

# **Abstracts BFR 2001**

## **Part 5**

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## Levels and Trends of PBDEs in North American Environment

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### **SUMMARY:**

A summary of physical and chemical properties of polybrominated brominated diphenyl ethers (PBDEs) recently determined in North American is presented. The focus of this overview is on the majority of data available from investigations in North American, which consists of levels and trends of PBDEs; however limited data of other brominated flame-retardants (BFRs) such as polybrominated biphenyls (PBBs) in lake trout from the Great Lakes and tetrabromobisphenol A (TBBPA) in sewage sludge are also available.

### **Physical Properties:**

Vapor pressures of various PBDE congeners were recently determined by Wong et al.<sup>i</sup>, and Tittlemier and Tomy<sup>ii</sup>. PBDE vapor pressures ranged between 0.1 Pa and  $10^{-6}$  Pa for BDE-2 and -190, respectively. These results indicate that PBDE congeners such as BDE-47 and -99 are mainly in the vapor phase and may travel further than higher molar mass congeners such as BDE-153 or -209, which are partially or almost totally transported in the particulate phase.  $K_{oa}$ s for PBDEs determined by Harner<sup>iii</sup> are presented at this workshop.

### **LEVELS:**

#### **Biological Compartment:**

Shortly after Andersson and Blomkvist<sup>iv</sup> first reported the occurrence of PBDEs in biota from Viskan River, Stafford<sup>v</sup> reported the presence of PBDEs in eggs and tissues of fish-eating birds from six states in the US and from Ontario, Canada. Recently, Simon and Wakeford<sup>vi</sup> demonstrated the presence of PBDEs and their metabolites in wildlife tissue and egg homogenates.

In freshwater ecosystem, Sergeant et al.<sup>vii</sup> reported the levels of PBDEs in CRMs, which consisted of lake trout from Lake Ontario (23.5 ng/g wet weight) and herring from the Pacific Ocean (1.4 ng/g wet weight). Alae et al.<sup>viii</sup> reported 540 ng/g lipid weight, 240 ng/g lipid weight and 140 ng/g lipid weight of PBDEs in lake trout from Lakes Ontario, Huron,

and Superior respectively. Hale et al.<sup>ix</sup> reported elevated concentrations of PBDEs (>1000 ng/g lipid weight) in fish from 9 out of 50 sites along Roanoke and Dan rivers in Virginia, USA. Crappie and bluegill fish from Hadley Lake in Indiana, USA were collected near a local source contained higher levels of BDE-153 and BDE-154, while the same type of fish collected from Lake of the Ozarks in central Missouri, USA had higher levels of BDE-47 followed by -99 and -100. <sup>x</sup>Concentrations of BDE-153 and-154 were significantly lower in the fish from Lake of the Ozarks than those reported from Hadley Lake.

In marine ecosystem, Kuehl et al.<sup>xi</sup> reported 180-220 ng/g lipid weight of PBDEs in bottlenose dolphins from the south Atlantic US coast. Later on, Kuehl and Haebler <sup>xii</sup> reported levels up to 8000 ng/g lipid weight of PBDE in bottlenose dolphins from the Gulf of Mexico. Harbor seals from California had mean concentration of 1280 ng/g lipid weight (sum of BDE-47, -99 and -153).<sup>xiii</sup> Ring seals from the Canadian Arctic had mean concentration 10 and 19 ng/g lipid weight for females and males respectively; belugas from the same region had 29 and 57 ng/g lipid weight for females and males respectively. Concentrations of PBDEs in marine environments from the Canadian West Coast were reported by Ikononou et al.<sup>xiv</sup>. PBDE concentrations in dungeness crab ranged between 50 and 310 ng/g lipid weight; and for porpoise ranged between 300 and 2300 ng/g lipid weight. Lebeuf and Trottier<sup>xv</sup> reported PBDE levels in marine mammals and fish from St. Lawrence Estuary; PBDE concentrations in fish ranged between 12 and 275 ng/g wet weight, and in beluga ranged between 22 and 933 ng/g wet weight.

### **A-biotic Compartments:**

There are limited data available on a-biotic compartments in North America. Concentrations of PBDEs in air samples collected from the Great Lakes area ranged between 77 pg/m<sup>3</sup> for Chicago and 6.9 pg/m<sup>3</sup> for Eagle Harbor. PBDE concentrations in Arctic air samples collected in 1994 ranged between 5 pg/m<sup>3</sup> for Dunai, Russia and 2000 pg/m<sup>3</sup> for Tagish, Yukon, Canada<sup>xvi</sup>. The high levels observed in air samples from the Yukon can be attributed to waste incineration near the sampling site.

M<sup>c</sup>Crea et al.<sup>xvii</sup> reported the concentration of PBDEs in dissolved water from Lake Ontario. Using Infiltrax devices, in excess of 100 L of water was extracted *in situ* with XAD resin. PBDE concentrations in suspended sediments from Wapiti River ranged between 0.9 and 2-ng/g dry weight. PBDEs have also been detected in both freshwater and marine sediments. The surface sediment from a sediment core collected from the western basin of Lake Ontario contained 20 ng/g dry weight PBDEs (di-deca); the concentration of BDE-209

in this sample was 13 ng/g. PBDEs have also been detected in marine sediments from St Lawrence Estuary<sup>xviii</sup>, and Strait of Georgia<sup>xix</sup>.

## **TRENDS:**

### **Biota:**

There is conclusive evidence that the levels of PBDEs are increasing steadily in the North American environment during the past 20 years as confirmed by reports of levels in lake trout from Lake Ontario<sup>xx</sup>, gull eggs from Snake Island in Lake Ontario<sup>xxi</sup>, seal from Holman Islands NWT, Canada, and beluga from the eastern Arctic Ocean<sup>xxii</sup>. PBDE concentration in lake trout from Lake Ontario increased from 3 ng/g lipid weight in 1978 to 945 ng/g lipid weight in 1998. Trends in gull eggs homogenate increased from 2ng/g lipid weight to 610 ng/g between 1981 and 1999. The concentrations of PBDEs increased by 70 folds seals from Holman island and in belugas from the eastern Arctic Ocean by 80 folds.

### **Sediment cores:**

Sediment cores can provide a record of the fluxes of contaminants including PBDEs into the environment. Sediment cores from Lake Ontario show a steady increase in the flux of PBDEs into Lake Ontario over the past thirty years. Interestingly, there was an unexpected rise in the flux of PBDEs about 1950<sup>xxiii</sup>.

## **CONCLUSION:**

PBDEs are ubiquitous contaminants in the North American environment. In general similar patterns and levels of PBDEs are observed in Europe, Asia and North America. Most of the PBDEs observed in biota are BDE- 47, 99, and 100, which are the principal components of the penta-BDE formulation. Recently the increase in PBDE concentrations in biota appears to have slowed down in Europe<sup>xxiv</sup>, while continued usage of the penta-BDE formulation in North America is reflected in a corresponding increase in PBDE concentrations in biota<sup>xxv</sup>.

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## Levels and Trends of BFRs in the European Environment

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Recent results on levels and trends of several polybrominated diphenyl ethers such as 2,2',4,4'-TeBDE (BDE-47), 2,2',4,4',5-PeBDE (BDE-99), 2,2',4,4',6-PeBDE (BDE-100) and decabrominated diphenyl ether (BDE-209) are presented. Some other BFRs are included such as tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD).

**Air:** Swedish air samples contained 1-8 pg/m<sup>3</sup> of sumPBDE (sum of BDE-47, -99 and -100) as well as 5.3-6.1 pg/m<sup>3</sup> HBCD<sup>1</sup>. Air samples collected at one rural site in southern England (Stoke Ferry) and one semi-rural site in northwestern England (Hazelrigg) contained tri- to heptaBDEs with sum concentrations of BDE-47, -99 and -100 of 7 - 28 pg/m<sup>3</sup> at Hazelrigg and 11 - 67 pg/m<sup>3</sup> at Stoke Ferry<sup>2,3</sup>.

**Sewage sludge:** Sewage sludge from a plant with input from a plastics industry using TBBPA and a plant having no known sources of TBBPA had levels of 56 and 31 ng/g dw, respectively<sup>4</sup>. Digested sewage sludge samples collected in 1998 from Stockholm showed the presence of BDE-47 (39-91 ng/g dw), BDE-99 (48-120 ng/g dw), BDE-100 (11-28 ng/g dw) and BDE-209 (140-350 ng/g dw) as well as TBBPA (2.9-76 ng/g dw)<sup>5</sup>. HBCD was also present.

**Sediments:** Sediment samples collected up- and downstream of a Swedish plastics industry using TBBPA contained TBBPA and dimethylated TBBPA (MeTA) (4) as well as BDE-47, -99 and -100<sup>6</sup> with found in higher concentrations downstream of the plant than upstream: 270, 1500, 490, 750 and 170 ng/g dw, respectively, in the downstream samples. Surficial sediment samples from a Swedish river with numerous textile industries had increasing concentrations of BDE-47, -99, -100 and -209 as well as HBCD further downstream as more industries were passed<sup>7</sup>. The range of sumPBDE levels were nd-9.6 ng/g dw, BDE-209 were nd-360 ng/g dw and HBCD were nd-1600 ng/g dw. Twenty surficial sediment samples taken from numerous sites in the Baltic Sea had sumPBDE levels of nd-1.1 ng/g dw<sup>8</sup>.

Several BFRs were analyzed in sediments collected from the mouths of major European rivers<sup>5,9</sup>. BDE-47 and -99 concentrations were highest in two Great Britain rivers (Humber and Mersey) and two in the Netherlands (1.61-13.1 ng/g dw). Highest 2,2',4,4',5,5'-HxBB levels were found in the Seine (France), three rivers in the Netherlands, the rivers Schelde (Belgium), Forth (Great Britain) and Ems (Germany) (0.013-0.056 ng/g dw). Levels of DeBB were highest in sediment from the Seine (2.4-3.9 ng/g dw). BDE-209 levels were highest in the River Mersey (Great Britain), followed by the Schelde and River Liffey (Ireland) (34-1800 ng/g dw). PBDE were analyzed in sediments from several rivers and estuaries in the United Kingdom up- and downstream of suspected sources and at a reference site. Concentrations ranges were <0.3-368 ng/g dw for BDE-47, <0.6-898 ng/g dw for BDE-99 and <0.6-3190 ng/g dw for BDE-209 quantified as the technical product DE-83<sup>10</sup>. Sediment cores from a freshwater lake in Germany, the Wadden Sea and from Drammenfjord (Oslo fjord) all contained measurable amounts of BDEs -28, -47, -66, -99, and -100<sup>11</sup>. The Drammenfjord and lake samples also contained BDEs -153 and -154, and the Wadden Sea and lake samples contained BDE-209 (Drammenfjord had not been analyzed yet).

**Biota:** Levels of sumPBDE are low in herbivorous mammals and birds from the terrestrial ecosystem: 5.7-13 ng/g lipid weight (lw) in starlings, 0.47-1.7 ng/g lw in reindeer and moose (all from Sweden)<sup>6,12,13</sup> and 2.5-4.5 ng/g fat in German cow's milk<sup>14</sup>. BDE-47, -99 and -153 have recently been quantified in global butter samples and highest sumPBDE levels were found in Great Britain (2.5 ng/g lipid), followed by Mexico, Germany and the USA (0.4-0.55 ng/g lipid)(K.C. Jones and A. Kierkegaard, personal communication). However, concentrations of PBDEs in eggs from pilgrim falcon from northern and southern Sweden contain high concentrations: BDE-47, 15-3800 ng/g lw; BDE-99, 110-9200 ng/g lw; BDE-100, 77-5200 ng/g lw; BDE-153, 270-16000 ng/g lw; BDE 154, 50-4400 ng/g lw, BDE-183, 56-1300 ng/g lw; BDE-209, 28-430 ng/g lw<sup>15</sup>. HBCD was also present in high concentrations (approx. 34-2400 ng/g lw). PBDE concentrations found in freshwater fish depend on the species and the collection site. In eels from Dutch rivers and lakes (10 locations), levels of BDE-47 ranged from <20 to 1700 ng/g lw<sup>16</sup>. Several species of freshwater fish from North-Rhine Westphalia contained 18-983 ng PBDE/g lw<sup>14</sup>. Various fish species studied from background areas in Sweden had sumPBDE concentrations ranging from 26-1200 ng/g lw<sup>6,12,13</sup>. Along the River Viskan, upstream and downstream of textile industries using BFRs, sumPBDE concentrations in pike ranged from nd-4600 ng/g lipid and HBCD ranged from nd-8000 ng/g lw<sup>7</sup>. Several species of flatfish were collected in the estuaries of rivers in the

United Kingdom up- and downstream of suspected sources and at a reference site. Concentration ranges were 73-9500 ng/g lw for BDE-47 and 16-790 ng/g lw for BDE-99<sup>10</sup>. Cod liver collected from three regions of the North Sea had sum levels of BDEs -47 and -99 of 1.9-360 ng/g lw<sup>17,18</sup>. SumPBDE levels in herring from five sites along the Swedish coast ranged from 17-62 ng/g lw<sup>6,13</sup> and in the Baltic Sea, 3.2 to 32 ng/g lw<sup>19</sup>. Levels of 8.4-100 ng/g lw were found in herring from three regions in the North Sea<sup>16,18</sup>. BDE-47 and -99 levels in Baltic salmon were 167-190 and 52 ng/g lw, respectively<sup>19,20</sup>.

SumPBDE concentrations in osprey found dead in Sweden were 2100 ng/g lw<sup>6,12,13</sup> and levels in white-tailed sea eagle collected from the Baltic Sea were 350 ng/g lw<sup>21</sup>. Common guillemots collected in 1979-81 from the Baltic and North Seas contained 370 and 80 ng PBDE/g lw and Brunnich's guillemot from Svalbard (Arctic) contained 130 ng PBDE/g lw<sup>21</sup>. Baltic guillemot eggs collected in 1994 contained sumPBDE of 570 ng/g lw<sup>6</sup>.

Female ringed seals collected in 1981 from Svalbard contained sumPBDE levels of 40-51 ng/g lw<sup>6,13,21</sup>. Baltic Sea harbour seal contained 90 ng PBDE/g lw, and harbour seal from the North Sea contained 10 ng PBDE/g lw<sup>6,21</sup>. Female grey seals from the Baltic Sea collected in 1979-1985 contained 730 ng/g lw<sup>6,12,13</sup>. Blubber from Baltic grey and ringed seals collected between 1981 and 1988 contained 419 and 350 ng/g lw, respectively<sup>19</sup>. Harbour seal from the Dutch coast contained 605-6010 ng/g lw<sup>22</sup>.

De Boer et al.<sup>22</sup> found PBDE levels of 187-349 ng/g lw in sperm whale, 869 ng/g lw in minke whale and 7700 ng/g lw in white-beaked dolphin collected along the Dutch coast in 1998. Long-finned pilot whales from the Faroe Islands had PBDE concentrations (19 congeners) ranging from 843-3160 ng/g lw<sup>23</sup>.

**Temporal trends:** Temporal trends in biological samples indicate increasing levels of BDE-47, -99 and -100 in the environment since the 1970s. The trends in guillemot indicate that levels of BDEs -47, -99 and -100 have begun to decline in the Baltic Sea in the 1990s<sup>24</sup>. The trends in pike from Lake Bolmen, Sweden, indicate a levelling off of PBDE levels in the 1990s. However, the human breast milk trend indicates that levels are increasing exponentially, doubling every five years<sup>25</sup>. Temporal trends in sediment cores from Drammenfjorden, a German freshwater lake and the Wadden Sea show that the lower brominated BDEs appear in the 1960s and BDE-209 appears about 10 years later<sup>11</sup>. The core from Drammenfjord shows increasing trends for all BDEs up to 1999 (BDE-209 not analyzed yet).

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## **Brominated Flame Retardants in the UK Environment**

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### **Abstract**

This paper summarises available data for the brominated flame retardant compounds - the polybrominated biphenyls and diphenyl ethers, in the UK environment prior to 2001.

Polybrominated biphenyls were either undetectable or (for BB209) found occasionally at low concentrations. High concentrations of brominated diphenyl ethers were found in some samples, particularly in the Rivers Skerne and Tees in NE England.

### **Introduction**

Historically there have been few studies on the occurrence and environmental concentrations of brominated flame retardants in the UK environment, to the extent that when the European Union called for data to be submitted for an assessment of the risk accompanying the continued use of these compounds within the Union, the Department of the Environment, Transport and the Regions in the UK had to commission a special survey. In 1997 the Oslo and Paris Commissions Secretariat also released the results of an initial European survey known as DIFFCHEM. The data from these studies, both of which considered only two classes of flame retardants, the polybrominated biphenyls and diphenyl ethers, are summarised in this paper.

### **The OSPAR DIFFCHEM study**

The DIFFCHEM study of contamination from diffuse sources drew on samples from 8 countries (Ireland, UK, France, Belgium, The Netherlands, Germany, Sweden and Norway) and 22 estuaries within Western Europe. Three sediment samples were taken in 1995 from each of the 22 sites, and, following analysis, the mean values were reported. Other contaminants were also determined in addition to the flame retardant compounds, and in order to avoid problems of data comparability, all analyses for specific compound groups were undertaken in a single laboratory. For the polybrominated biphenyls (PBBs) and diphenyl ethers (PBDEs), this was the Institute of Applied Environmental Research at Stockholm University<sup>1</sup>. Samples were collected using corers or grabs, transferred to glass jars and frozen at -20°C prior to analysis. The analytical method was after that of Nylund *et al.*<sup>2</sup>, and involved extraction using acetone and *n*-hexane of the dried < 63 µm fraction, elimination of

elemental sulphur using Jensen's reagent<sup>3</sup>, clean-up with sulphuric acid, fractionation using HPLC on an amino column, and instrumental analysis using GC-NICIMS with ammonia as reagent gas. The ions due to bromine at 79 and 81 Da were monitored. Separate columns were used for the determination of the decabrominated compounds (BB209 and BDE209; 15m length) and the other brominated compounds (30m length), so as to prevent thermal degradation of the decabromo-compounds on the chromatographic column during the analysis. The compounds determined are listed in Table 1.

