements have been performed by e.g. Örn et al. (1996), Marsh et al. (1999), Tittlemier and Tomy (2001), Wong et al. (2001), Harner and Shoeib (2002), Tittlemier et al. (2002) and Braekevelt et al. (2003). Experimentally derived properties for a large number of PBDE congeners are, however, still lacking and the need for further measurements have been pointed out by e.g. Palm et al. (2002).

A major concern when interpreting the results from different experimental studies is that the reported properties sometimes vary by several orders of magnitude. This is the case for many chemical groups (Mackay et al. 1999) and relates to the different methodologies used, the analytical methods and other, often unknown parameters. Table A 1 shows examples of reported vapour pressures for PBDEs from various experimental studies as well as QSPR (Quantitative Structure-Property Relationship)-calculated values.

**Table A 1. Example of reported vapour pressures (in Pa) from experimental studies and estimated values of selected PBDE homologues and congeners.  $P^S_L$  denotes vapour pressure of the liquid state of the compound,  $P^S_s$  the vapour pressure of the solid state.**

Homologue class	Watanabe & Tatsukawa (1989) $P^S_s$ (Pa)	Tittlemier and Tomy (2001) $P^S_L$ (Pa)	Tittlemier et al. (2002) $P^S_L$ (Pa)	Wong et al. (2001) $P^S_L$ (Pa)	ECB (2002a) $P^S_s$ (Pa)	Estimated* $P^S_s$ (Pa)
Tri	$(1.5-2.7) \times 10^{-3}$	$1.7 \times 10^{-4}$ (# 28)	$2.19 \times 10^{-3}$ (# 28)	$2.19 \times 10^{-2}$ (# 17) $4.56 \times 10^{-3}$ (# 30) $2.25 \times 10^{-3}$ (# 32) $1.78 \times 10^{-3}$ (# 33) $1.39 \times 10^{-3}$ (# 35) $1.02 \times 10^{-3}$ (# 37)		$3.1 \times 10^{-4}$
Tetra	$(2.6-3.3) \times 10^{-4}$	$2.1 \times 10^{-5}$ (# 47)	$1.86 \times 10^{-4}$ (# 47) $1.22 \times 10^{-4}$ (# 66) $6.79 \times 10^{-5}$ (# 77)	$3.19 \times 10^{-4}$ (# 47) $2.38 \times 10^{-4}$ (# 66) $4.00 \times 10^{-4}$ (# 69) $4.92 \times 10^{-4}$ (# 75) $1.56 \times 10^{-4}$ (# 77)	$5.2 \times 10^{-4}$	$3.2 \times 10^{-5}$
Penta	$(2.9-7.3) \times 10^{-5}$	$3.6 \times 10^{-6}$ (# 85) $1.2 \times 10^{-5}$ (# 99)	$9.86 \times 10^{-6}$ (# 85) $1.76 \times 10^{-5}$ (# 99) $2.86 \times 10^{-5}$ (# 100)	$2.81 \times 10^{-5}$ (# 85) $6.82 \times 10^{-5}$ (# 99) $4.99 \times 10^{-5}$ (# 116) $8.07 \times 10^{-5}$ (# 119)	$5.4 \times 10^{-5}$	$3.3 \times 10^{-6}$
Hexa	$(4.2-9.4) \times 10^{-6}$	$1.9 \times 10^{-6}$ (# 138)	$1.58 \times 10^{-6}$ (# 138) $2.09 \times 10^{-6}$ (# 153) $3.80 \times 10^{-6}$ (# 154)	$8.43 \times 10^{-6}$ (# 153)	$5.5 \times 10^{-6}$	$3.8 \times 10^{-7}$
Hepta		$2.3 \times 10^{-7}$ (# 190)	$4.68 \times 10^{-7}$ (# 183) $2.82 \times 10^{-7}$ (# 190)	$9.05 \times 10^{-7}$ (# 190)	$5.7 \times 10^{-7}$	$4.4 \times 10^{-8}$
Octa	$(1.2-2.2) \times 10^{-7}$				$5.9 \times 10^{-8}$	$4.9 \times 10^{-9}$
Nona					$6.1 \times 10^{-9}$	$5.4 \times 10^{-10}$
Deca					$6.2 \times 10^{-10}$	$5.7 \times 10^{-11}$

\* Estimated with EPIWIN estimation software (Meylan, 1999)

Similar discrepancies are found when comparing reported values of water solubility or log  $K_{OW}$  for highly hydrophobic compounds, such as the PBDEs (see e.g. Palm et al., 2002). In order to achieve “best-estimates” for properties of chemicals, a common approach is to apply QSPRs. The basic idea behind QSPRs is to use a molecular descriptor such as e.g. molecular mass or volume, number of substitutes or relative retention time on a gas chromatographic column and to plot the properties of well-studied compounds against this descriptor. The regression relationship obtained can then be used to derive the properties of the unknown compound. This kind of approach is particularly advantageous for chemicals belonging to a group with similar structures and behaviour, such as the PCBs, the halogenated benzenes or the PBDEs.