Table 1. Brominated flame retardant compounds determined in DIFFCHEM survey.

Congener	Compound
BB153	2, 2', 4, 4', 5, 5'-hexabromobiphenyl
BB209	Decabromobiphenyl
BDE47	2, 2', 4, 4'-tetrabromodiphenyl ether
BDE99	2, 2', 4, 4', 5-pentabromodiphenyl ether
BDE209	Decabromodiphenyl ether

Within the DIFFCHEM survey, for the bromobiphenyls, BB153 was not detected in any of the 6 samples from the UK (limit of detection 0.009  $\mu\text{g kg}^{-1}$  dry weight). BB209 was detected in 3 of the UK samples, at concentrations of 0.1 (Thames), 0.18 (Clyde) and 0.33 (Mersey)  $\mu\text{g kg}^{-1}$  dry weight. The highest values observed in the study for BB153 and BB209 were 0.05 and 3.4  $\mu\text{g kg}^{-1}$  dry weight respectively, both in the Seine estuary in France. For the brominated diphenyl ethers, all three BDE congeners were detected in all UK samples. Concentrations of BDE47 ranged from 0.2 to 5.8  $\mu\text{g kg}^{-1}$  dry weight, and for BDE99 the range was similar; 0.4 to 6.9  $\mu\text{g kg}^{-1}$  dry weight. In both cases the highest value was observed in the Humber. For BDE209 the range was 2.1 to 1,700  $\mu\text{g kg}^{-1}$  dry weight, with the highest value in the Mersey. For all three BDE congeners, the UK maximum value was the highest observed across all 22 samples.

#### Initial UK pilot survey

Allchin *et al.*<sup>4</sup> analysed samples of sediment and fish tissue in the vicinity and downstream of potential sources of brominated flame retardants, including sites of use and manufacture. Samples were collected during 1995/96. The methodology involved Soxhlet extraction of dried samples with acetone/*n*-hexane, alumina clean-up, and analysis using GC-ECD with confirmation by GC/MS in some samples. PBBs were screened on a formulation basis, and PBDEs were analysed both as formulations and as 3 specific congeners (BDE47, BDE85 & BDE100; also, the formulation DE-83 is essentially BDE209). No PBBs were detectable in any of the samples, at a limit of detection of 5  $\mu\text{g kg}^{-1}$  (on a formulation basis as Firemaster

BP-6). BDEs were detected in all but one of the 23 fish and shellfish samples analysed, including those taken at 5 offshore sites established under the UK National Monitoring Programme at 10 miles from the coast. BDE47 was the most abundant congener, the highest concentration observed being 1,290  $\mu\text{g kg}^{-1}$  wet weight in a flounder liver from Tees Bay. High concentrations of BDEs were found in sediments from both the River Skerne and the River Tees, in the latter case from the confluence of the two rivers right down to the lower estuary. This is downstream of a former production site, although there may also be additional local point sources within the catchment area. The formulation data indicated that the major part of the contamination was due to the penta- and octa-mixes of the polybrominated diphenyl ethers, such as DE-71 and DE-79. The highest concentration of BDE209, 3,190  $\mu\text{g kg}^{-1}$  dry weight, were seen in the River Calder below a sewage treatment works; BDE209 was also detected at lower concentrations in the River Ribble, near Avonmouth in the Bristol Channel, and in the Skerne and Tees Rivers.

### **Subsequent work**

These studies demonstrated significant contamination of the UK environment by PBDEs from industrial sources, and wider studies are now underway. Analysis of marine mammals has shown widespread contamination with these compounds, in both harbour porpoises and a number of species of pelagic whales and dolphins which feed primarily in deep offshore waters<sup>5,6</sup>. Further studies are continuing, both within the UK and in collaboration with two institutes in the Netherlands, and additional data will become available during 2001/02.

### **Acknowledgement**

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# LEVELS OF SOME POLYBROMINATED DIPHENYL ETHER (PBDE) FLAME RETARDANTS IN ANIMALS OF DIFFERENT TROPHIC LEVELS OF THE NORTH SEA FOOD WEB.

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## Summary

The levels of polybrominated diphenyl ethers (PBDE) have been studied in a model food chain of the North Sea. A clear geographical trend was observed in the levels found in the invertebrates, where the highest levels of the dominant congener of PeBDE occurred near the English coast.

## Introduction

Many plastics in household equipment, car interiors and textiles contain brominated flame retardants for fire safety reasons. The most frequently used PBDE (30,000 tons in 1992) is currently decabromodiphenylether (DeBDE); other PBDE flame retardants are pentabromodiphenyl ether (PeBDE; e.g. Bromkal 70-5DE), and octabromodiphenyl ether (OcBDE). PeBDE's main use is flame-retarded flexible polyurethane foam.

Like related organochlorines, the PBDEs are very hydrophobic ( $\log K_{ow}$  values 4-10) and resistant to degradation<sup>1</sup>. The water solubility and vapour pressure of the PBDEs decrease with increasing degree of bromination. Thus, these parameters have the lowest values for BDE 209.

Three major components of commercial PeBDE, i.e. the BDE congeners 47, 99 and 153 (numbering according to the IUPAC nomenclature for PCBs) showed even higher bioaccumulation factors as the comparably chlorinated PCBs in blue mussels, despite their larger molecular size<sup>1</sup>. These congeners, and BDE 100, are also widespread in biota<sup>2-5</sup>. The presence of tetra, penta- and hexa-brominated diphenyl ether congeners in deep-sea foraging animals as sperm whales indicates that these PBDEs can be regarded as globally occurring chemicals<sup>6</sup>.

Measurements of the levels of anthropogenic compounds in biota are often used for identifying geographical and temporal trends, and to obtain information about the availability of such compounds to humans. Because of their possible environmental spread, the inclusion of certain PBDEs in monitoring programmes is appropriate. The present study focussed on their determination in a number of animal species from the North Sea representing different trophic levels of the food web. Since the production figures of especially PeBDE formulations are momentarily decreasing, whereas those of DeBDE remain similar, the bioaccumulation potential of the fully brominated congener BDE 209 (>97% of commercial DeBDE) is of special interest.

### **Methods and materials**

*Invertebrates and fish:* The majority of the samples were taken during a cruise with the RV Pelagia in August-September 1999. The herring samples were caught at 51°34' N and 2°47' E by the fishing vessel TX 37. The following tissues were analysed: sea star: pyloric caeca; hermit crab: abdomen; whelk: whole body except the shell; fish: liver and fillet. No differentiation was made between the sexes. The levels of the PBDEs are expressed on the basis of extractable lipids<sup>7, 8</sup>.

*Marine mammals:* Samples of blubber and liver were analysed. The cetacean samples were obtained from Dr. Chris Smeenk. The samples of harbour seals were obtained from Dr. Ursula Siebert and originated from Wadden Sea area of Schleswig-Holstein (Germany). All samples came from beach-stranded animals, or animals drowned in fishing nets.

*Extraction:* Tissue amounts corresponding to approximately 50 mg lipid were extracted, using an ultra-Turrax method. After extraction with pentane and acetone, the sample was treated with sulphuric acid and a silica clean-up was performed.

*Analysis:* The levels of 15 individual PBDEs were determined by GC/MS. The GC was a Hewlett Packard 6890; the mass-selective detector a Hewlett Packard 5973. GC specifications: split-splitless injection, split valve closed for 1.5 min.  $T_{\text{injector}}$  270°C. Column: stationary phase CP Sil-8, 25 m \* 0.25 mm \* 0.25  $\mu\text{m}$  (Chrompack, NL). Carrier gas He; linear gas velocity 74  $\text{cm s}^{-1}$ , constant flow programmed. Oven temperature program: 90°C (1.5') / 20°C  $\text{min}^{-1}$  / 190°C (0') / 4.5°C  $\text{min}^{-1}$  / 270°C (5') / 10°C  $\text{min}^{-1}$  / 320°C (10'). MSD specifications: negative chemical ionisation (NCI) in the SIM mode at the m/z ratios of both bromine isotopes (79 and 81) and m/z=487 (for BDE 209 only). Ionisation gas  $\text{CH}_4$ .  $T_{\text{ion source}}$  210°C;  $T_{\text{transferline}}$  320°C;  $T_{\text{quadrupole}}$  160°C.

## Results and discussion

The results discussed here concern the sea star *Asterias rubens* and the hermit crab *Pagurus bernhardus*. The results are shown in fig. 1. In general it can be said that the geographical trend is highly similar in both species, the concentrations of BDEs in the abdomens of hermit crabs being slightly above those in the pyloric caeca of sea stars. BDE-47 is usually present in the highest concentrations, followed by the penta-BDEs 99 and 100, and the hexa-BDEs 153 and 154.

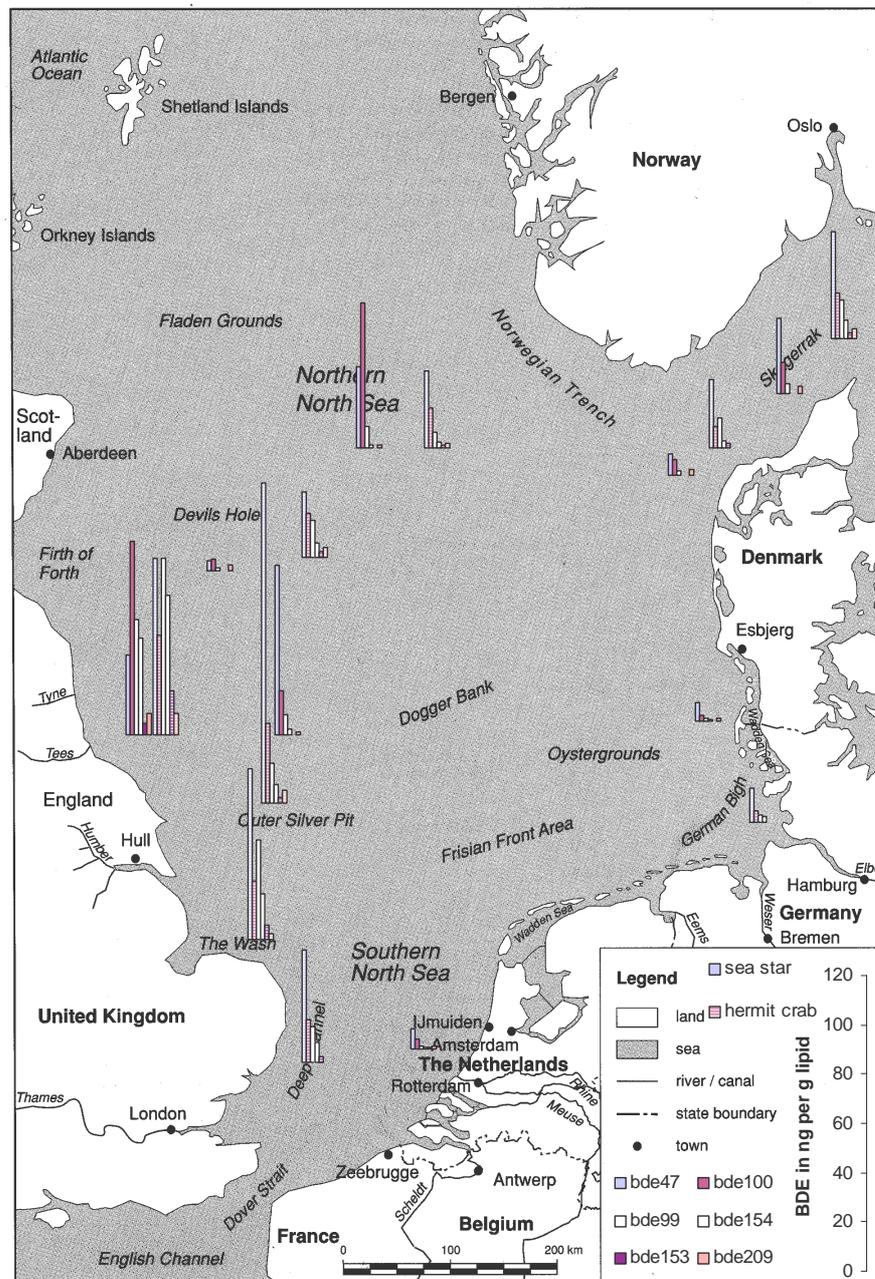


Figure 1. The concentrations of BDE congeners in sea stars and hermit crabs from the North Sea.

BDE-209 was sometimes present just above the detection limit. However, when the samples contain parts of the digestive system, the presence of BDE-209 above the detection limit cannot be interpreted as unambiguous proof for uptake by the organism. Instead, these levels may represent remainders of food present in the digestive system. Other studies have confirmed that the bioaccumulative properties of BDE 209 are much lower than those of the dominant congeners in PeBDE<sup>9</sup>; some studies have reported a complete lack of proof of uptake from river sediment<sup>1</sup>, whereas others have reported a low, but measurable uptake efficiency<sup>10</sup>.

The highest levels of PBDEs in these invertebrates occurred near the English coast, especially at the latitude of the estuaries of the rivers Tyne and Tees, but also further south. Surprisingly low levels of PBDEs were found along the coasts of continental Europe, showing that the major rivers there (Rhine, Meuse, Elbe) do not appear to be major sources for the North Sea ecosystem. This geographical distribution of the PBDEs is in sharp contrast to what was observed in the early eighties for PCBs in the polychaete *Nephtys spp.*<sup>11</sup>. In the Skagerrak, the levels seem to increase from west to east, representing an increase influence of the Baltic, which is known to contain elevated levels of PBDEs<sup>12; 13</sup>. Since these invertebrates do not migrate over large distances, they are more representative for the site of capture than fish and marine mammals.

Another item discussed will be the biomagnification of the main PBDE congeners with increasing trophic level of the organisms (invertebrates-fish-marine mammals).

### **Acknowledgement:**

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## Brominated diphenyl ethers in land-applied sewage sludges in the US

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Sewage sludges destined for land-application were collected from four different regions of the US. Brominated diphenyl ethers (BDEs) suggestive of both Deca- and Penta- commercial products were present, ranging from <75 to 9160 and from 1100 to 2290 µg/kg (dry weight basis), respectively. Burdens of Penta-like BDEs surpassed those typically reported in European sludges by over 10-fold. Flame-retarded polyurethane foams may deteriorate after weathering into minute, easily transportable fragments. Direct release of these, in conjunction with land application of contaminated sewage sludges, may introduce significant amounts of Penta-related BDEs into the environment.

BDEs are used as additives to polymers and textiles, presumably nondispersive applications<sup>1</sup>. Consumption of Penta-, a class of commercial BDE products consisting of congeners with 4 to 6 bromines, has decreased in Europe. However, overall global Penta- demand has continued to climb, with greater than 97% (8290 tons in 1999) in North America<sup>2</sup>. Penta- is used principally to flame-retard polyurethane foams, largely employed in furniture and related padding applications<sup>1</sup>. While BDEs levels in the US environment have received minimal attention, we recently observed that tetra- to hexa- BDEs were detectable in 85% of Virginia fish examined (DL ~5 ug/kg)<sup>3</sup>. In a number of instances fillet concentrations in the mg/kg (lipid) range were encountered. This suggests that significant pathways for the release of BDEs exist and the chemicals are bioavailable. Deca-, a commercial product consisting predominantly of BDE209, is used in greater amounts than Penta-. Global demand was 54,800 tons in 1999<sup>2</sup>. Most Deca- is consumed in North America (44%), followed by Asia (42%) and Europe (14%)<sup>2</sup>. While reported in increasing frequencies in sediments near point sources, it has seldom been detected in wildlife<sup>4</sup>. This has been attributed to its low bioavailability. Deca- is used predominantly on textiles and in denser plastics, such as housings for electronics<sup>1</sup>.

Disposal of sewage sludge in the US has proven increasing expensive and problematic as ocean dumping has been banned, available landfill space is dwindling and siting of incinerators has become more and more difficult due to objections from local residents. In

response, over half of the 6.9 million tons of “biosolids” generated in 1998 by US wastewater treatment plants (WWTPs) were land-applied<sup>5</sup>, often on agricultural fields. Regulation of biosolids “recycled” in this manner focus primarily on pathogen and metal content. While hydrophobic, persistent organic pollutants (POPs) may concentrate in WWTP sludges, few have been examined in detail. Rationales supporting this tact include the fact that production of the most notorious POPs, e.g. PCBs and organochlorine pesticides, have been reduced and more stringent wastewater pretreatment requirements now exist<sup>5</sup>. Due to the large volumes of biosolids released into the US environment annually and the high use of flame retardants here, we investigated BDE burdens in eleven sewage sludges destined for land-applications.

### **Methods:**

Eleven biosolid samples were obtained from four different regions of the US: the Mid-Atlantic (N=4), West (N=4), Northeast (N=2) and South (N=1). Samples were lyophilized, spiked with a surrogate standard (PCB30, 65, 121 and 204) and subjected to enhanced solvent extraction with methylene chloride. Extracts were purified by size exclusion and silica gel chromatography. Sulfur was removed with activated copper. Purified extracts were analyzed on a 60 m DB5 (0.32 mm ID, 0.25  $\mu$ m film) GC column. A 15 m (0.25 mm ID, 0.10  $\mu$ m film) was used for BDE209. Carrier gas was He and injections were made in the splitless mode. Quantitation was by halogen selective electrolytic conductivity detection.

Pentachlorobenzene was used as an internal standard. Data were corrected for PCB204 recovery. BDE standards included individual congeners (Cambridge Isotope Laboratories, Inc; Wellington Laboratories), as well as commercial Deca- (Fluka Chemie) and Penta-products (DE-71, Great Lakes Chemical Corp.). Compound identities were further confirmed in selected samples by full scan, low-resolution electron ionization mass spectrometry (MS).

### **Results and Discussion:**

BDEs were the dominant halogenated compounds observed in the biosolids. Deca-concentrations ranged from <75 to 9160  $\mu$ g/kg (dry weight basis). Photolysis of Deca- has been proposed as a potential source of less brominated congeners to the environment. However, evidence of this occurring on a significant scale, under realistic field conditions, is currently not available. This is of particular interest as the less brominated congeners appear to be more bioaccumulative and toxic than BDE209. BDEs with congener distributions reflective of the Penta- commercial mixture (Fig. 1) used to flame-retard foam were present in

the biosolids at relatively consistent levels, i.e. from 1100 to 2290 µg/kg. This suggests a steadier input of Penta- related congeners to WWTPs, compared with Deca-

During manufacture, Penta- is added to the polyurethane precursors. Subsequent foam polymerization is exothermic (>100°C). Considerable CO<sub>2</sub> is released, generating the foam's spongy structure. Volatile organic solvents, e.g. methylene chloride, are often used as additional "blowing agents", further reducing the foam's density<sup>6</sup>. Release from manufacturing facilities of resulting vapors may serve to transport associated BDEs. We have observed elevated concentrations of low brominated congeners in soils near a North Carolina foam production facility. However, alteration of the Penta- congener pattern is to be expected, except at the immediate point of release. Spillage and wastewater are also potential sources, but would not explain the consistency of levels observed in the biosolids. Outgassing and leachability of BDEs from in-service products is relatively modest due to the constituents' low volatilities and would result in a congener pattern different from the Penta-profile.

Degradation of polyurethane foam itself has received minimal attention. We observed that exposure of Penta-containing polyurethane for four weeks to outdoor Virginia summer conditions resulted in discoloration, embrittlement and subsequent erosion of the foam's surface. Treated foams may contain up to 30% Penta- by weight<sup>5</sup>. Thus, disintegration of a modest portion of the total foam produced and subsequent transport of the resulting minute fragments could facilitate dispersal of significant amounts of BDEs. If these fragments reach WWTPs they would collect in resulting sludges, largely preserving the original congener pattern of the Penta- product, as seen in the biosolid samples we examined.

The data presented suggest that BDEs are under-appreciated POPs of concern in the US, ironic considering their high use here. Despite reductions in consumption in Europe, Penta-constituents will remain a worldwide issue due to their potential for long distance transport by global circulation and their high bioaccumulation potential. Laudable lobbying efforts aimed at reducing fire-related deaths in the US, by ameliorating the flammability of polyurethane foam in residential furniture, may further increase Penta- demand. Land application of BDE-containing biosolids, a massive and expanding sludge disposal practice, provides a ready pathway for BDE release to the environment.

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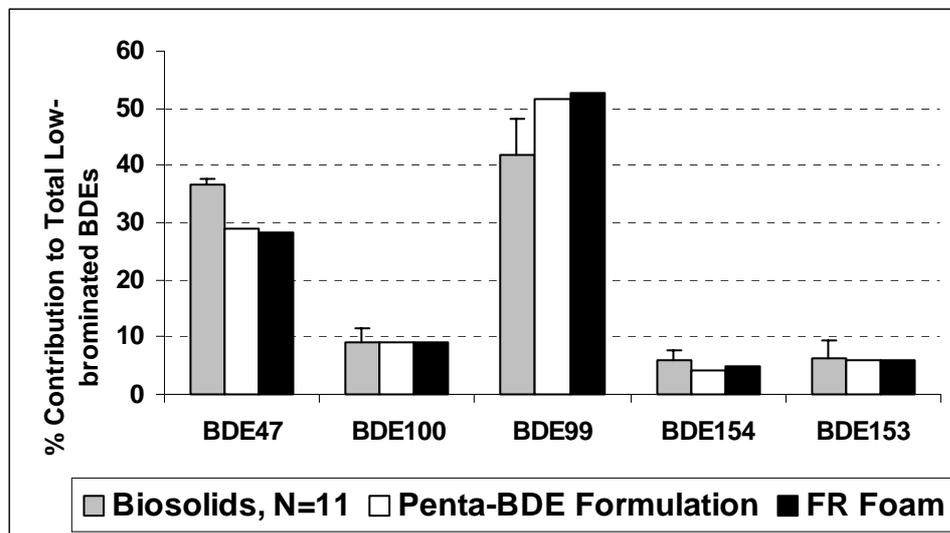


Fig. 1. Comparison of the relative contributions of the dominant low brominated congeners in biosolids, from four different regions of the US, to those in flame retardant-treated foam and a Penta- BDE product.

## POLYBROMINATED DIPHENYL ETHERS IN NORTH SEA GREY SEAL PUPS

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### SUMMARY

Blubber biopsies from identified grey seal pups at weaning and after several months at sea were analysed for polybrominated diphenyl ether congeners (PBDEs). The  $\Sigma$ PBDE concentrations ranged from 4500 to 30000 pg/g fat. Concentrations found in blubber showed a significant negative correlation with weight change between weaning and recapture.

### EXPERIMENTAL

#### **Seal sampling**

Blubber biopsies from Grey Seal (*Halichoerus grypus*) pups on the Farne Islands (off the north-east coast of England) were taken at weaning (October/November 1998) and after several months at sea in April/May 1999. 170 pups were tagged at weaning and 14 of these pups were recaptured in the 1999 exercise. The weight and girth of the seals were also recorded so that total fat content could be estimated.

#### **Analysis**

The entire blubber sample (approx 0.2 g) was chopped finely and extracted using DCM on a 'hot Soxhlet' apparatus for 4 hours. Extracted lipid determination was performed on an aliquot of this extract. The remaining extract was evaporated and cleaned using acidified silica (1:2 by weight conc. H<sub>2</sub>SO<sub>4</sub> and activated silica gel) and activated silica gel chromatography columns, then analysed by GC-NCI MS using ammonia as the reagent gas. Unlabelled PBDEs and <sup>13</sup>C<sub>12</sub> labelled PCBs were used as recovery and internal standards. The following PBDEs were quantified in each sample: 17, 28, 35, 37, 47, 49, 66, 71, 75, 85, 99, 100, 120, 153, 154.

## RESULTS

$\Sigma$ PBDE concentrations measured ranged from 4500 to 25000 pg/g fat at weaning, whereas after about 6 months foraging at sea the range became 9200 to 23000 pg/g fat for the same animals. BDE 47 dominated all samples, contributing approximately 65 % of the total with congeners 99, 100 and 153 each contributing approximately 10 % of the total. A typical seal blubber PBDE congener profile is shown in Figure 1.

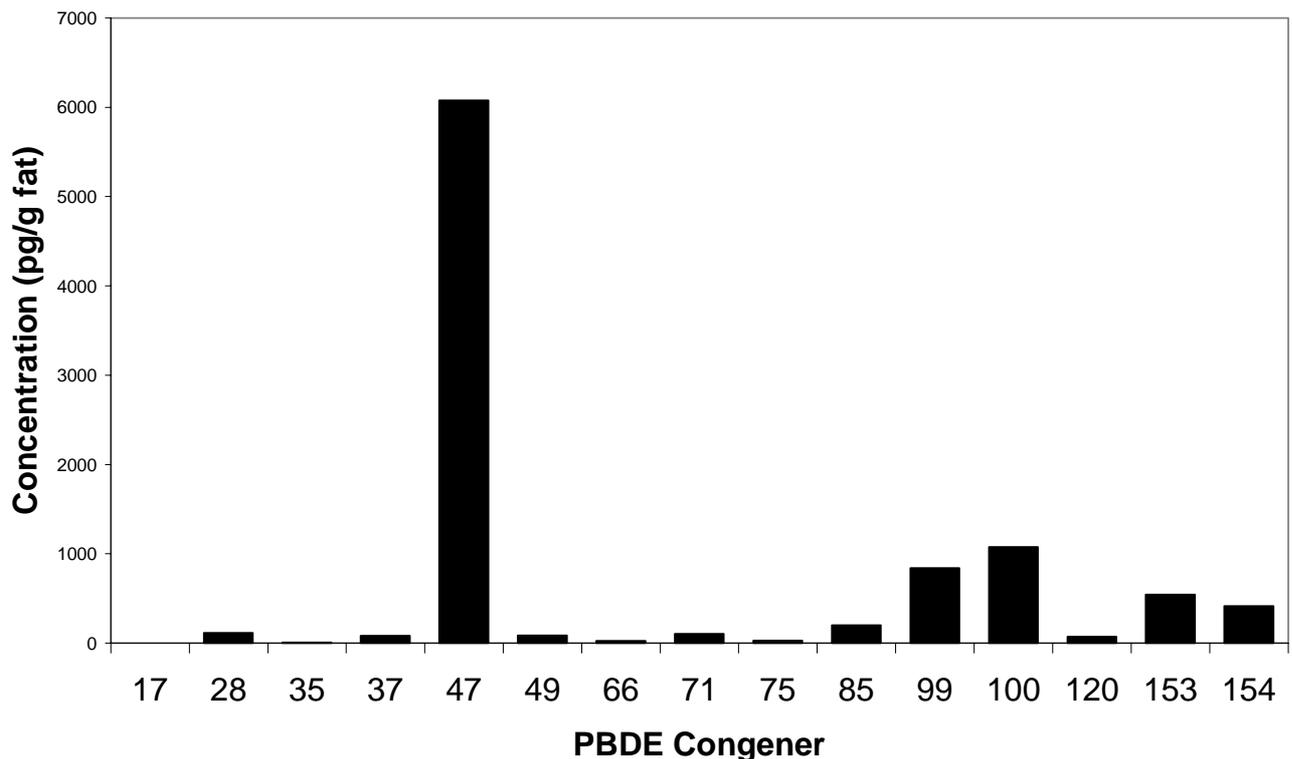


Figure 1. Congener pattern of PBDEs in North Sea grey seal pups

Most seals lost condition (i.e. blubber) between weaning and the spring re-capture due to the difficulties they face finding food at this stage of life. PBDE concentrations in blubber generally increased from the weaning sample to the spring re-capture for the same individual. Significant negative correlations were found between the change in blubber PBDE concentrations between captures and the amount (or percentage) weight change for the more brominated compounds (BDE 85 and above). Figure 2 shows the change in BDE-99 blubber concentration between captures and the percentage weight change observed. The less brominated BDEs showed less significant negative correlations.

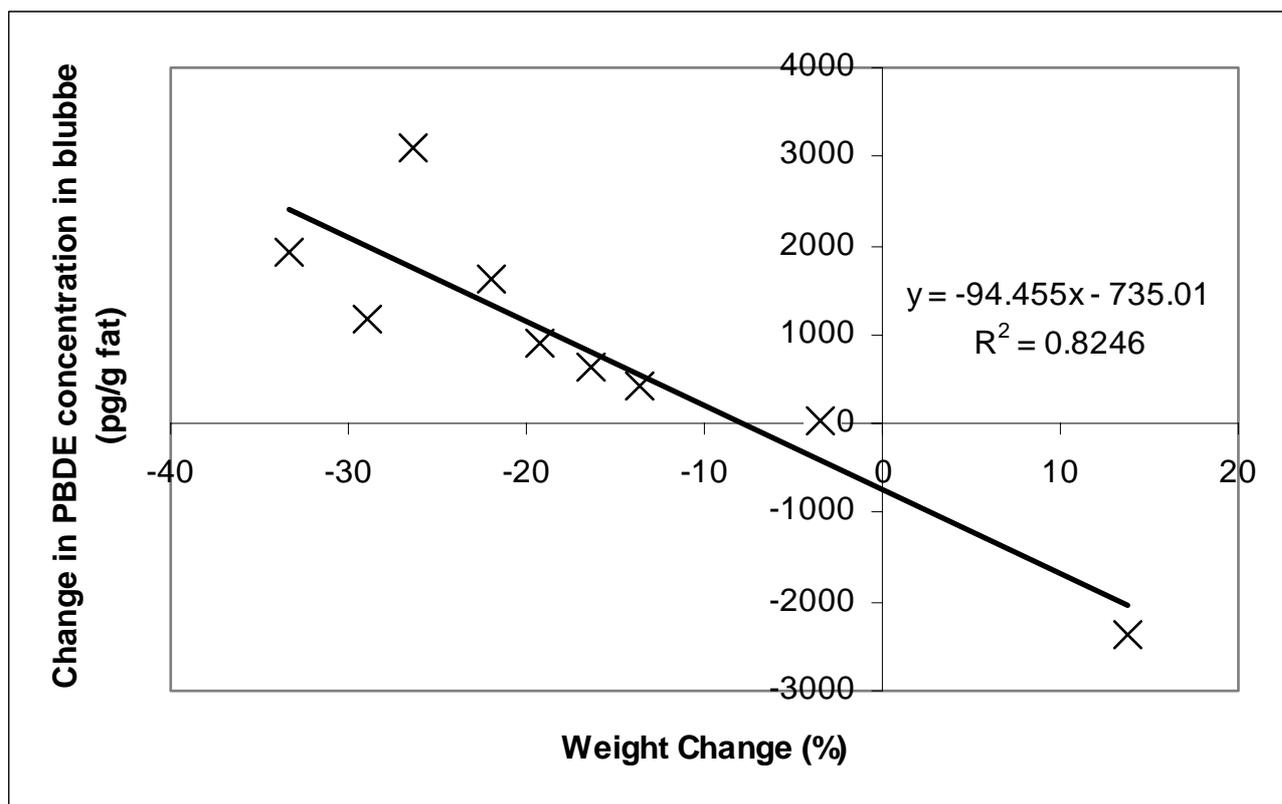


Figure 2. BDE-99 concentration and weight change between captures

De Boer<sup>1</sup> reported concentrations of BDE-47 of 8.4 - 100 ng/g fat in herring in the North Sea. The concentrations of BDE-47 found in seal blubber ranged from approximately 3 – 15 ng/g fat, either indicating that concentrations of this compound in the North Sea may have fallen throughout the 1990s, or that seals do not bio-magnify this compound.

PBDE concentrations from Baltic grey seal blubber samples from the literature are shown in table 1. The seal blubber samples analysed ranged from approximately a factor of 100 below to approximately a factor of 10 below the concentrations of total PBDEs reported in reference 3, also for juvenile seals. Individual PBDE concentrations were similarly approximately 2 orders of magnitude lower in this study than reported in the Baltic for samples taken in the 1980s<sup>2,4,5</sup>. This may indicate a general reduction in PBDE concentrations in the marine environment during the 1990s.

Table 1 – Concentrations of BDEs in Baltic grey seal blubber from the literature

BDE concentration (ng/g lipid)				Years	Age	Reference
47	99	100	ΣBDE			
650	40	NR	NR	1979-88	Adult	2
308	54	NR	NR	1981-88	Adult	3
NR	NR	NR	300-310	1980s	Juvenile	4
650	40	38	NR	1979-85	Adult	5

NR – not reported

The total body fat content was estimated from the girth and length measurements taken of each seal using an equation developed using tritiated water studies. Combined with the PBDE concentrations in the blubber, and assuming that PBDEs are predominantly found in the blubber, the total body burden of PBDEs in the seals were estimated to be 83 – 280 ng ΣPBDE in October 1998 and 150 – 500 ng ΣPBDE in April/May 1999. This may indicate that seal pups accumulate approximately the same total amount of PBDEs in the first 6 months foraging for food as during gestation and suckling.

A two day mass balance study on a captive seal was also carried out, for which results will be presented.

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# SPATIAL AND TEMPORAL TRENDS OF POLYBROMINATED DIPHENYL ETHERS DETECTED IN GREAT LAKES HERRING GULLS, 1981 to 2000

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## Summary

Polybrominated diphenyl ethers (PBDEs) were found at total concentrations ranging from 200-1400 ng/g (wet weight) in herring gull eggs from 15 colonies in the Great Lakes. Highest levels were in Lake Michigan and near Detroit, Hamilton and Toronto, suggest a broad urban source. Temporal trends, 1981-2000, at three of the colonies indicated exponential increases with doubling times of 3-5 years.

## Introduction

The number of reports of measurable quantities of PBDEs found in environmental samples such as sediment, fish, marine mammals, air (1), (2), (3) (4) and human milk (5) is increasing. PBDEs, as a whole, are both persistent and lipophilic, and have the potential to biomagnify (6). PBDEs were found to be increasing in Swedish breast milk, in contrast to other POPs (5). It is important to establish sources and if concentrations of these chemicals are increasing everywhere in the environment.

The Canadian Wildlife Service (CWS) has been using eggs of the herring gull (*Larus argentatus*) as a biomonitor of temporal and spatial trends of POPs in the Great Lakes since the late 1960's (7). The data are one of the most geographically comprehensive and continuous sets of POPs concentrations in the world. Subsamples of eggs were archived, allowing analysis of trends of 'new' POPs to be carried out.

We report results on the identification and concentration of PBDE compounds in herring gull eggs from fifteen Great Lakes sites, providing a snapshot of the current spatial distribution of PBDEs in the Great Lakes. Additionally, archived eggs from Lakes Huron, Michigan, and Ontario collected between 1981 and 2000 were analyzed to determine temporal trends.