### Deriving properties using a QSPR-method

Cole and Mackay (2000) illustrated a QSPR method named “the three solubility approach” and applied it to the chlorobenzenes while Cousins and Mackay (2000) later applied it to the phthalate esters. With this method, all available experimental data for the constituents of a certain chemical group are collected and, if necessary, complemented with estimated data. Correlations are then sought between the molecular descriptor chosen and the “solubilities” ( $\text{mol/m}^3$ ) of the liquid state of the compounds in air, water and octanol ( $S_A$ ,  $S_W$ ,  $S_O$ ), with octanol representing a surrogate for media in



the environment containing organic carbon or lipids (i.e. soils, sediments, biota, vegetation). The correlations obtained are then used to calculate “best-estimates” of the solubilities of individual compounds in these three media. Other properties, such as partition coefficients ( $K_{OW}$ ,  $K_{AW}$ ,  $K_{OA}$ ), vapour pressure (Pa) and water solubility ( $\text{g/m}^3$ ), can then be derived from these three solubilities.

Palm et al. (2002) applied the three solubility approach to the PBDEs and calculated “best estimates”, considering all the available experimental data on physical-chemical properties and complementing estimated values. Since then, additional experimental studies have been performed (Tittlemier et al. 2002; Braekevelt et al. 2003). Estimated property data generally differ considerably from experimental data (Palm et al. 2002; see also Table A 1), but estimations may sometimes be necessary, if experimentally derived data are lacking. Following the approach outlined in Palm et al. (2002), we recalculated the solubility equations, including only the experimental data and excluding software estimated data. The underlying data included in the calculations are shown in Table A 3. The equations obtained were as follows:

$$\text{Log}(S_A) = 3.58 - 0.036V \quad r^2 = 0.87 \quad \text{SE} = 0.55 \quad (\text{A1})$$

$$\text{Log}(S_W) = 2.42 - 0.021V \quad r^2 = 0.75 \quad \text{SE} = 0.50 \quad (\text{A2})$$

$$\text{Log}(S_O) = 2.95 - 0.001V \quad r^2 = 0.02 \quad \text{SE} = 0.38 \quad (\text{A3})$$

where  $V$  is the molar volume ( $\text{cm}^3/\text{mol}$ ) calculated with the Le Bas method (Reid et al., 1987). From eq. A1-A3 the equations for the partition coefficients were derived:

$$\text{Log}(K_{OW}) = 0.53 + 0.02V \quad (\text{A4})$$

$$\text{Log}(K_{AW}) = 1.16 - 0.015V \quad (\text{A5})$$

$$\text{Log}(K_{OA}) = -0.63 + 0.035V \quad (\text{A6})$$

Figure A 1a shows that the solubility in air falls with increasing bromination with a slope similar to that of the chlorobenzenes and PCBs. The absolute values are about a factor of  $10^2$  to  $10^4$  lower for the PBDEs at the same molar volume, which is similar to the findings by Palm et al. (2002). The decrease in  $S_A$  is 0.84 log units per bromine added i.e. a factor of 7.0. The solubility in water also decreases with increasing degree of bromination (0.49 log units or a factor of 3.11 per bromine added, see Figure A 1b) to a greater extent than the solubility in octanol, which decreases only by 0.03 log units or a factor of 1.1 per bromine (Figure A 1c). The standard errors (S.E.) of the regression lines are less than one log unit.

Plots of the three partition coefficients are given in Figure A 2. The octanol-water partition coefficient increases by 0.46 log units (factor of 2.9) per bromine added, which is a result of the faster decrease in water solubility with molar volume than the decrease in octanol solubility, as discussed above. The reported values for  $\log K_{OW}$  for one substance sometimes vary by one log unit (factor of 10) which is of concern since  $K_{OW}$  is used to estimate sorption and bioaccumulation.

The “experimental”  $K_{AW}$  data (as calculated from experimental data of water solubility and vapour pressure), which are essential for estimating air-water exchange of PBDEs, show considerable scatter, indicating a need to perform direct measurements of this quantity. It is of concern that different estimates range over a factor of  $10^{2.2}$ . The  $K_{AW}$  is estimated to decrease by 0.35 log units (factor of 2.2) per bromine added, which implies a decreasing preference for air relative to water with increasing bromination. Excluding

software estimated data significantly changes the air-water partitioning trend with increasing molar volume. In Palm et al. (2002),  $K_{AW}$  was found to increase with increasing substitution, while the opposite is shown here. This decreasing trend is observed also for other groups of compounds such as PAHs (de Maagd et al., 1998). The large scatter in estimated values of  $K_{AW}$  is reduced to some extent when only using experimentally derived data.