## Materials and Methods

Herring gulls eggs were collected from fifteen locations on the Great Lakes, connecting channels, or rivers. The sampling colonies are shown on Figure 1. Samples were homogenized and pooled (n=13) prior to analysis. In brief, egg homogenates were ground with anhydrous sodium sulfate and extracted with 1:1 DCM /hexane. Extracts were spiked with BDE surrogate spiking solutions containing  $^{13}\text{C}_{12}$  labeled BDE-47 (10000 pg/g),  $^{13}\text{C}_{12}$  BDE-100, -99 and -126 (15000 pg/g each),  $^{13}\text{C}_{12}$  BDE-28, -154 and -183 (25000 pg/g each). Lipid removal was accomplished by GPC, followed by Florisil chromatography (8). Samples were spiked with  $^{13}\text{C}_{12}$  BDE - 77 as a performance indicator standard and reduced to final volume for analysis.

Samples were analyzed using a VG AutoSpec double focusing mass spectrometer operated at 7000 resolution in the electron impact ionization using selected ion monitoring. Five chromatographic windows were used to monitor the following isomer groups:  $\text{Br}_1 + \text{Br}_2$ -DE,  $\text{Br}_3$ -DE,  $\text{Br}_4$ , +  $\text{Br}_5$ -DE,  $\text{Br}_5 + \text{Br}_6 + \text{Br}_7$ -DE. The two strongest ions of the molecular cluster for each native analyte and labeled surrogate were monitored. PBDEs were quantitated using the isotope dilution method. For those congeners that internal standards were not available relative response factors from the appropriate homologue were used.

## Results and Discussion

### Spatial distribution:

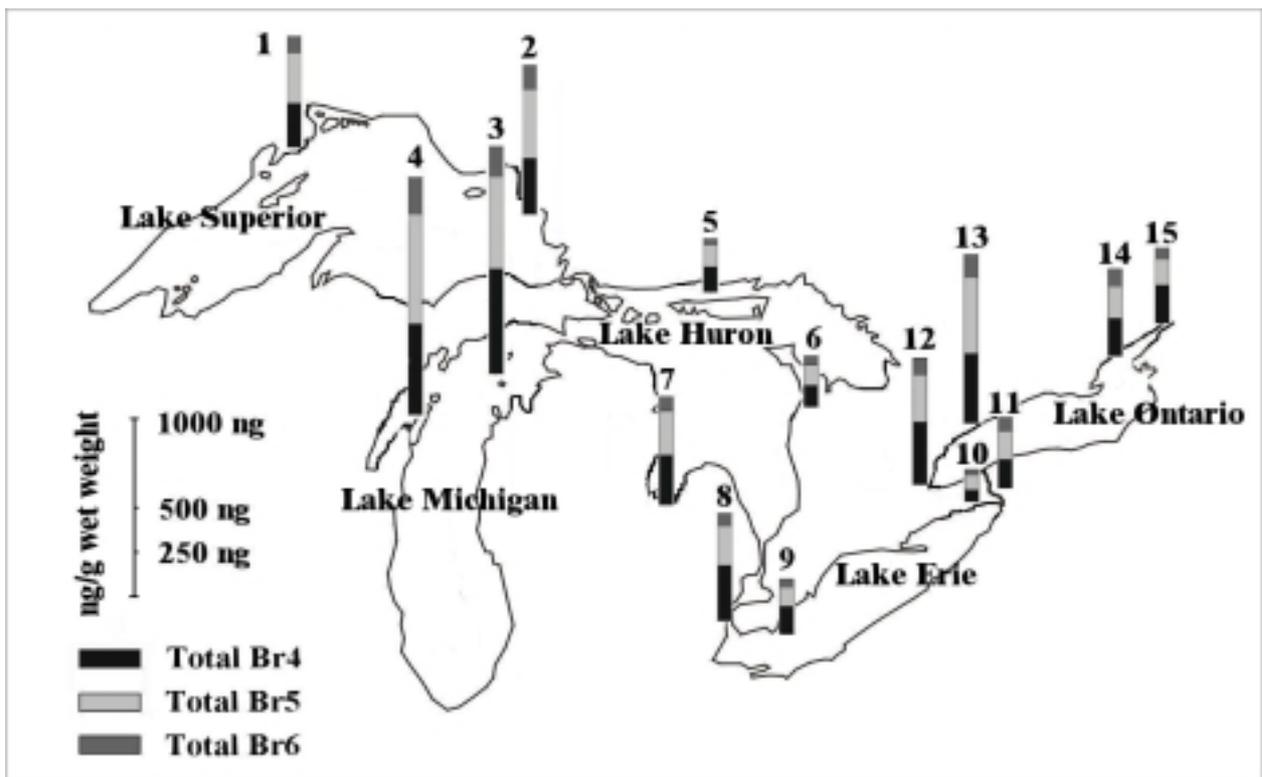
$\text{Br}_4$ DEs to  $\text{Br}_6$ DEs made the most significant contribution to the total PBDEs. In most cases, six congeners constituted at least 90 percent of the total BDE concentration. In all samples, BDE-47 was the dominant congener, followed by BDE- 99, -100, and -153. This agrees with previously published data on trout, marine mammals, and seals (9) (10) (11).

The PBDE concentrations are shown in Figure 1 of  $\Sigma\text{Br}_4$ -,  $\Sigma\text{Br}_5$ - and  $\Sigma\text{Br}_6$ DEs. Concentrations are corrected for recoveries (53 -101%). The levels of PBDEs ranged from 1400 ng/g wet weight of whole egg at site 4 in Lake Michigan, to 200 ng/g at site 10 in Lake Erie. High total concentrations of PBDEs in remote northern sites (Granite Island, Agawa Rock) that are not located near any major industrialized areas are most likely a result of the winter migration patterns of the gulls. Lake Superior Gulls tend to move to southern Lake Michigan, which remains ice-free year round (12). Highest concentrations outside of Lake Michigan and Lake Superior appear to be associated with nearby large urban areas: site 8

(Detroit), site 12 (Hamilton) and site 13 (Toronto), suggesting that the source is widespread, and not associated with point source input.

Figure 1: Concentrations of BDEs in herring gull eggs (ng/g wet weight) :

1, Granite Island; 2, Agawa Rock; 3, Gull Island; 4, Big Sister Island (Green Bay); 5, Double Island; 6, Chantry Island; 7, Channel/Shelter Island (Saginaw Bay); 8, Fighting Island (Detroit River); 9, Middle Island; 10, Port Colbourne; 11, Niagara River; 12, Hamilton Harbour; 13, Leslie Street Spit; 14, Snake Island; 15, Strachan Island (St Lawrence River).



Temporal Trends:

Temporal trends, 1981-2000, of total BDE isomer groups at three sites are shown in Table 1.  $\Sigma$ BDEs were increasing in Herring Gull eggs throughout this period. Statistical analysis revealed a significant exponential increase of the major component BDEs at all three sites. Doubling times were calculated for total  $\Sigma$ Br<sub>4</sub>-,  $\Sigma$ Br<sub>5</sub>- and  $\Sigma$ Br<sub>6</sub>DEs (Table 1). Levels of  $\Sigma$ Br<sub>4</sub>DEs and  $\Sigma$ Br<sub>5</sub>DEs were increasing at a similar rate (doubling time 2.5-2.9 years), with the exception of  $\Sigma$ Br<sub>4</sub>DEs at site 7, which were doubling every 3.5 years.  $\Sigma$ Br<sub>6</sub>DEs were increasing more slowly (doubling time 3.4-5.9 years). At different times over the past 19 years, depending on the site, the relative proportion of  $\Sigma$ Br<sub>4</sub>DEs and  $\Sigma$ Br<sub>5</sub>DEs switch as the major isomer group in the samples. Doubling times of  $\Sigma$ BDEs ranged from 3-5 years.

At these rates of increase, in 8 years  $\Sigma$ BDE concentrations will have reached or surpassed those of PCBs in the Great Lakes (7). Norén and Meironyté (5) found a doubling time of 5 years for  $\Sigma$ BDEs in Swedish human milk. The similarity in rates of increase over such a distance and in very different food chains suggest that PBDEs are rapidly becoming a global problem.

Table 1 Temporal Trend Data for years 1981-2000.

Levels are in ng/g (wet wt.) and corrected for recoveries. For  $y(t)=ae^{bt}$ , rate constant =  $b$  ( $\text{yr}^{-1}$ ), and doubling time ( $\text{yr}$ ) =  $K(2) = \ln(2)/b$ .

Year	Shelter Island (site 7)				Gull Island (site 3)				Snake Island (site 14)			
	$\Sigma \text{Br}_4$	$\Sigma \text{Br}_5$	$\Sigma \text{Br}_6$	$\Sigma \text{BDE}$	$\Sigma \text{Br}_4$	$\Sigma \text{Br}_5$	$\Sigma \text{Br}_6$	$\Sigma \text{BDE}$	$\Sigma \text{Br}_4$	$\Sigma \text{Br}_5$	$\Sigma \text{Br}_6$	$\Sigma \text{BDE}$
1981	7	2	14	23	5	5	6	15	3	2	4	9
1983	9	5	18	32	5	5	8	19	4	3	6	13
1987	32	19	21	71	45	41	26	111	17	13	105	135
1988	44	31	34	109	54	57	31	142	46	34	85	165
1989	na	na	na	na	na	na	na	na	49	40	53	142
1990	55	35	52	142	na	na	na	na	na	na	na	na
1991	na	na	na	na	na	na	na	na	54	55	59	168
1992	89	70	56	215	99	100	37	237	84	64	58	207
1993	127	104	52	283	165	265	290	721	na	na	na	na
1994	na	na	na	na	na	na	na	na	123	89	56	268
1996	129	158	84	371	268	290	105	663	129	98	60	287
1998	212	182	88	482	367	801	323	1492	162	138	72	372
1999	209	301	119	630	320	353	134	807	234	210	96	540
2000	294	257	82	633	612	539	180	1331	223	185	101	509
<b>b</b>	0.20	0.26	0.12	0.14	0.25	0.27	0.20	0.23	0.24	0.25	0.14	0.19
<b>K(2)</b>	3.52	2.69	5.92	4.95	2.79	2.53	3.38	2.97	2.89	2.77	5.10	3.72
<b>r<sup>2</sup></b>	0.91	0.94	0.95	0.97	0.87	0.63	0.41	0.74	0.90	0.92	0.45	0.85
<b>p</b>	<0.0001	<0.0001	<0.0001	<0.0001	0.0001	0.0062	0.0367	0.0008	<0.0001	<0.0001	0.0141	<0.0001

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## **Higher brominated PBDEs found in eggs of Peregrine Falcons (*Falco peregrinus*) breeding in Sweden.**

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### **Summary**

Concentrations of BDE-47, -99, -100, -153, -154, -183, -209, BB-153 and HBCD were analyzed in peregrine falcon eggs collected in 1988-1999 representing females from three different populations: northern Sweden, southwestern Sweden and a captive breeding population. All BFRs analyzed for were found, including BDE-183 and -209, and concentrations were much higher in wild falcons than in captive falcons.

### **Introduction**

Peregrine falcons feed almost exclusively on other birds and most populations of the species were previously endangered in the northern hemisphere because of high concentrations of DDT-, dieldrin-, aldrin-, and mercury affecting both reproduction and survival. The peregrine falcon is therefore a species where highly bioaccumulating environmental contaminants can be expected to be found and this species has therefore been used in environmental monitoring programs in North America, Europe and the Arctic.

Most analyses of PBDE in Swedish fauna have been on species belonging to marine/aquatic food webs or at low trophic positions in the terrestrial food web<sup>1,2,3,4,5</sup>. For predatory birds, only muscle samples from osprey (*Pandion haliaetus*) have previously been analysed<sup>1,3,4</sup>. No analyses have been reported for predatory birds in the terrestrial food web.

### **Materials and methods**

Peregrine falcon eggs were collected within the Swedish Society for Nature Conservation inventory program and with permission from the Swedish EPA. Egg contents were removed from the eggs and stored frozen in tinted glass jars. Material came from either unfertilised eggs collected during the nesting period or eggs that did not hatch that were collected after the

nesting period. In some cases, eggs were collected during different years from the same female (max 4-year interval). For southwestern Sweden, 24 eggs from 17 females were analysed. For northern Sweden, 18 eggs from 18 females were analysed. For the captive breeding population, 10 eggs from 8 females were analysed. All but one of these females were hatched in captivity or collected as nestlings. Twenty-one eggs were analysed for BDE-209 and HBCD (4 from the captive population, 9 from the southern population, 8 from the northern population). Where several eggs from one female were analysed, the average values were calculated and used in the statistical analysis.

Eggs were homogenized and extracted with acetone/hexane and then diethyl ether/hexane<sup>6</sup>. The organic phase was washed with a sodium chloride/phosphoric acid buffer, the solvent evaporated and the remaining lipid determined gravimetrically. The lipids were dissolved in trimethyl pentane and treated with sulphuric acid to remove the lipids.

Standards used included individual BDE congeners (Cambridge Isotope Laboratories) as well as commercial DeBDE (Dow FR-300BA, Dow Chemicals, Midland, MI, USA), Firemaster BP-6 for BB-153 (EPA, USA) and HBCD (Michigan Chemical, St. Louis, MI, USA). Dechlorane (Hooker Chemical Corp.) was used as internal standard. The GC (Carlo Erba MEGA MFC 500) was equipped with either a 40 m DB5MS (methyl+5% phenyl) capillary column for analysis of BDEs -47 to -183 and BB-153 or a 12.5 m DB5MS (methyl+5% phenyl) capillary column for analysis of BDE-209 and HBCD. The GC was connected to a VG Trio-1000 massspectrometer run in chemical ionising mode measuring the negative ions formed (MS-ECNI). Ion source temperature was 200 C (220 C for BDE-209). Ammonia was used as reaction gas. The mass fragments monitored for quantitation were m/z -79 and -81 for brominated substances and -237 and -239 for dechlorane. QA/QC samples and procedural blanks were also run.

## **Results and discussion**

The wild falcons had statistically significantly higher PBDE concentrations than the captive falcons, which are raised on a controlled diet of chickens (Fig. 1). BDE-209 was found in 18 of 21 analysed eggs (range 28-430 ng/g lw). BDE-183 was found in all eggs, with much higher concentrations in the two wild populations (range 56-1300 ng/g lw) compared to the captive falcons (range 6-19 ng/g l.w.). This is the first time, to our knowledge, that these two congeners have been found in wildlife high up in the food web.

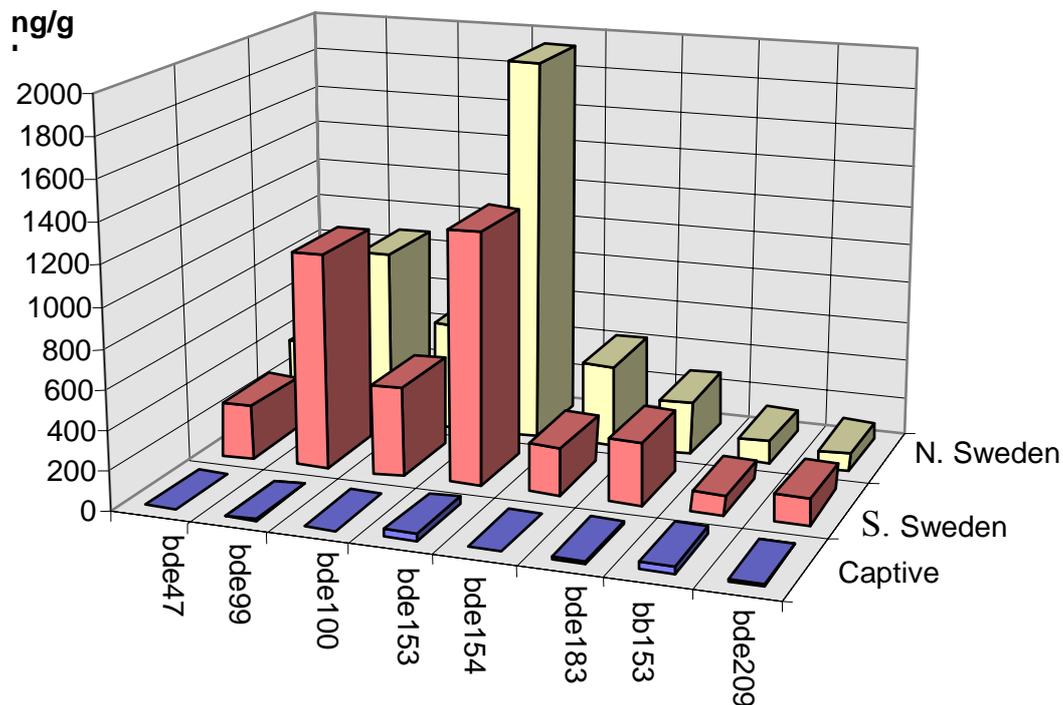


Figure 1. Concentrations (ng/g lipid weight) of BDE-47, -99, -100, -153, -154, -183, -209 and BB-153 in eggs from three populations of peregrine falcon.

Concentration ranges for the other BFRs in the wild populations were 15-3800 ng/g lw for BDE-47; 110-9200 ng/g lw for BDE-99; 77-5200 ng/g lw for BDE-100; 270-16000 ng/g lw for BDE-153; 50-4400 ng/g lw for BDE-154 and 26-370 for BB-153. HBCD was also present (approx. 34-2400 ng/g lw). The largest difference was for BDE-99 where the arithmetic mean was about 400 times higher in wild falcon eggs compared with captive eggs. There were no statistically significant differences in PBDE concentrations between the falcons from the northern and southwestern populations, in spite of them having different diets during breeding. The northern population feeds on waders and ducks, while the southern population feeds on birds in the terrestrial food web. However, peregrine falcons, as well as many of their prey, migrate to wintering grounds along the coasts of southern Europe, where they may be exposed to PBDE. A study of sediments from many European river mouths has shown the presence of elevated concentrations of PBDEs and PBBs in sediments<sup>7,8,9</sup>.