Accurate estimates of  $K_{OA}$  are essential to accurately predict environmental phase partitioning between air and various terrestrial surfaces, such as soils and vegetation. Figure A 2c indicates that  $K_{OA}$  increases by 0.8 log units (factor of 6.5) per bromine added. The calculated values are generally between 0.1-1.5 log units lower than the corresponding measured values (Harner and Shoeib, 2002). This discrepancy is lower than what was reported in Palm et al. (2002) but it is still significant. As suggested in Beyer et al. (2002), the observed difference between measured and calculated values of log  $K_{OA}$  (Figure A 2c) might be a result of the different measurement techniques when determining  $K_{OW}$  and  $K_{OA}$ , which may imply that a correction factor is required when estimating  $K_{OA}$  from measured values of  $K_{OW}$  according to  $K_{OA} = K_{OW}/K_{AW}$ .

Due to the uncertainties mentioned above, it is desirable to further determine melting point, entropy of fusion,  $K_{OW}$ ,  $K_{AW}$ ,  $K_{OA}$  and  $S_o$  experimentally for a few selected congeners to ascertain the trend with bromination more accurately. For modelling exercises, all physical-chemical properties are of importance, but the parameters of main uncertainties and thus the ones where major focus should lie in future research efforts, are the degradation rates in various media, particularly in soils and sediments, as PBDEs are likely to be distributed here. Degradation rates in air are certainly also important, as they have strong impact on the LRT potential of PBDEs. However, there are fairly well established structure-property relationships for POP reaction with hydroxyl radicals, which is believed to be the most important degradation process in the atmosphere. Thus, current estimation methods used to calculate degradation rates in air are believed to be more reliable than for other media.

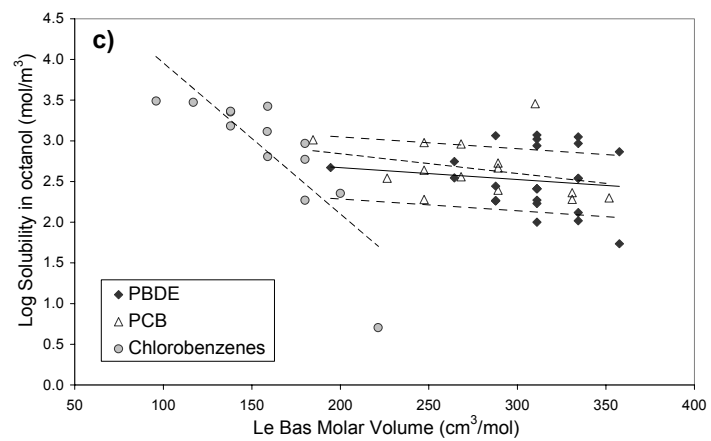
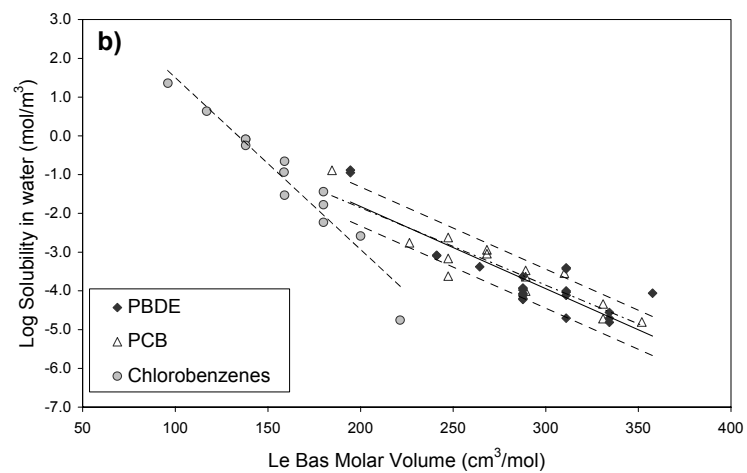
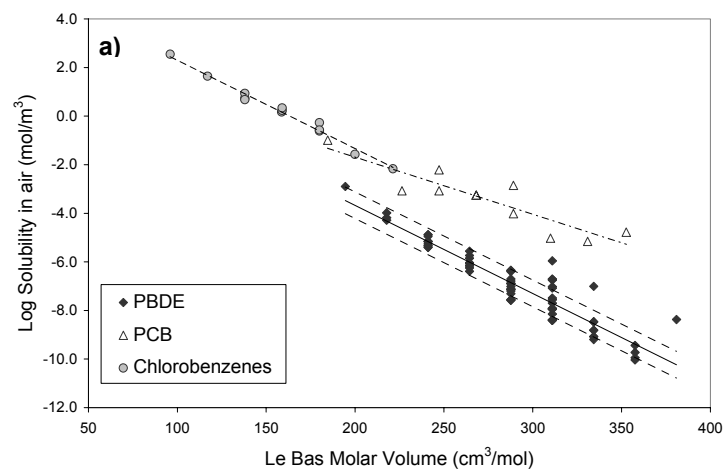
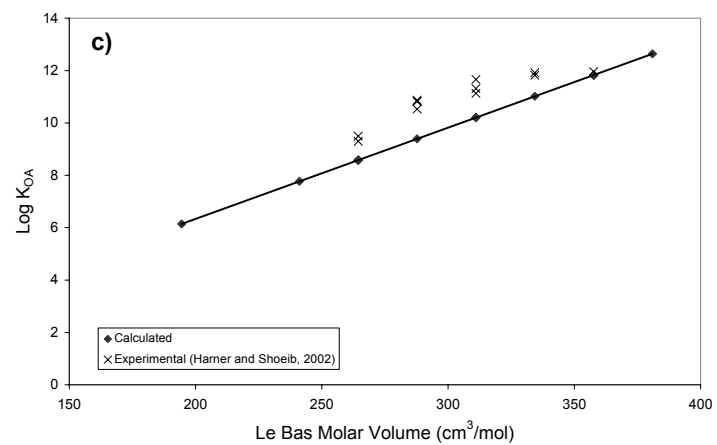
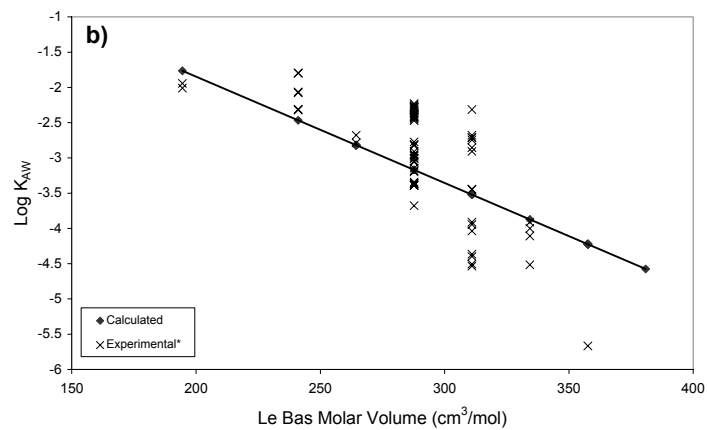
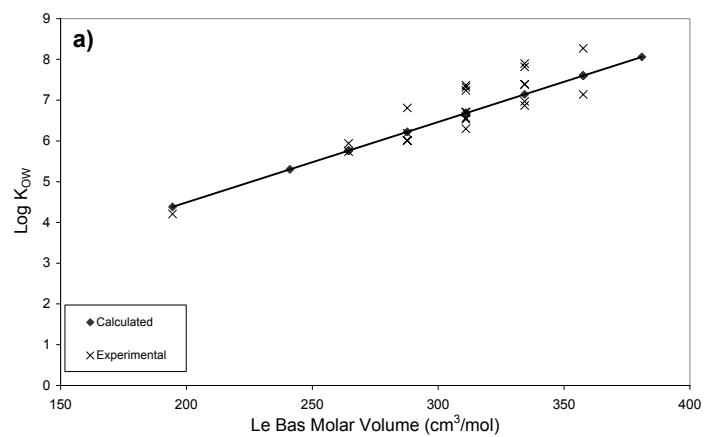


Figure A 1. Plots of log Solubility in air (i.e. vapor pressure/RT), water and octanol (i.e.  $K_{OW} \times S_W$ ) (mol/m<sup>3</sup>) for the liquid state at 25°C for PBDEs, chlorobenzenes and PCBs. The Le Bas Molar Volumes for penta, octa and decabrominated congeners are 311, 358 and 428 cm<sup>3</sup>/mol, respectively.



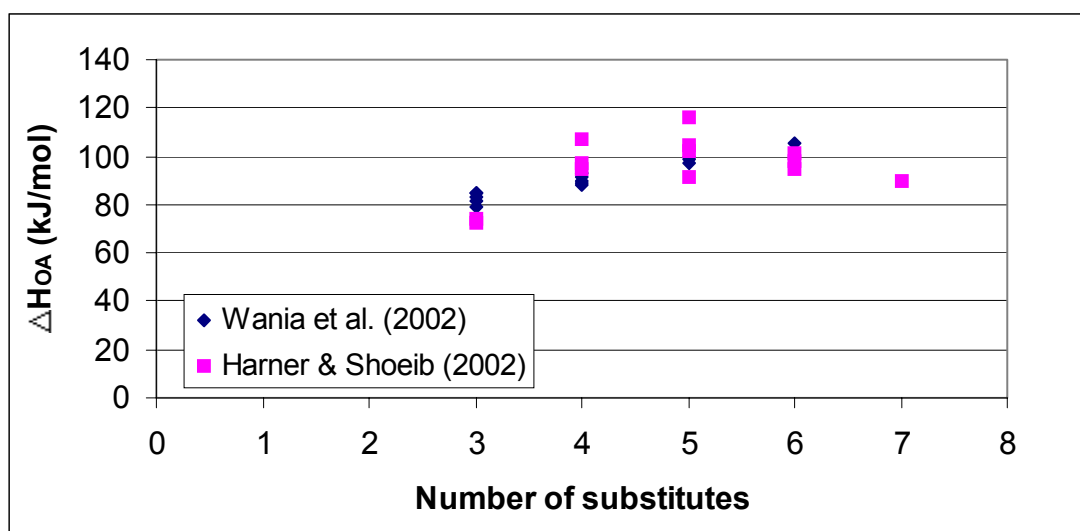
**Figure A 2. Plots of  $\text{Log } K_{ow}$ ,  $\text{Log } K_{aw}$  and  $\text{Log } K_{oa}$  versus Le Bas Molar Volume. \*Experimental values of  $\text{Log } K_{aw}$  were calculated from experimentally derived solubilities.**