The pattern of PBDE congeners is different in peregrine falcons when compared to previous analyses in other animals. Compared to guillemot eggs (*Uria aalge*) from the Baltic Sea<sup>1</sup>, the falcon eggs contained several higher brominated PBDE. Dominant congeners in

falcon eggs were BDE-99 and -153, as compared to BDE-47 in guillemot eggs. The BDE-47, -99, -100, -153 and -154 concentrations from 1999 were also much higher in falcon eggs (means of 290, 850, 460, 1800 and 390 ng/g lw, respectively) than in guillemot eggs (means of 130, 13, <7, <3, and <5 ng/g lw, respectively).

One argument used for the use of decaBDE (BDE-209) is that the molecule is so large that it is not bioavailable, and therefore can not accumulate in living organisms. Our study indicates that this is not correct. Eggs from the wild populations had significantly higher BDE-209 concentrations than the captive population feeding on chickens. This is an indication that this congener is present in the environment and may bioaccumulate. Only lower brominated BDE congeners are found in fish-eating guillemots which indicates that organisms in the terrestrial environment may be more highly exposed to the higher brominated BDEs.

We thank the Swedish Society for Nature Conservation and TCO-Development AB for funding and Kerstin Nylund, ITM, for technical assistance.

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## Environmental measurements and the global distribution of PBDEs

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### INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) represent important additive flame retardants with numerous uses within industrial and domestic electronic equipment and textiles. Due to very stringent fire regulations since 1988, and an increased use of plastic materials and synthetic fibres in general, their use has increased significantly in the last 20 years in the UK. PBDEs are similar in behaviour (hydrophobic, lipophilic, thermally stable) and toxicity to the well studied contaminants PCBs, although unlike PCBs, little is known about their physico-chemical properties. Growing evidence suggests that PBDEs are widespread global environmental pollutants and that they are capable of bioaccumulation in remote foodchains. Detectable levels have been reported in a variety of media including air, water, soil, sediments, sewage sludge (de Boer et al., 2000), aquatic and terrestrial vertebrates (Ikonomou et al., 2000; Dodder et al., 2000; Allchin et al., 1999), a variety of lipid-rich foods (Kalantzi et al., 2000), in blood (Paterson et al., 2000; Papke et al., 2000) human breast milk (Ryan 2000). Several studies have reported rising trends in environmental concentrations of PBDEs (Stern and Ikonomou 2000; Papke et al., 2000; Noren 1998) and these represent an area of particular environmental health concern. Concern has been expressed about continued elevated concentrations of congener BDE-47, an important constituent of the restricted penta product, in several matrices including air, foods and human tissues. We hypothesise that its continued presence in the environment could be evidence of a slow release of BDE-47 from large historical reservoirs and/or recycling of products within waste streams. Interestingly, there is also evidence that PBDEs undergo photolytic debromination in the presence of UV light leading to the formation of lower brominated PBDE congeners (Soderstrom et al., 1998). This formation mechanism has been put forward as an explanation for the continued abundance of BDE-47, but little data had been generated to support this claim. Limited monitoring has been carried out in the UK and this has been restricted to sediments and fish (Allchin et al., 1999) and ambient air (Peters et al., 2000). We have several ongoing

studies which aim to characterise not only the contemporary UK distribution of PBDEs but also their temporal trends and global distribution.

### **UK distribution of PBDEs in Air**

We have monitored two sites in the UK for PBDEs since 1997: Hazelrigg and Stoke Ferry. The Hazelrigg site is situated at the Lancaster University experimental field station, approximately 7 km from the Irish Sea coast. The Stoke Ferry site is situated in the grounds of a water treatment works, approximately 60 km from the North Sea coast. Graseby-Andersen model PM10 High Volume samplers equipped with a glass fibre filter (GFF) and 2 polyurethane foam (PUF) plugs were used for sampling. Individual congeners were measured in ranges of 0.1 - 70 and 0.1 - 130 pg m<sup>-3</sup> for Hazelrigg and Stoke Ferry, respectively, with mean total PBDE concentrations at these 2 sites of 85 and 100 pg m<sup>-3</sup>, respectively. Highest concentrations were measured for BDE-47. From Spring 97 to Spring 98, there is some evidence that concentrations of tri- and tetra-brominated diphenyl ethers have decreased. Further long-term observations will confirm this trend.

### **Global distribution of PBDEs in Air**

#### **(i) Atlantic Cruise data**

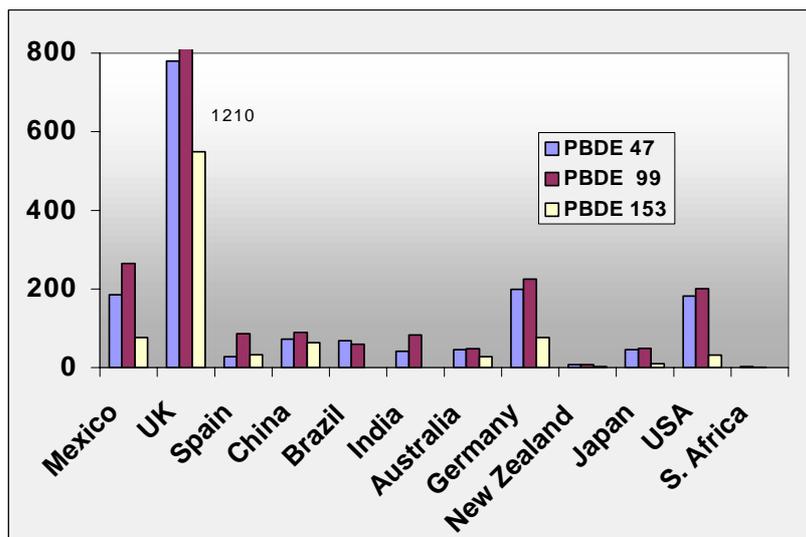
We have collected data on the atmospheric concentrations of PCDD/Fs, PCBs and organochlorine pesticides along a global north-south transect through the Atlantic (Lohman et al., 2000). Results supported the fact that PCDD/Fs are ubiquitous in the atmosphere even in remote regions in the southern hemisphere. The extracts produced in this study are undergoing reanalysis for PBDEs and will show the distribution of these chemicals from the industrial north Atlantic to the remote Southern Ocean.

#### **(ii) Global butter survey**

We have recently used samples of butter collected from different countries to identify the global distribution of polychlorinated biphenyls (PCBs) and a range of OC pesticides (Kalantzi et al., 2001). Butter  $\Sigma$ PCB concentrations varied by a factor of ~60 in 63 samples from 23 countries. We found that European and North American butter had the highest PCB levels. Lower contaminant levels were found in samples from the Southern Hemisphere, including Australian and New Zealand butter. These findings mirror known patterns of chemical usage and estimated emissions, suggesting that butter could be used globally as an effective monitor of a range of atmospheric contaminants. Analysis of a preliminary sub-set of samples has shown variations in PBDE levels in these butter samples highlighting the

significance of foodchain transfer of these compounds (see Figure 1). UK butter had the highest levels of PBDEs, exceeding samples from Mexico, Germany and the USA (approximately equal as the next most contaminated samples) by approximately a factor of 6.

Figure 1: PBDE congeners in world butter samples (pg/g lipid)



### Global distribution of PBDEs in Soil

As part of the GLOBAL-SOC project, surface soil samples have been obtained from 200 remote sites world-wide (Figure 2). Samples from these sites have been analysed for PCBs and for all PCB congeners analysed, concentrations were found to be greatest at locations between 30 and 60° N – the region of greatest use (and release) of these compounds. These data suggest that there has been little

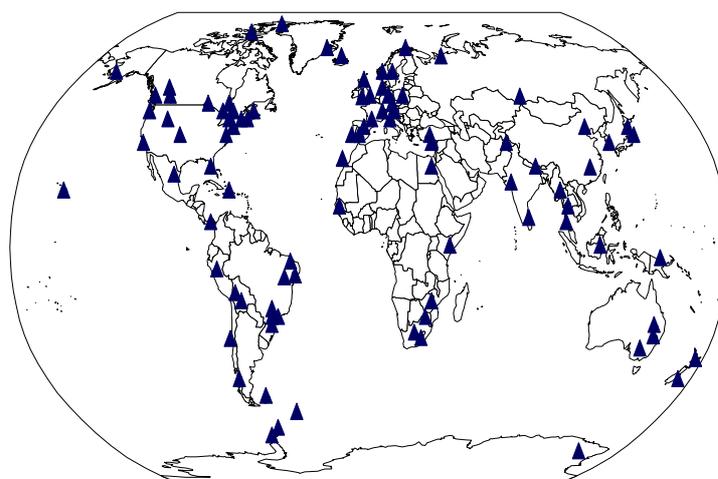


Figure 2: Location of major soil sampling locations

movement of PCBs away from regions of use and manufacture. We are currently reanalysing these samples for PBDEs so that their global land-based distribution can be estimated.

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**Polybrominated Diphenyl Ethers (PBDEs) in shorthorn sculpin  
(*Myoxocephalus scorpius*) from 3 locations in Southern Greenland**

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Summary

Levels of PBDEs were measured in shorthorn sculpin (*Myoxocephalus scorpius*) from three locations in southern Greenland; Usuk (no population), Igaliko (population 40), and Qaqortoq (population 3200). The highest levels were found in Qaqortoq followed by Igaliko and Usuk indicating local emission of PBDEs in Igaliko and Qaqortoq.

Introduction

PBDEs with an estimated production of 40.000 tonnes world-wide in 1992<sup>1</sup> is the group of brominated flame retardants (BFRs) most frequently measured in the environment and the group of BFRs measured in highest concentrations, as well. In 1981 Andersson and Blomkvist reported the presence of PBDEs in samples of Pike collected along River Viskan in Sweden<sup>2</sup>. These measurements were the first to indicate the presence of brominated flame retardants in biota, and since then PBDEs have been measured in more than 50 species at different trophic levels in Asia, Europe, North America and in the Arctic environment. Compared to knowledge of polychlorinated biphenyls (PCBs) and chlorinated pesticides in biota from the Arctic environment little is known about the presence of PBDEs. PBDEs were reported for the first time in the Arctic environment by Sellström et al (1993)<sup>3</sup>. They measured the sum of three PBDE congeners (BDE-47, BDE-99 and BDE-100) in a ringed seal (*Pusa hispida*) collected at Svalbard in 1981 to 51 µg kg<sup>-1</sup> lipid weight in a blubber sample<sup>3</sup>. In 2000 Lucross et al reported PBDEs in marine mammals from the Canadian Arctic for the first time, suggesting that PBDEs are ubiquitous pollutants in the Arctic environment<sup>4,5</sup>. In this short paper, levels of PBDEs in shorthorn sculpins, collected at three locations in southern Greenland with different degrees of urbanisation, are presented.

## Method

### **Sampling**

Shorthorn sculpins were sampled at three locations in southern Greenland: Usuk (A) a reference area with low degree of human activity, Igaliko (B) a settlement with approximately 40 inhabitants, and Qaqortoq (C) a village with approximately 3200 inhabitants. All three locations are situated within 50 kilometres.

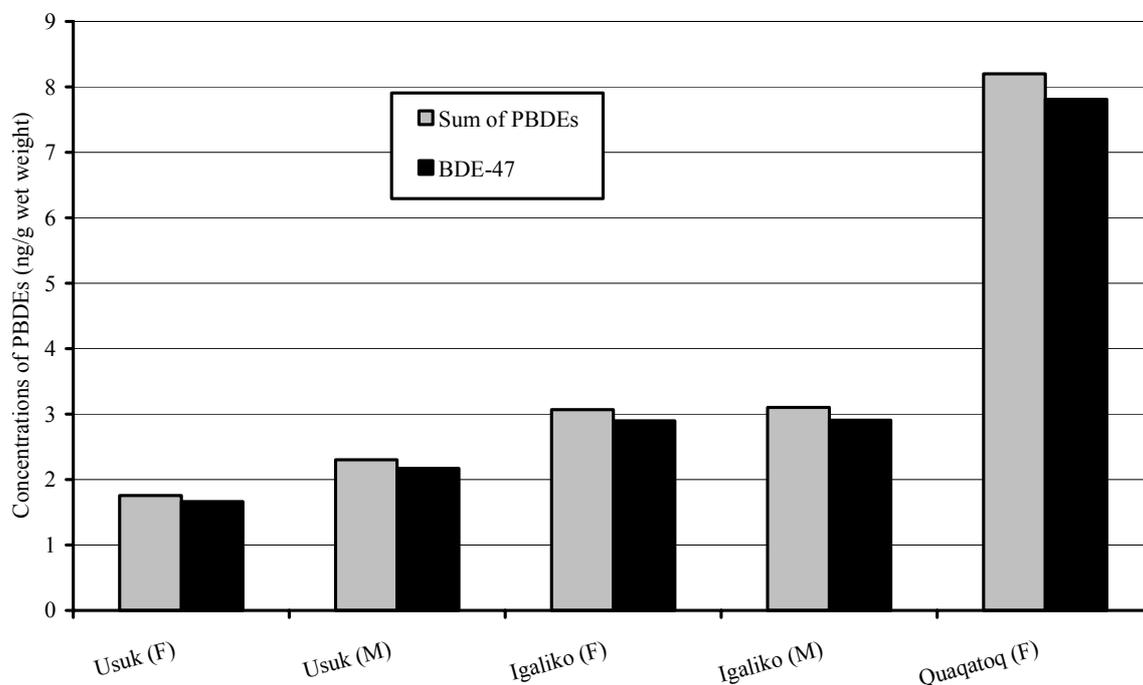
### **Chemical analysis**

Five liver samples, each pooled from 4-5 individuals of shorthorn sculpin, were analysed. The five samples consisted of females and males from Usuk and Igaliko, as well as females from Qaqortoq. The extraction and cleanup method is similar to the method used at the National Environmental Research Institute, Department of Environmental Chemistry for analysis of polychlorinated biphenyls (PCBs) and polychlorinated pesticides in biota. The method has previously been reported in detail<sup>6</sup>. Briefly, fish liver (2 g) was ground in a mortar with anhydrous sodium sulphate, soxhlet extracted with 350 ml of hexane:acetone mixture (4:1) and cleaned on a multilayer glass column (1 (i.d.) x 20 cm) packed from the bottom with: 5 g aluminum oxide activated at 160°C for 24 h and deactivated with 10% water, 1 g silica activated at 160°C for 24 h, 5 g silica activated and impregnated with concentrated sulfuric acid, and 1 cm anhydrous sodium sulphate. The sample was applied to the column and eluted with 200 mL hexane. The hexane extract was concentrated to 1 mL and analysed by gas chromatography-mass spectrometry (GC-MS) with negative chemical ionisation (NCI). CB-198 was added as recovery standard prior to soxhlet extraction, whereas CB-207 (PCB congeners) was applied as internal standard. The mass fragments were monitored using selected ion monitoring (SIM). The quantifying ions were  $m/z$  -78.9 and -80.8 for tetra-hexa BDEs -359.8 and -393.7 for CB-198 and -393.7 and -429.7 for CB-207.

### **Results and discussion**

The average sum concentrations (females and males) of BDE-47, BDE-99, BDE-100 and BDE-153 in shorthorn sculpin collected at Qaqortoq, Igaliko and Usuk, were 8.2, 3.1, and 2.1  $\mu\text{g kg}^{-1}$ . In Figure 1 the concentration of BDE-47 and the sum concentration of the four PBDEs in shorthorn sculpin collected at the three sampling areas, are compared. Shorthorn sculpin is a stationary species and it can be assumed that the captured individuals have lived

most of their lives close to the sampling site. The concentration of PBDEs is highest in Qaqortoq followed by Igaliko and Usuk.



**Figure 2:** Concentrations of BDE-47 and the sum of tetra-hexa BDEs in liver samples from shorthorn sculpin (Female, Male) collected at Usuk, Igaliko and Qaqortoq.

The higher level of PBDEs found close to populated areas suggests local sources of pollution in addition to long-range transport. In Igaliko a small waste incinerator was located close to the sampling site. Burning, at low temperatures, of materials containing PBDEs could result in the slightly higher levels of PBDEs at Igaliko compared to Usuk only five kilometres away. In Qaqortoq the sampling site was located inside the harbour. Within a kilometre from here the refuse dump, receiving all kind of waste from the town, is situated on a small hill at the seashore. Washout and emission from the dump could therefore most likely be a source of PBDE contamination to the marine environment close to Qaqortoq. The observed PBDE levels in fish liver samples are 10-100 times lower than concentrations measured in liver samples from dab (*Limanda limanda*), whiting (*Merlangius merlangus*), flounder (*Platichthys flesus*), and plaice (*Pleuronectes platessa*) collected between 1994 and 1996 down stream potential point sources in the UK ( $15\text{-}1300 \mu\text{g kg}^{-1}$  wet weight)<sup>7</sup>.

## Conclusions

PBDEs have been measured in shorthorn sculpin sampled at three locations in southern Greenland; Usuk (no population), Igaliko (population 40) and Qaqortoq (population 3200). The highest PBDE levels were found in Qaqortoq followed by Igaliko and Usuk. The measured sum concentrations of BDE-47, BDE-99, BDE-100 and BDE-153 in shorthorn sculpin collected at Qaqortoq, Igaliko and Usuk, were 8.2, 3.1, and 2.1  $\mu\text{g kg}^{-1}$  wet weight, respectively. It is shown that the human activity in Igaliko and Qaqortoq has an effect on the level of PBDEs in liver samples of shorthorn sculpins.