The obtained equations (A1) – (A6) yield property data, which agree well with recent estimates by Wania and Dugani (2003). Table A 2 shows a comparison between property data derived here, to those in the study by Wania and Dugani (2003). On the average, the property data differ by 0.2 log units (factor of 1.6), with LogK<sub>OA</sub> disagreeing to a somewhat larger extent than the other properties. For lower brominated congeners (di-hexa), Wania and Dugani used an alternative method for deriving "best-estimates", which has been described in Beyer et al. (2002). The general agreement between the two property data sets is considered good, which is not surprising, since both studies were based on similar sets of existing reported property data. This indicates that for achieving internally consistent data sets for physical-chemical properties, either the three-solubility approach (Cole and Mackay, 2000) or the technique described in Beyer et al. (2002) may be used.

**Table A 2. Comparison between physical-chemical properties generated in this study, and recent estimates by Wania & Dugani (2003). Numbers have been rounded to two significant figures.**

<i>Homo logue</i>	<i>Log P<sub>L</sub> (Pa)</i>		<i>Log S<sub>L</sub> (mol/m<sup>3</sup>)</i>		<i>Log K<sub>OA</sub></i>		<i>Log K<sub>OW</sub></i>		<i>Log K<sub>AW</sub></i>	
	Wania & Dugani (2003)	This study	Wania & Dugani (2003)	This study	Wania & Dugani (2003)	This study	Wania & Dugani (2003)	This study	Wania & Dugani (2003)	This study
Mono	-1.3	-0.9	-2.1	-2.2	7.8	7.0	5.1	4.8	-2.5	-2.1
Di	-2.0	-1.8	-2.6	-2.7	8.6	7.8	5.5	5.3	-2.8	-2.5
Tri	-2.8	-2.6	-3.1	-3.2	9.4	8.6	5.8	5.8	-3.1	-2.8
Tetra	-3.7	-3.7	-3.7	-3.7	10	9.4	6.4	6.2	-3.4	-3.2
Penta	-4.4	-4.3	-(4.0-4.2)	-4.2	11	10	6.8	6.7	-(3.7-3.8)	-3.5
Hexa	-5.0	-5.1	-4.6	-4.7	12	11	6.5	7.1	-3.9	-3.9
Hepta	-6.0	-6.0	-5.1	-5.2	13	12	7.5	7.6	-4.2	-4.2
Octa	-6.7	-6.8	-5.6	-5.7	14	13	7.9	8.1	-4.5	-4.6
Nona	-7.5	-7.7	-6.0	-6.2	14	13	8.3	8.5	-4.8	-4.9
Deca	-8.3	-8.5	-6.5	-6.7	15	14	8.7	9.0	-5.1	-5.3

Apart from partition coefficients, enthalpies of phase transfer, reaction rates with OH radicals and environmental half-lives in different media are also required as model input. As discussed above, it is desirable to use property data that are as internally consistent as possible. Values of log K<sub>OW</sub> and log K<sub>AW</sub> for congeners of varying degree of bromination were derived from Equations A4-A6. Enthalpies of octanol-air transfer ( $\Delta H_{OA}$ ) have been derived by Wania et al. (2002) and Harner and Shoeib (2002). The measured values obtained for individual congeners in these studies differ somewhat and are shown in Figure A 3.



**Figure A 3. Measured values of  $\Delta H_{OA}$  for PBDEs of varying degree of bromination from Wania et al. (2002) and Harner & Shoeib (2002).**

The results from the individual studies of  $\Delta H_{OA}$  are all in the same order of magnitude but the obtained trends are not identical. The average values from these studies for each degree of bromination were used for the modelling study (see Table 4.3). As shown in Figure A 3,  $\Delta H_{OA}$  has not been measured for higher substituted compounds than heptaBDE. It is thus not clear whether  $\Delta H_{OA}$  continues to decrease for higher brominated compounds, as indicated in the study by Harner and Shoeib (2002), or rises, as in Wania et al. (2002; see Figure A 3). However, surface-air exchange should be of less importance for higher brominated congeners due to their low volatility, thus we use the values for heptaBDE for all the higher brominated compounds (Gouin et al., 2002).

The enthalpy change for the phase transfer of the dissolved compound from air to water ( $\Delta H_{AW}$ ) was determined from:

$$\Delta H_{AW} = \Delta H_{OW} - \Delta H_{OA} \quad (A7)$$

where  $\Delta H_{OW}$  is the enthalpy change for the phase transition of the dissolved compound from octanol to water, which was assumed to be 15, 20 and 25 kJ/mol for tri-, tetra- to hexa- and hepta- to deca-substituted congeners respectively, which is similar to the default values adopted by Wania and Dugani (2003), with the deviation that we assume a somewhat lower enthalpy of phase change for lower brominated compounds and a slightly higher one for the higher brominated congeners.