## Acknowledgements

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## Flame Retardants in Longitudinal Profile of Elbe River Sediments - first Review and Assessment

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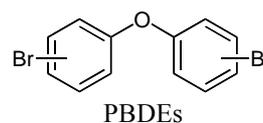
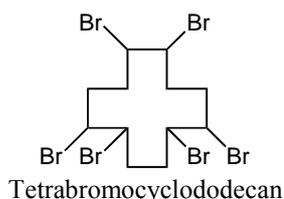
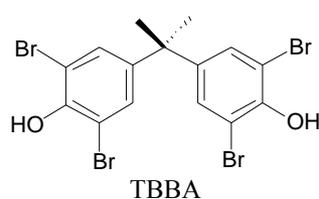
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In a pilot study, sediment samples have been collected from monitoring stations along the longitudinal profile of the Elbe river. These have been analyzed for polybrominated and organo phosphate flame retardants. The poster will present first results for these class of compounds in Elbe sediments.

Recently, much research interest has been focused on anthropogenic compounds and their metabolites mimicking the effect of hormones. Exposure to such endocrine-disrupting chemicals has been associated with various adverse effects on the endocrine and reproductive functions in animals and has also been linked to negative health outcomes in humans. Due to structural similarities with hormones, such as 17 $\beta$ -estradiol and thyroxine, phenolic compounds with one or two hydroxyl groups may play a key role as competitors of the natural hormones.

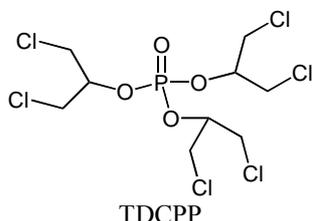
Two important representatives of brominated phenols were selected in this study, which are polybrominated biphenylethers (PBDEs) and tetrabromo bisphenol-A (TBBA). PBDEs were widely used as flame retardants in electronic equipment, plastics, textiles, building materials, carpets, automobiles and aircrafts.

TBBP-A is one of the most commonly used flame retardant worldwide; over 60 000 tons per year which comprises about 30% of the total amount of brominated flame-retardants. It is mainly incorporated as a reactive flame retardant in epoxy resins used in printed circuit boards, but also as an additive in ABS (acrylonitrile–butadiene– and -styrene) systems.

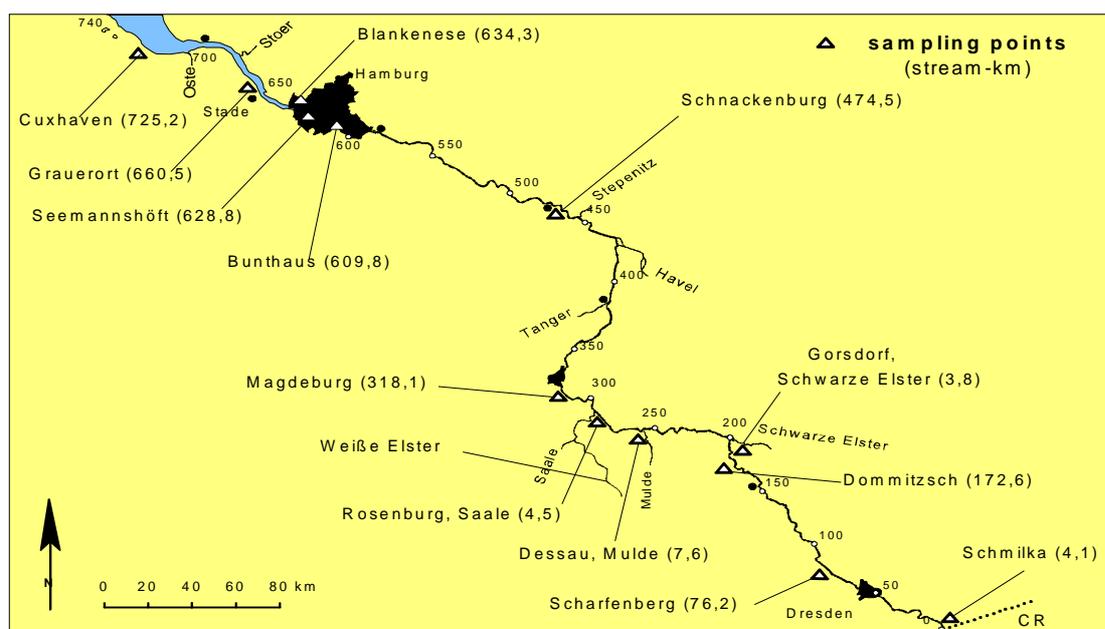


Beside brominated organo phosphates are used as flame retardant. They are widely used to control the flammability of rigid polyurethane foams and polyester foam systems. Latest publications indicated their toxic potential to ecosystem and mammals. Sublethal effects to

rats were found down to a dietary dose of 5 mg/kg/day TDCPP. This study focuses on four widely used representatives Tris-(1,3-chloro 2-propyl) phosphate (TDCPP, Fyrol FR2), Tris-(2-chloro-2-propyl) phosphat (Fyrol PCF), Tris-(2-chloro-ethyl) phosphate and Tris-(2-butoxyethyl) phosphate.



To estimate the ecological impact of flame retardants sediment samples were taken from five monitoring stations along the Elbe river and its tributaries (fig. 1). On line samplers collected suspended matter/sediments over a period of one month. January and February 2001 were selected in this study.



**fig. 1** sampling sites along the longitudinal profile of Elbe river

The poster will present the applied analytical methodology and a critically assessment of the results with special emphasis on ecological impacts.

**Species dependent distribution of polybrominated biphenyls  
and diphenylethers in eggs of Norwegian birds of prey**

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Summary

For the first time, the brominated flame retardant contamination in eggs of Norwegian birds of prey were investigated. The polybrominated diphenylethers (PBDE) showed a species dependent congener pattern in the analysed eggs. In addition, polybrominated biphenyls (PBB) were also detected in most of the analysed samples. The tetra- and hexabrominated congeners dominated the PBB pattern in the analysed egg samples.

Introduction

In recent years brominated flame retardants have come into public focus as new emerging environmental pollutants (Pijnenburg et al. 1995; Sellstrom et al. 1993). In Norway no brominated flame retardants were produced, but import and use is still relatively unrestricted. Due to long-range transport as well as uncontrolled point sources, brominated flame retardants were detected in the Norwegian environment and at Svalbard (Burkow et al. 2001; Herzke, Schlabach M., & Planting S. 2000; Thomsen et al. 2001).

Polybrominated diphenyl ethers (PBDEs) belong to the most abundant and persistent group of the as additives used brominated flame retardants (BFRs). Findings of PBDE in air and biological samples from remote areas as the Arctic indicate an ubiquitous distribution (Alaee et al. 1999; Jansson, 1987; Jansson et al. 1993; Stern, Addison R.F., & Ikonomou M. 2000). Polybrominated biphenyls (PBB) have been mostly used in form of the technical mixture BP6 ("Firemaster") until the eighties, containing up to 56% 2,2',4,4',5,5'-hexabromobiphenyl (PBB 153) (Gupta et al. 2001), and in later years as 97% pure decabromobiphenyl. The market for PBB in Western Europe today is relatively small with a yearly production of about 600 t/a compared to 7,050 t/a for PBDE. PBB is added mostly to thermoplastic polyesters in

contact with live parts of electric appliances and machines (Danish Environmental Protection Agency 1999).

Top predatory bird species are very sensitive indicators of low level contamination of organohalogene compounds, with great compound- and species variation (Hoffman et al. 1998). Especially members of the order *Falconiformes* have proven to be very sensitive to contamination with organochlorines (Fyfe et al. 1976). A mixture of insecticides (DDT and its metabolites), PCB, dieldrin and other structurally related organochlorine chemicals evidently caused the dramatic reduction of local bird populations characterised by reduction of eggshell thickness and egg fertility (Newton 1979, Newton 1988, Nygård 1999). The presence of brominated flame retardants were recently confirmed in substantial amounts in the marine ecosystem, confirming the urgent need of studying the contamination status of top predators (e.g., birds of prey) with this specific compound group (de Boer et al. 1998; Jansson, 1987).

### Results and Discussion

A set of 39 eggs from nine different species, representing different food chains, was analysed for the content of PBB and PBDE (table 1).

Table 1: Average sum PBDE and PBB levels in bird species selected for the initial BFR survey (ng/g ww).

Species	Scientific name	Main food objects	No. of samples	Σ PBDE	Σ PBB
Merlin	<i>Falco columbarius</i>	Passerines and small waders	3	36	7,5
White-tailed Sea Eagle	<i>Haliaeetus albicilla</i>	Fish and seabirds	5	411	44
Goshawk	<i>Accipiter gentilis</i>	Medium-sized birds, small mammals	7	200	42
Golden Eagle	<i>Aquila chrysaetos</i>	Mammals and game birds	9	7	9
Peregrine Falcon	<i>Falco peregrinus</i>	Medium-sized birds	6	224	49
Osprey	<b>Pandion haliaetus</b>	Freshwater fish	4	113	20
Gyrfalcon	<i>Falco rusticolus</i>	Medium-sized birds	2	18	3
Eagle Owl	<i>Bubo bubo</i>	Medium-sized birds and mammals	1	513	70
Sparrowhawk	<i>Accipiter nisus</i>	Passerines	2	732	163

A variety of PBDE and PBB congeners could be quantified in the analysed samples with capillary gas chromatography coupled to low resolution mass spectrometry (GC/LR-EIMS).

Capillary gas chromatographic coupled to high resolution mass spectrometry was performed for a selected number of samples and confirmed the GC/LR-EIMS detection of PBDE and PBB congeners quantified. PBDE was detected in all egg samples analysed with species dependent differences in the congener distribution patterns. Eggs from Sparrowhawk, Goshawk, White-tailed Sea Eagle and Osprey were higher contaminated with PBDE 47 compared to PBDE 99 and, thus, expressed the typical PBDE pattern documented for biota samples (Jansson et al. 1993). However, species, mainly feeding on migrating passerines, thus being exposed to contaminants from regions close to potential sources, showed a different pattern. Eggs from Peregrine Falcons, Merlins and Gyrfalcons showed a higher proportion of PBDE 99 and 153 compared to PBDE 47. In general, the PBDE patterns found indicate the influence of habitat and food specialisation on the contamination pattern in birds of prey. The eggs from the fish feeding White-tailed Sea Eagle were highest contaminated with PBDE, followed by Peregrine Falcon, Goshawk and Osprey (table 1). Golden Eagle, Gyrfalcon and Merlin had the lowest PBDE levels (between 5 and 40 ng/g ww). The one Eagle Owl egg analysed was relatively highly contaminated too, but we cannot claim that this egg is representative for the species. Compared with the technical PBDE mixture Great Lakes DE 71, Sparrow Hawk, Goshawk and Osprey eggs showed a similar distribution pattern, indicating source near contamination.

PBB compounds were not as abundant in the analysed egg samples as the PBDE congeners. The highest contamination was found in egg samples from Eagle Owl and Sparrowhawk (table 1). In general, the limited sample numbers available for these two species restrict a general conclusion. Sum PBB concentrations in eggs of White-tailed Sea Eagle, Peregrine Falcon and Goshawk (average concentration: 40 ng/g ww) were up to ten-times lower than for PBDE. Only a few eggs of Golden Eagle, Gyrfalcon and Merlin contained measurable amounts of PBB (maximum concentration: 20 ng/g ww). The tetra- and hexabrominated congeners dominated the PBB pattern in the analysed egg samples. No significant similarities were found compared to the pattern of the technical mixture Firemaster BP6.

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## PBDEs on the rise: as reflected by aquatic species from British Columbia and the Arctic

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PBDE levels determined in Ringed seal from Holman Island, Northwest Territories showed a 10 fold increase from 1981 to 2000. A pronounced increase in PBDE levels was also observed in whitefish from the Columbia River, British Columbia from 1992 to 1996. Congener 47 was the major contributor to the total PBDE detected in the Ringed seal whereas congener 99 in the whitefish.

### Introduction

Used as additive flame retardants, polybrominated diphenyl ethers (PBDEs) are produced as a series of commercial mixtures containing tetra-deca congeners. PBDEs have become a concern due to their bioaccumulation, potential toxicity, large production quantities, and presence in all environmental compartments at levels that are increasing. Even though 75% of PBDE production is based on deca-BDE, only major amounts of tetra and penta congeners (mostly 47 and 99) have been found in biota.<sup>1</sup> In beluga whales of Cumberland Sound, the total PBDE increased 8 fold from 1982-97 (2-16 ppb lipid) with a congener pattern change of decreasing tetra contributions.<sup>2</sup> A large increase in PBDE levels was also reported in Lake trout of the Great Lakes, Canada from 1978-98 (3-915 ppb lipid)<sup>3</sup> as well as in Swedish human milk from 1972-97 (0.07-4.02 ppb lipid)<sup>4</sup>. This study focuses on examining the temporal trends and congener distributions of PBDEs in environmental samples from two different regions: a) blubber of Ringed seals from Holman Island in the Northwest Territories and b) muscle tissue of whitefish from the Columbia River.

### Materials and Methods

**Samples:** Several blubber samples were obtained from Ringed seals (*Phoca hispida*) (35 males and 14 females, age range 0-35 years) that had been obtained from Holman Island, Northwest Territories (NWT) during 1981, 1991, 1996 and 2000. The whitefish (*Prosopium williamsoni*) (muscle tissue of 14 males and 1 female, age range 2-12 years) were collected in 1992 and 1994-1996 from Slocan River acting as the reference site which feeds into

Columbia River, British Columbia (BC) as well as from regions within the Columbia River that are enclosed by dams, namely near Genelle and Beaver Creek.

Analysis: Blubber (0.2 g) and muscle tissue (10 g) were processed according to a multiresidue method<sup>5</sup> for GC/HRMS using a DB-5HT column and EI/SIR mode. Mono to deca congeners were monitored<sup>5</sup>, but only the mono-hepta congeners are reported as the levels of the higher brominated congeners are those of the procedure blanks. All data was lipid normalised.

## Results and Discussion

The PBDE levels were measured in Ringed seal from Holman Island, NWT obtained during 1981, 1991, 1996 and 2000 (Figure 1). In 1981 the levels were low (0.6 ppb total PBDE), close to that of the procedure blank. However, a large increase has occurred in the later years, reaching 6 ppb total PBDE in 2000. The females showed lower levels than the males of the corresponding collection year which is consistent with the marine-mammal trend of females unloading lipophilic contaminants to their young via lactation<sup>6</sup>. These levels are low in comparison to those found in the blubber of Harbour porpoises from the Strait of Georgia<sup>5</sup> which contained up to 2 ppm total PBDE (lipid normalised, as are all of the following literature values used for comparison purposes). However, it is of concern that PBDEs are even found in this remote northern region and, more importantly, that their levels are rapidly increasing. The major contributing congeners constituting ca. 90% of the total are given in Figure 1. Consistent with most other biota

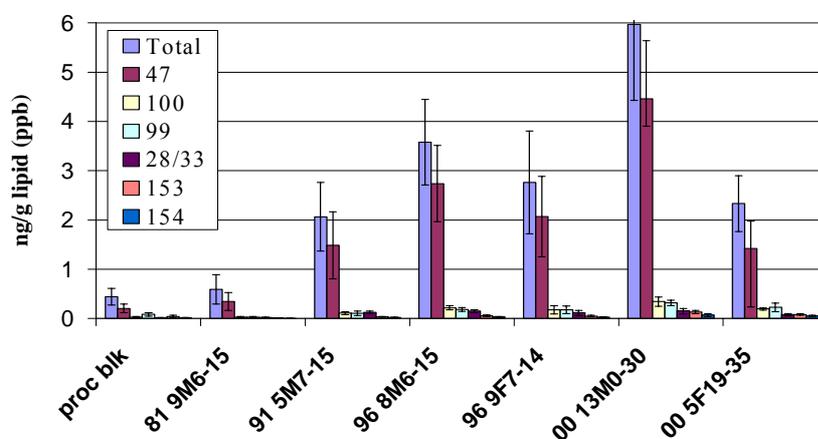


Figure 1. PBDE in blubber of Ringed seals from Holman Island, NWT in 1981-2000. Data labels give the year (81-00), number of individuals, and sex (M/F) followed by the age range.

studies, congener 47 contributed the most (ca. 70%) whereas congeners 99 and 100 contributed similarly (ca. 6%). A PBDE total of ca. 400 ppb has been reported in Ringed seals from the more contaminated Baltic Sea with a ca. 70% contribution of congener 47.<sup>7</sup> A recent study on Harbour seal blubber from San Francisco Bay revealed a 1 ppm mean (congeners 47, 99 and 153) with congener 47 as the main contributor.<sup>8</sup> Exploratory work on PBDE levels in various BC biota revealed higher levels (300-400 ppb) in whitefish from Columbia River compared to various BC fish (most <200 ppb).<sup>5</sup> The Columbia River regions sampled are subject to input from industry (smelter, pulp mill) and municipal sewage of small towns; however, at present a direct point source is not known. This prompted the study of sampling whitefish from different regions along the Columbia River. As the whitefish are enclosed within dams along the Columbia River, they reflect the contamination within a limited region. In 1992, the whitefish from the Genelle region (downstream of a bleached kraft pulp mill) and those from the Beaver Creek region (downstream of a lead/zinc smelter) had total PBDE levels of 66 and 56 ppb, respectively which are more than 4 fold higher than those from the reference site, Slocan River (14 ppb) (Figure 2). Similar to the arctic seal samples, PBDE levels in the whitefish showed a large increase from 1992-96 (reaching levels up to 0.8 ppm for Genelle whitefish in 1995, Figure 2).