Half-lives for different environmental media and reaction rates with OH radicals in the atmosphere were estimated with the Estimations Programs Interface for Windows (EPIWIN) software (Meylan, 1999, see the Syracuse Research Corporation Inc. web site at <http://esc.syrres.com/interkow/epi.htm> for a description of the estimation software). The EPIWIN software estimates physical-chemical properties and reaction rates from structure alone and is now widely used by chemical regulators, particularly in the US. For the purpose of consistency, all first order biodegradation rate constants were estimated using EPIWIN. It should be noted that the estimated half-lives are extremely uncertain, and may be underestimated. It has been observed that EPIWIN largely overestimates the reactivity of well-known POPs (see further section 7). However, for PBDEs experimentally derived half-lives are not available, and thus

EPIWIN estimates were used. Estimated activation energies (J/mol) were taken from Wania and Dugani (2003).

**Table A 3. Reported properties of polybrominated diphenyl ethers**

<i>Substitution</i>	<i>Wsol (mg/L)</i>	<i>log K<sub>OW</sub></i>	<i>log K<sub>OA</sub></i>	<i>P<sup>S</sup> (Pa)</i>	<i>MP (°C)</i>
<b>0</b>	18 <sup>a</sup> 21 <sup>b</sup>	4.21 a		2.99 a	27.45 a
<b>1</b>				P <sub>L</sub> <sup>S</sup> : 0.163 (# 1), 0.128 (# 2)e P <sub>L</sub> <sup>S</sup> : 0.259 (# 3)h	
<b>2</b>	0.13 ± 0.02 (# 15)h	5.03 c		(1.27-1.89)×10 <sup>-2</sup> c P <sub>L</sub> <sup>S</sup> : 1.68×10 <sup>-2</sup> (# 7), 1.37×10 <sup>-2</sup> (# 8), 2.77×10 <sup>-2</sup> (# 10), 1.19×10 <sup>-2</sup> (# 12), 1.13×10 <sup>-2</sup> (# 13) 9.84×10 <sup>-3</sup> (# 15) e P <sub>L</sub> <sup>S</sup> : 1.73×10 <sup>-2</sup> (# 15)	56-56.5 (#15)f 57-58 (#15)h
<b>3</b>	(7.0 ± 1.0) × 10 <sup>-2</sup> (# 28) <sup>h</sup>	5.47-5.58 <sup>c</sup> 5.74 ± 0.22 (# 17), 5.94 ± 0.15 (# 28) <sup>m</sup>	9.3 (# 17), 9.5 (# 28) <sup>d</sup>	(1.5-2.7)×10 <sup>-3</sup> c P <sub>L</sub> <sup>S</sup> : 2.19×10 <sup>-3</sup> (# 17), 2.01×10 <sup>-3</sup> (# 25) 1.6×10 <sup>-3</sup> (# 28) 4.56×10 <sup>-3</sup> (# 30), 2.25×10 <sup>-3</sup> (# 32), 1.78×10 <sup>-3</sup> (# 33), 1.39×10 <sup>-3</sup> (# 35), 1.02×10 <sup>-3</sup> (# 37) <sup>e</sup> P <sub>L</sub> <sup>S</sup> : 1.7×10 <sup>-4</sup> (# 28) <sup>g</sup> P <sub>L</sub> <sup>S</sup> : 2.19×10 <sup>-3</sup> (# 28) <sup>h</sup>	64-64.5 (# 28) 85-86 (# 30) 77-77.5 (# 32), 48-49 (# 37) <sup>f</sup> 64-64.5 (# 28) <sup>h</sup>
<b>4</b>	1.09×10 <sup>-2</sup> b 1.53×10 <sup>-2</sup> g (1.5 ± 0.2) × 10 <sup>-2</sup> (# 47), (1.8 ± 0.3) × 10 <sup>-2</sup> (# 66), (6.0 ± 0.1) × 10 <sup>-3</sup> (# 77) <sup>h</sup>	5.87-6.16 <sup>c</sup> 6.19 <sup>g</sup> 6.81 ± 0.08 (# 47) <sup>m</sup>	10.53 (# 47), 10.82 (# 66), 10.87 (# 77) <sup>d</sup>	2.6-3.3×10 <sup>-4</sup> c P <sub>L</sub> <sup>S</sup> : 3.19×10 <sup>-4</sup> (# 47), 2.38×10 <sup>-4</sup> (# 66), 4.0×10 <sup>-4</sup> (# 69), 4.10×10 <sup>-4</sup> (# 71), 4.92×10 <sup>-4</sup> (# 75), 1.56×10 <sup>-4</sup> (# 77) <sup>e</sup> P <sub>L</sub> <sup>S</sup> : 2.1×10 <sup>-5</sup> (# 47) <sup>g</sup> P <sub>L</sub> <sup>S</sup> : 1.86 × 10 <sup>-4</sup> (# 47), 1.22×10 <sup>-4</sup> (# 66), 6.79×10 <sup>-5</sup> (# 77) <sup>h</sup>	78.5-79 (# 47) 96-97 (# 51) 134-135 (# 71) 134.5-135.5 (# 75) 94-95 (# 77) <sup>f</sup> 83.5-84.5 (# 47) 104-108 (# 66) 96.5-98 (# 77) <sup>h</sup> 82-82.5 (# 47) <sup>i</sup>
<b>5</b>	(6.0 ± 0.1) × 10 <sup>-3</sup> (# 85), (9.4 ± 0.8) × 10 <sup>-3</sup> (# 99), (4.0 ± 1.0) × 10 <sup>-2</sup> (# 100) <sup>h</sup> 9.0 × 10 <sup>-7</sup> j 2.4 × 10 <sup>-3</sup> (# 99) <sup>k</sup>	6.46-6.97 <sup>c</sup> 6.57 <sup>g</sup> 7.37 ± 0.12 (# 85) 7.32 ± 0.14 (# 99) 7.24 ± 0.16 (# 100) <sup>m</sup>	11.66(# 85), 11.31 (# 99), 11.13 (# 100), 11.97(# 126) <sup>d</sup>	2.9-7.3×10 <sup>-5</sup> c P <sub>L</sub> <sup>S</sup> : 2.81×10 <sup>-5</sup> (# 85), 6.82×10 <sup>-5</sup> (# 99), 4.99×10 <sup>-5</sup> (# 116), 8.07×10 <sup>-5</sup> (# 119) <sup>e</sup> P <sub>L</sub> <sup>S</sup> : 3.6×10 <sup>-6</sup> (# 85) 1.2×10 <sup>-5</sup> (# 99) <sup>g</sup> P <sub>L</sub> <sup>S</sup> : 9.86×10 <sup>-6</sup> (# 85), 1.76×10 <sup>-5</sup> (# 99), 2.86×10 <sup>-5</sup> (# 100) <sup>h</sup>	123.3(# 85), 92.3 (# 99) <sup>i</sup> 97-98 (# 100), 199.5-200 (# 116), 86-87 (# 119) <sup>f</sup> 119-121 (# 85) 90.5-94.5 (# 99) 100-101 (# 100) <sup>h</sup>



<b>6</b>	$(8.7 \pm 0.6) \times 10^{-4}$ (# 153) $(8.7 \pm 0.9) \times 10^{-4}$ (# 154) <sup>h</sup>	6.86-7.92 <sup>c</sup> 7.90 ± 0.14 (# 153) 7.82 ± 0.16 (# 154) <sup>m</sup>	11.82 (# 153), 11.92(# 154), 11.97(# 156) <sup>d</sup>	4.2-9.4×10 <sup>-6c</sup> P <sub>L</sub> <sup>S</sup> : 8.43×10 <sup>-6</sup> (# 153) <sup>e</sup> P <sub>L</sub> <sup>S</sup> : 1.9×10 <sup>-6</sup> (# 138) <sup>g</sup> P <sub>L</sub> <sup>S</sup> : 1.58×10 <sup>-6</sup> (# 138), 2.09×10 <sup>-6</sup> (# 153), 3.80×10 <sup>-6</sup> (# 154) <sup>h</sup>	180-181 (# 140) 142-143 (# 154) 183.5-184.5(# 166) <sup>f</sup> 160-163 (# 153) 131-132.5 (# 154) <sup>h</sup> 182.3-182.8 (# 128), <sup>i</sup> 134.2 (# 138), 157.6 (# 153) <sup>i</sup>
<b>7</b>	$(1.5 \pm 0.3) \times 10^{-3}$ (# 183) <sup>h</sup>	8.27 ± 0.26 (# 183) <sup>m</sup>	11.96(# 183) <sup>d</sup>	P <sub>L</sub> <sup>S</sup> : 9.05 × 10 <sup>-7</sup> (# 190) <sup>e</sup> P <sub>L</sub> <sup>S</sup> : 2.3×10 <sup>-7</sup> (# 190) <sup>g</sup> P <sub>L</sub> <sup>S</sup> : 4.68×10 <sup>-7</sup> (# 183) 2.82×10 <sup>-7</sup> (# 190) <sup>h</sup>	156-157 (# 181), 197-197.5 (# 190) <sup>f</sup> 171-173 (# 183) <sup>h</sup>
<b>8</b>		8.35-8.9 <sup>c</sup>		1.2-2.2×10 <sup>-7 c</sup>	206 <sup>i</sup>
<b>9</b>					
<b>10</b>		9.97 <sup>c</sup>			

<sup>a</sup>SRC (2000), <sup>b</sup>EU (2000), <sup>c</sup>Watanabe and Tatsukawa (1989), <sup>d</sup>Harner and Shoeib (2002), <sup>e</sup>Wong et al. (2000), <sup>f</sup>Marsh et al. (1999), <sup>g</sup>Tittlemier and Tomy (2001), <sup>h</sup> Tittlemier et al. (2002), <sup>i</sup>Örn et al. (1996), <sup>j</sup>WHO (1994), <sup>k</sup>Stenzel and Markley (1997), <sup>l</sup>Lassen et al. (1999), <sup>m</sup>Braekvelt et al.(2003)