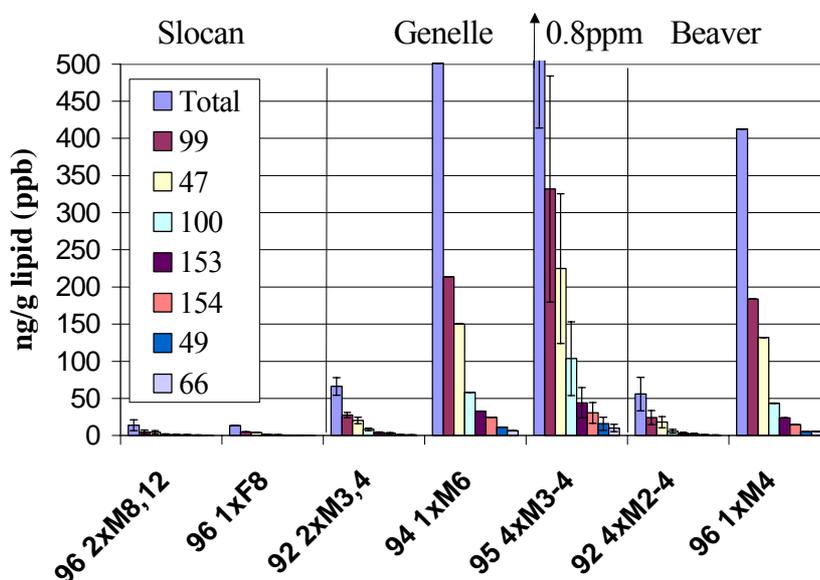


Figure 2. PBDE levels in muscle tissue of whitefish from Columbia River, BC 1992-1996. Data labels give the year (92-96), number of individuals, and sex (M/F) followed by the age(s).

Lake trout from the Great lakes in 1997 contained comparable levels (177-604 ppb) to those in the whitefish. For all the sampling years, the whitefish displayed a similar congener pattern that is distinct from other BC fish species<sup>5</sup> and Great Lakes Lake trout<sup>3</sup> in that congener 99 contributes more than 47. Various fish species from the Virginia Rivers showed a large variation in congener patterns although congener 47 tended to contribute ca. 70%.<sup>9</sup> The analysis of more whitefish collected in 2000 from the Columbia River is planned to determine whether this PBDE rise is continuing. FA/PCA will be applied to the whitefish and seal data above as well as other BC data in an effort to determine potential congener pattern similarities.

#### Acknowledgements

Gratefully acknowledged are Environment Canada for their contribution in collecting the whitefish, Tom Smith for collecting the seal samples, and the RDL staff for their dedicated efforts in analysing the samples. DFO, TCP and TSRI supplied funding for this study.

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## Brominated Flame Retardants in Dutch North Sea Surface Sediments

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### Abstract

Brominated flame retardant (BFR) concentrations were determined in the fine fraction (<63µm) of 10 surface sediments located in the southern part of the Dutch section of the North Sea Continental Shelf. Concentrations generally decreased with increasing distance from the Dutch shore. Highest levels were found off the Western Scheldt, which is in accordance with findings reported by other authors.

### Introduction

Early 2000, the managing authorities of the Dutch North Sea, the North Sea Directorate, requested a report on the distribution of 'new', potentially harmful compounds in surface sediments and sediment cores in the southern part of the North Sea. Compounds selected for this project were Irgarol 1051 (an antifouling agent), phthalates (o.a., plastizisers), and brominated flame retardants (BFR), i.e. Polybrominated Biphenyls (PBBs), Polybrominated Diphenylethers (PBDEs) and hexabromocyclododecane (HBCD).

In this paper, the results will be presented of BFR analyses in ten surface sediments off the Dutch coast, locations chosen to cover both remote off-shore areas as well as near-shore coastal sediments.

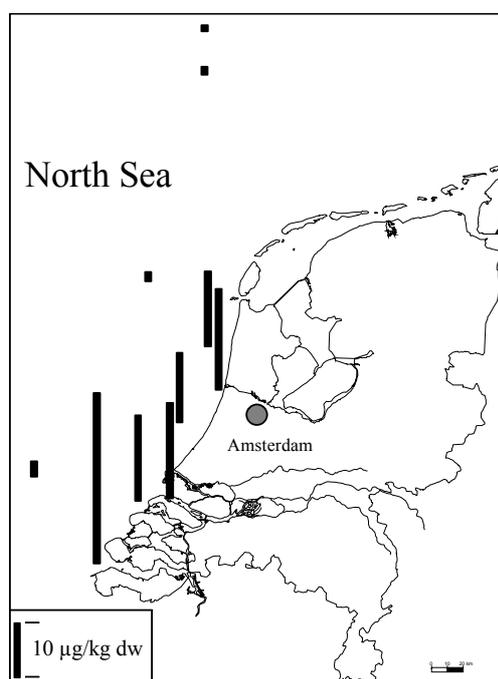
### Methodology

Surface sediments were sampled using a box-core; at each location, the top 5 cm of six individual cores were pooled and further treated as one sample. Each sample was sieved through a 63µm nylon mesh, freeze-dried and homogenized. BFR were determined after hexane:acetone Soxhlet extraction, clean-up over two PL gel columns and further purification by elution over a silica column and sulphuric acid treatment. The final analyses were carried out on GC/MS, using EC/NCI with methane as reagent gas. Peak identification was based on retention time and the recognition of the Br<sup>-</sup>-ion (m/z 79/81). The following compounds were

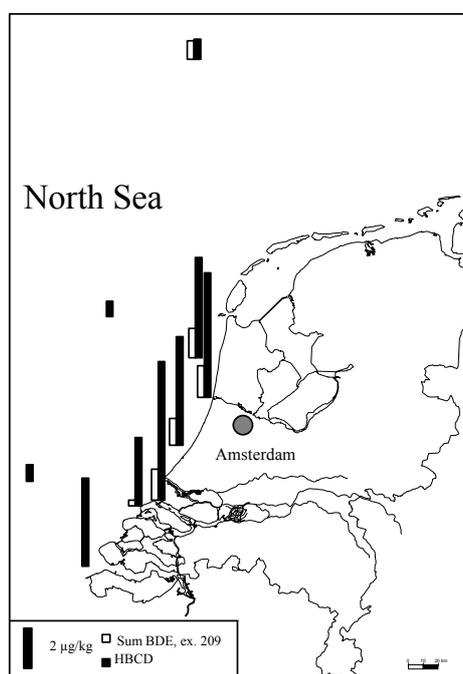
determined: PBB congeners 15, 49, 52, 101, 153 and 209; PBDE congeners 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 190 and 209, and hexabromocyclododecane (HBCD; PBB and PBDE nomenclature being similar to that of the PCBs; Ballschmiter *et al.*, 1992).

## Results and Discussion

Decabromobiphenyl (PBB 209) levels were below 0.54-0.70  $\mu\text{g}/\text{kg}$  dry weight (d.w.; average  $0.63 \pm 0.06$ ), with no apparent relationship between location and PBB 209 level. PBDE 209 levels, however, showed a clear trend with remote locations having lower and near-shore levels having higher levels: Figure 1.



**Figure 1:** PBDE 209 levels in North Sea surface sediments (fraction  $<63\mu\text{m}$ ).



**Figure 2:** Levels of PBDE and HBCD in North Sea surface sediments (fraction  $<63\mu\text{m}$ ).

With  $32 \mu\text{g}/\text{kg}$  d.w., PBDE 209 levels off the Western Scheldt were higher than those reported by de Boer *et al.* (2000), who found a decreasing trend in the Western Scheldt from  $510 \mu\text{g}/\text{kg}$  at the upper estuary to less than  $4 \mu\text{g}/\text{kg}$  near Vlissingen at the mouth. As the PBDE levels in suspended matter in the Western Scheldt were variable and depended on sampling period (de Boer *et al.*, 2000), the results of the present study are probably within the normal concentration range of these compounds.

Figure 2 shows levels of the sum of the determined PBDE congeners minus PBDE 209, as well as the levels of HBCD. Locations with high PBDE 209 levels (Figure 1) were generally

high in these other BFRs as well.

With the exception of PBB 169, all PBB levels were below 0.10 µg/kg d.w.; PBB 169 levels were between 0.05 and 1.10 µg/kg, without apparent relationship between location and contaminant level.

HBCD and PBDE 209 levels showed a positive correlation between locations; contrary, PBDE 209 and PBB 169 levels were *inversely* correlated. This may suggest a different source (either in time or space) of the brominated biphenyls with respect to the other BFR compounds.

From Figures 1 and 2 it becomes evident that the highest BFR contamination is found in near-coastal sediments. This corresponds with the fresh water plumes of the rivers Scheldt and Rhine, being pushed towards the Dutch coast through the counter-clockwise orientated residual currents of the North Sea.

On the sideline of this study, additional parameters (e.g., sediment toxicity) were determined that could be used as indications of sampling site contamination. The genotoxicity of sediment extracts was determined using the Mutatox bacterial genotoxicity test (Klamer *et al.*, 1997). In this assay, incubation of a dark strain of otherwise light-emitting bacteria in the presence of genotoxic compounds (i.e. an extract), may result in a restoration of bioluminescence. The lowest concentration that induces significant light emission was recorded. BFR levels generally correlated positively with genotoxicity; as, however, BFR compounds themselves are not genotoxic in this assay (de Boer *et al.*, 1998), the positive correlation is probably indicative for the presence of unknown genotoxic compounds.

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**Polybrominated diphenyl ethers in Beluga Whales (*Delphinapterus leucas*)  
from the St Lawrence Estuary, Canada: levels and temporal trends**

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Summary

Polybrominated diphenyl ethers (PBDEs) were measured in beluga whales from the St Lawrence Estuary. A significant increase of PBDE concentrations was observed in blubber samples of beluga whales during the last 10 years. These findings are in agreement with temporal trends reported in other studies and provide further evidence that levels of PBDEs have recently increased in the Canadian environment.

Introduction

Polybrominated diphenyl ethers (PBDEs) are aromatic hydrocarbons used as flame retardants in a wide range of manufactured products such as paints, polymers and textiles (WHO, 1994). Total consumption of PBDEs worldwide has doubled from the 1980's to the 1990's. Since that time, the demand for PBDEs has increased in many countries and continues to rise (de Boer et al. 2000). The main source of PBDEs in the environment is probably the disposal of the waste products of flame-retardants, by incineration or burial in landfills. The properties of PBDEs are comparable to those of other persistent lipophilic organic pollutants such as PCBs and DDTs. Recent studies have shown that PBDEs are ubiquitous in the marine environment and are bioaccumulated by the food web (de Boer et al. 2000). However, information on levels of PBDEs in North American environments, particularly in eastern Canada, remains limited. In this study we report current levels and temporal trends of PBDEs in beluga whales from the St Lawrence Estuary.

Materials and Methods

*Samples.* Blubber samples were obtained from stranded adult male (n=14) and female (n=15) beluga whales (*Delphinapterus leucas*) found on the shores of the St Lawrence Estuary between 1997 and 1999. We also analyzed archived blubber samples, obtained from male (n =

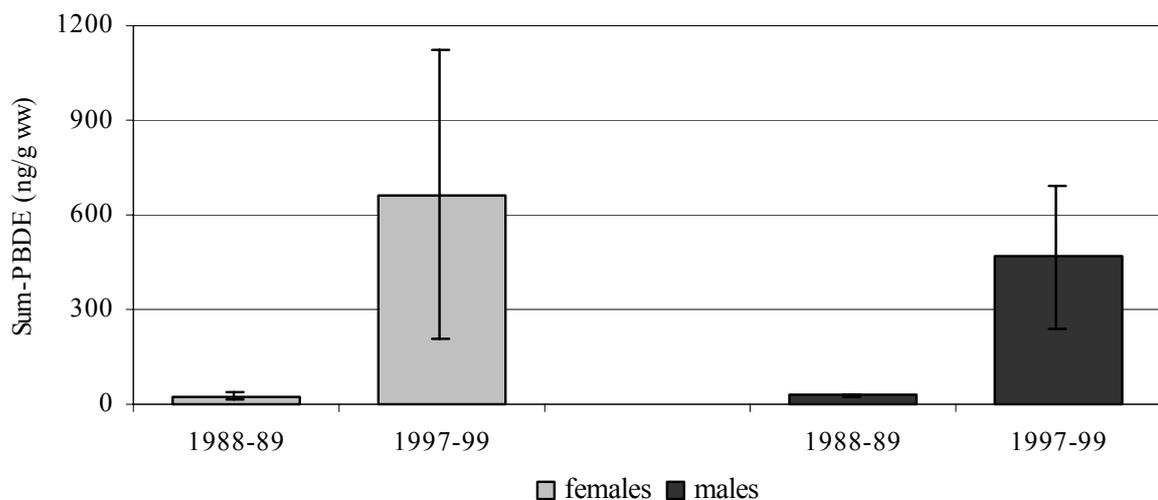
6) and female (n=6) beluga whales which were found dead on the coasts of the Estuary between 1988 and 1990. A sample of blubber extending the depth of the blubber layer was taken from a larger piece of blubber collected from the dorso-lateral region of each individual. Blubber samples were either placed in a solvent rinsed glass jar or wrapped in solvent rinsed aluminium foil and placed in a sealed plastic bag and stored at  $-20^{\circ}\text{C}$  until analysis.

*Analysis of BDPEs.* The skin was removed from the blubber samples (0.5-1 g wet weight), which were then chemically dried with sodium sulphate before being transferred to a glass column. One  $^{13}\text{C}_{12}$  PBC was added to the column before the extraction procedure. Lipids and lipophilic compounds were extracted from the sample with dichloromethane-hexane (50:50). The extraction solution was fractionated in three portions, one of them received a mixture of four  $^{13}\text{C}_{12}$  PBDEs and was prepared for purification. Lipids were removed from the remaining extract by gel permeation chromatography. The extract was further cleaned by elution through a two-layer column packed with neutral silica and alumina. The final extract was reduced in volume and spiked with an instrument performance solution containing two  $^{13}\text{C}_{12}$  PCBs. Quantification of forty individuals PBDEs was performed using a gas chromatograph equipped with an ion trap mass detector. Chromatographic separation of the contaminants was achieved using a 30m DB-5MS column (0.25 mm ID, 0.25  $\mu\text{m}$  film thickness) with helium as the carrier gas. The ion source was operated in electron impact ionisation mode and the ion trap in MS/MS mode. Concentrations of PBDE congeners were calculated using relative response factors (RRFs) determined from a three-point calibration curve.

### Results and Discussion

*Contamination levels.* PBDE levels in male and female beluga whales, expressed as the sum of forty congeners, are shown in the figure. Concentrations of polybrominated diphenyl ethers in beluga whales collected between 1997 and 1999 were unexpectedly similar in both females ( $665 \pm 457$  ng/g wet weight) and males ( $466 \pm 230$  ng/g wet weight). Levels of persistent organochlorinated contaminants in adult beluga whales are generally higher in males than in females (Muir et al, 1996a,b; Lebeuf et al, 2001). This trend in bioaccumulation is attributed to the transfer of contaminants from a mother to her young, via the placenta and mother's milk, and was confirmed for PCBs and DDTs measured in the same blubber samples. These observations suggest that the transfer of BPDEs from the females to the calves is not as important for PBDEs as it is for PCBs and DDTs. On the other hand, males could be more efficient than females in eliminating PBDEs. This last assumption is in agreement with the

relatively lower capacity of female mammals to transform contaminants, as reported by Aguilar et al. (1999). Contamination levels of PBDEs in male beluga whales from the St Lawrence are more than 25 times higher than in male beluga whales collected in 1997 from the SE Baffin and Cumberland Sound (Stern and Ikonomou, 2000). Although there is increasing evidence of long range transport of PBDEs, contamination in the St Lawrence Estuary very likely originates, as for most organic contaminants, from fluvial inputs from the St. Lawrence River and the Great Lakes.



*Temporal trends.* Concentrations of PBDEs in beluga whales from the St Lawrence increased significantly during the last 10 years (see figure). PBDE levels in blubber samples of belugas collected between 1988 and 1990 were similar in both males and females but were approximately 20 times lower than levels in the 1997-1999 samples. The similar current levels of PBDEs in males and females could also be a consequence of the relatively recent introduction of these compounds in the St Lawrence Estuary. Under these new environmental conditions, PBDEs would tend to be much more accumulated by both male and female belugas, rather than be eliminated. The increase of PBDE levels in St Lawrence beluga whales during the last 10 years is in agreement with temporal trends reported in other studies, such as those for lake trout from the Great Lakes (Luross et al., 2000), and for beluga whales from the SE Baffin and Cumberland Sound (Stern and Ikonomou, 2000). The temporal trend of PBDEs in beluga whales from the St Lawrence Estuary provides further evidence that these compounds have recently increased in the Canadian environment.

## Conclusion

The growing use of PBDEs as flame-retardants has resulted in an increasing contamination of beluga whales from the St Lawrence Estuary. However, levels of PBDEs in male and female belugas are unexpectedly similar, unlike the trend shown with other persistent organic compounds. These results can be explained by the relatively recent history of BPDEs contamination in the St Lawrence Estuary or the greater capacity of male beluga whales to biotransform these compounds when compared to female animals.

## Acknowledgements

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## Establishing Baseline Levels of Polybrominated Diphenyl Ethers in Lake Ontario Surface Waters

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Analysis of large volume water samples, field concentrated by glass fiber filters and XAD-2<sup>®</sup> (XAD) resin determined that polybrominated diphenyl ethers (PBDEs) in Lake Ontario surface waters ranged between 4 and 13 pg/L in 1999. Two PBDE congeners, 2,2',4,4'-tetrabromo-diphenyl ether (BDE-47) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), made up >70% of the total. Dissolved and particulate phases analyzed separately showed that ~90% of total measured PBDEs were in the dissolved phase. This may be the first report of PBDEs being measured in North American surface waters.