## Appendix 2 Estimates of global production and consumption of commercial PBDE products

Year	Global Br production (tonnes) <sup>1</sup>	BFR/bromine ratio <sup>2</sup>	Total BFR production <sup>3</sup>	PBDE/BFR ratio <sup>4</sup>	PBDE production <sup>5</sup>	penta/PBDE ratio <sup>6</sup>	PentaBDE Production	octa/PBDE ratio <sup>6</sup>	OctaBDE production	deca/PBDE ratio <sup>6</sup>	DecaBDE production
1970	210 000	0.01	2 100	0.33	693	0.1	69	0.15	104	0.75	520
1971	230 000	0.01	2 300	0.33	759	0.1	76	0.15	114	0.75	569
1972	265 000	0.01	2 650	0.33	875	0.1	87	0.15	131	0.75	656
1973	272 000	0.01	2 720	0.33	898	0.1	90	0.15	135	0.75	673
1974	289 000	0.01	2 890	0.33	954	0.1	95	0.15	143	0.75	715
1975	277 000	0.01	2 770	0.33	914	0.1	91	0.15	137	0.75	686
1976	309 000	0.01	3 090	0.33	1 020	0.1	102	0.15	153	0.75	765
1977	350 000	0.01	3 500	0.33	1 155	0.1	116	0.15	173	0.75	866
1978	361 000	0.01	3 610	0.33	1 191	0.1	119	0.15	179	0.75	893
1979	403 000	0.01	4 030	0.33	1 330	0.1	133	0.15	199	0.75	997
1980	343 000	0.05	17 150	0.33	5 660	0.1	566	0.15	849	0.75	4 245
1981	344 000	0.1	34 400	0.33	11 352	0.1	1 135	0.15	1 703	0.75	8 514
1982	383 000	0.15	57 450	0.33	18 959	0.1	1 896	0.15	2 844	0.75	14 219
1983	364 000	0.2	72 800	0.33	24 024	0.1	2 402	0.15	3 604	0.75	18 018
1984	397 000	0.25	99 250	0.33	32 753	0.1	3 275	0.15	4 913	0.75	24 564
1985	382 000	0.3	114 600	0.33	37 818	0.1	3 782	0.15	5 673	0.75	28 364
1986	375 000	0.32	120 000	0.33	39 600	0.1	3 960	0.15	5 940	0.75	29 700
1987	391 000	0.34	132 940	0.33	43 870	0.1	4 387	0.15	6 581	0.75	32 903
1988	370 000	0.36	133 200	0.33	43 956	0.1	4 396	0.15	6 593	0.75	32 967
1989	409 000	0.38	155 420	0.33	51 289	0.1	5 129	0.15	7 693	0.75	38 466

1990	390 000	0.4	156 000	0.33	51 480	0.1	5 148	0.15	7 722	0.75	38 610
1991	392 000	0.41	160 720	0.33	53 038	0.10	5 481	0.14	7 425	0.76	40 132
1992	397 000	0.43	170 710	0.33	56 334	0.11	6 009	0.13	7 323	0.76	43 002
1993	392 000	0.45	176 400	0.33	58 212	0.11	6 403	0.12	6 985	0.77	44 823
1994	420 000	0.47	197 400	0.33	65 142	0.11	7 383	0.11	7 166	0.78	50 594
1995	437 000	0.47	205 390	0.33	67 779	0.12	7 908	0.1	6 778	0.78	53 093
1996	483 000	0.38	183 540	0.33	60 568	0.12	7 268	0.09	5 451	0.79	47 849
1997	517 000	0.38	196 460	0.33	64 832	0.12	7 996	0.08	5 187	0.80	51 649
1998	514 000	0.38	195 320	0.33	64 456	0.13	8 164	0.07	4 512	0.80	51 779
1999	550 000	0.4	220 000	0.33	72 600	0.13	9 438	0.06	4 356	0.81	58 806
2000	542 000	0.4	216 800	0.33	71 544	0.13	9 301	0.06	4 293	0.81	57 951
2001	523 000	0.4	209 200	0.33	69 036	0.11	7 594	0.056	3 866	0.83	57 300

<sup>1</sup>USGS (2002), <sup>2</sup>1970-1993 data: assumed stepwise increase from 1980 to 1994 level; 1994-2001: Lyday (2001) <sup>3</sup> Calculated as  $BFR_{prod} = Br_{prod} \times BFR/Br \text{ ratio}$  <sup>4</sup> 1970 – 1990 data: KEMI (1994); 1990-1998: assumed stepwise increase to 1999 level; 1999-2001: BSEF (2000, 2003)

<sup>5</sup>Calculated as  $PBDE_{prod} = BFR_{prod} \times PBDE/BFR \text{ ratio}$  <sup>6</sup>1970 – 1990 data: KEMI (1994); 1990-1998: assumed stepwise increase to 1999 level; 1999-2001: BSEF (2000, 2003)