New York State Department of Environmental Conservation (NYSDEC) and United States Environmental Protection Agency (EPA) researchers collected large volume samples of Lake Ontario surface water in 1999 for persistent organic pollutant (POP) analyses. Lake Ontario is among 15 of the world's largest lakes and provides an important source of drinking water to surrounding US and Canadian metropolitan areas<sup>1</sup>. PBDEs were added to the list of analytes in response to recent Canadian reports that PBDEs have been detected in Lake Ontario fish tissue<sup>2</sup>. PBDEs are widely used as an additive flame retardant and are as bioaccumulative as polychlorinated biphenyls (PCBs)<sup>3,4</sup>.

Samples were collected from EPA's Great Lakes research vessel during fall isothermal conditions. Duplicate samples were collected in the eastern, central and western basins of the lake. Water was sampled continuously for 24 hr in each basin while covering an ~50 km<sup>2</sup> grid pattern. An intake tube was suspended from a boom off the side of the vessel and towed 1 m below the surface. Approximately 2,500 L of surface water was pumped through a glass fiber filter cartridge (1 mm nominal porosity) to capture contaminants bound to particulates. Several hundred liters of filtered water were then pumped through two

columns each holding 35 g of XAD resin (divinylbenzene-styrene copolymer) to capture dissolved hydrophobic contaminants. The XAD columns were placed in series in order to increase the total volume of resin available to capture dissolved contaminants. This also provides a means, by analyzing the columns separately, to evaluate the extraction efficiency of the first XAD columns. XAD has been a tool for concentration of environmental contaminants in water for over 25 years<sup>5-10</sup>.

In addition to PBDEs, glass fiber filter and XAD resin samples were analyzed for PCB congeners, dioxin/furan congeners, and organochlorine pesticides. A limited number of archived Lake Ontario sample extracts collected in 1997 with similar sampling equipment were also analyzed. Filter samples and XAD resins were spiked with a suite of <sup>13</sup>C labeled internal standards, Soxhlet extracted overnight with dichloromethane, and the extract fractionated on a Florisil<sup>®</sup> column. The Florisil column fraction containing ortho-substituted PCBs was concentrated down to 20 mL and analyzed for PBDEs using a pressure programmed DB-5HT column and detected by EI positive ion HRMS at 10,000 mass resolution, in selected ion mode, monitoring two peaks in the molecular ion cluster. The method was calibrated with a set of 41 PBDE congeners (mono to decabromo, based on Cambridge Isotope Labs analytical standard #EO-4980). PBDEs were quantitated against <sup>13</sup>C labeled internal standards and individual response factors were determined for each reported congener. Levels of PBDE congeners detected in procedural (method) blanks were used to correct field sample results.

The analytical results show that PBDEs in Lake Ontario surface waters ranged between 4 and 13 pg/L with ~ 90% in the dissolved phase. BDE-47 and BDE-99 were the most abundant congeners together making up >70% of total PBDEs. BDE-47 and BDE-99 have been reported to be the dominant congeners detected in Lake Ontario lake trout<sup>2</sup>. Results of first and second XAD columns analyzed separately show that the first column captured essentially all of the detected dissolved phase PBDEs. BDE-47 and BDE-99 were not detected on the second columns. Concentrations of PBDEs detected on filtered particulates were much lower and showed fewer consistent congener compositions than those detected in the dissolved phase samples. For example, detected levels of dissolved phase BDE-47 ranged between 0.06 and 3.6 pg/L compared to a range of 0.05 and 0.23 detected on particulates. This characterization of PBDEs in Lake Ontario surface waters will assist water quality experts evaluate the significance of these contaminants in the Great Lakes ecosystem.

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**Concentrations of BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and HBCDD  
in guillemot egg from the Baltic Proper 1996-2000.**

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Summary

**Guillemot eggs collected at St. Karlsö in the Baltic Proper between the years 1996-2000 have been used in this work. The egg content of analysed brominated flame-retardants (BFRs) is reported, with highest levels (given in ng/g lipid weight, geometric mean and 95% C.I.) for BDE -47 (87.5, 70.2-185.1) and for HBCDD (116.9, 112.3-135.2). No time trend for the BFRs in question is statistically proven for the investigated years.**

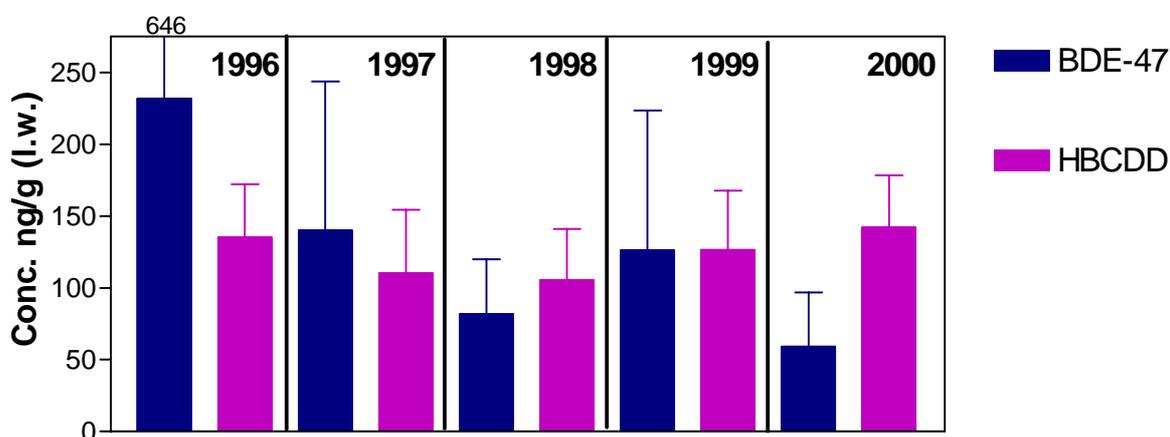
Guillemot (*Uria aalge*) is one of the few bird species that stay in the Baltic all year round. The bird feed on pelagic fish *i.e.* sprats (*Sprattus sprattus*) and herring (*Clupea harengus*) and the female normally lay one egg per year<sup>1</sup>. In the Swedish environmental monitoring program, 10 guillemot eggs are collected annually and analysed regarding both biological/morphological and chemical variables<sup>1,2,3,4</sup>. During the five years, 1996-2000, a total of 49 eggs were collected and analysed.

The concentrations of analysed BFRs for the years 1996-2000 are given in table 1.

**Table 1.** Guillemot egg collected between the years 1996-2000 and analysed for their content of PBDEs (-47, -99, -100, -153, -154) and HBCDD.  
*n*=number of eggs, *SD*=standard deviation, *lw*=lipid weight.

	n	Mean ± SD (ng/g lw)	Median (ng/g lw)	Geometric mean (ng/g lw)	Lower ; Upper 95% CI
BDE -47	49	127.70 ± 199.9	89.4	87.51	70.24 ; 185.1
BDE -99	49	13.15 ± 14.90	11.0	10.63	8.87 ; 17.43
BDE -100	30	37.75 ± 55.20	24.5	28.51	17.14 ; 58.37
BDE -153	10	1.41 ± 0.84	1.0	1.23	0.81 ; 2.01
BDE -154	10	3.57 ± 0.81	3.35	3.49	2.99 ; 4.15
HBCDD	49	123.7 ± 40.01	122.0	116.9	112.3 ; 135.2

Is there a time trend in the material? A PLS model<sup>5</sup> with year as Y and the analysed BFRs as the X-matrices has no significant components. When 2 components are forced on the data the resulting model has  $R^2X = 0.824$ ,  $R^2Y = 0.061$  and  $Q^2 = 0.000$  meaning that there is not enough systematic change over the 5 years for the model to have any predictive value. Interestingly, the multivariate model suggests that the HBCDD concentration tends to increase at the same time as the PBDEs are decreasing in concentration over the five years but this is not statistically proven and a longer time-series will have to be analysed. BDE-47 and HBCDD concentrations respectively are illustrated for the 5 years (1996-2000) in figure 1.



**Figure 1.** BDE -47 and HBCDD concentrations (mean  $\pm$  SD , ng/g lipid weight) in guillemot eggs collected at St. Karlsö in the Baltic Proper 1996-2000. (n=10 eggs each year).

## Acknowledgements

MISTRA for financially supporting Katrin Lundstedt-Enkel within the NewS programme. The data for BFRs in guillemot eggs was produced within the Swedish Environmental Monitoring Programme, Swedish Environmental Protection Agency. Umetrics for the software<sup>6</sup>.

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- <sup>6</sup>Simca 8.1 by Umetrics, [www.Umetrics.com](http://www.Umetrics.com)

**Multivariate modelling of concentrations of BDE-47, BDE-99, BDE-100 and HBCDD in relation to organochlorines in guillemot egg collected from the Baltic Proper 1996-2000.**

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Summary

Guillemot eggs collected from St. Karlsö in the Baltic Proper between the years 1996-2000 have been used in this work. The egg content of analysed brominated flame-retardants is modelled in relation to the egg biology/morphology and concentration of organochlorines. The model's predictive value is best for BDE-47 and BDE-99 and lowest for BDE -100 and HBCDD.

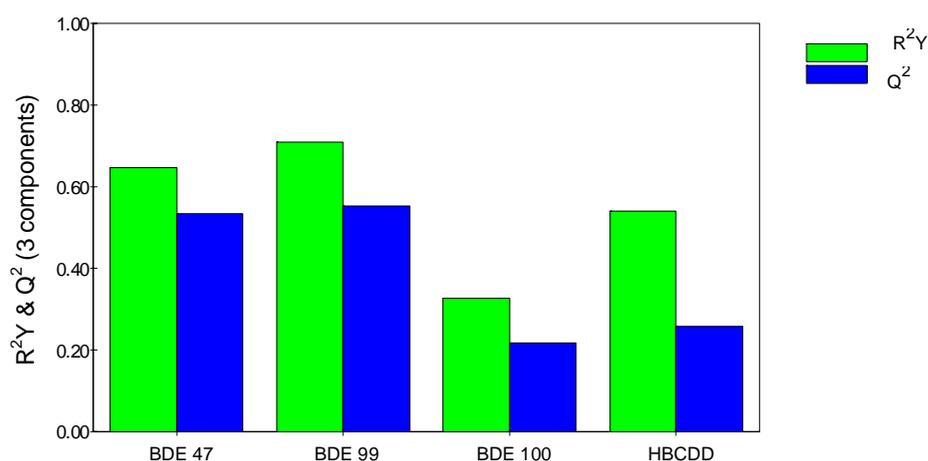
Guillemot (*Uria aalge*) is one of the few bird species that stay in the Baltic all year round. The bird feed on pelagic fish *i.e.* sprats (*Sprattus sprattus*) and herring (*Clupea harengus*) and the female normally lay one egg per year<sup>1</sup>. In the Swedish environmental monitoring program, 10 guillemot eggs are collected annually and analysed regarding both biological/morphological and chemical variables<sup>1,2,3</sup>. During the five years, 1996-2000, a total of 49 eggs were collected and analysed.

In this investigation a total of 27 variables, for each individual egg, were used for the multivariate modelling. Eight of the variables describe the egg biology/morphology *i.e.* shell weight, shell thickness, fat content, dry matter *etc.* and 19 variables describe the analysed concentrations of HOCs (halogenated organic compounds) *i.e.* DDT, DDE, DDD, PCB (congeners -28, -53, -101, -137, -180),  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, HCB, PBDE (congeners -47, -99, -100) and HBCDD<sup>2,3,4</sup>.

In this work we were interested in studying if variations in egg biology and content of organochlorines mirror variations in the egg content of analysed brominated flame-retardants (BFRs). The questions to be answered are; can a multivariate model, modelling the biology of an egg together with its content of organochlorines, be used to predict the egg BFR

concentrations? What variable/-s shows the best co-variation with the egg BFR concentrations?

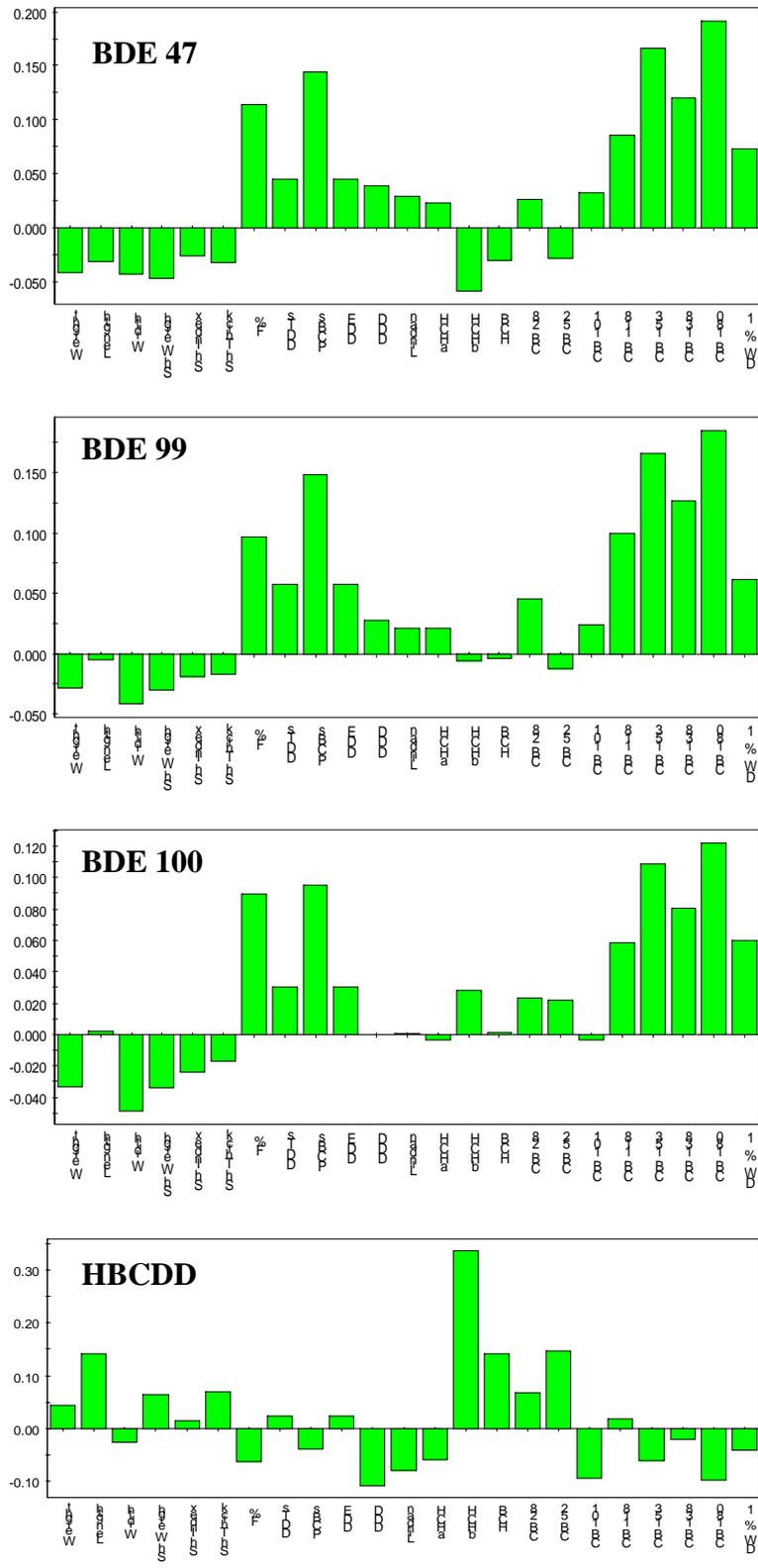
Initial principal component analysis (PCA) using 10 significant components explained 97 % of the variation in the measured variables. In the resulting loading plot, clear groupings were discernible (data not shown). More extensive modelling was carried out using Partial Least Squares regression - Projection to Latent Structures analysis (PLS) <sup>5</sup>. The resulting PLS model, using BDE-47, -99, -100 and HBCDD concentrations in the egg as Y-matrices and the biological/morphological and chemical variables as X-matrices, describes in mathematical terms the BFRs intrinsic relationship to the measured biological/morphological variables and analysed concentrations of organochlorines in the guillemot eggs. The PLS model uses 3 components ( $R^2X=0.61$ ,  $R^2Y=0.58$ ,  $Q^2=0.39$ ) where the predictive value is highest for BDE – 99 and -47 and lowest for BDE –100 and HBCDD (fig 1).



**Fig. 1.** Model summary for the PLS analysis. The concentrations of BDE –47, -99 –100 and HBCDD in guillemot eggs ( $n=49$ ) collected at St Karlsö in the Baltic Proper 1996-2000 are modelled as Y and egg biology/morphology and measured organochlorines as the X-matrices. Plot showing the respective Y variable's  $R^2Y$  value and predictive value,  $Q^2$ . 3 components.

BDE-99 and –47 has the highest values in the model summary plot.

For BDE-99;  $R^2Y = 0.71$ ,  $Q^2 = 0.553$  and for BDE-47;  $R^2Y = 0.647$ ,  $Q^2 = 0.533$ . For the other two BFRs the values are lower, HBCDD has  $R^2Y = 0.54$ ,  $Q^2 = 0.257$  and PBDE-100;  $R^2Y = 0.327$ ,



**Fig. 2.** Regression coefficients plots. PLS modelling with BDE -47, -99, -100 and HBCDD concentrations in guillemot eggs ( $n=49$ ) collected at St. Karlsö in the Baltic Proper 1996-2000 as Y and egg biology/morphology and measured organochlorines concentrations as X-matrices.  $R^2X=0.61$ ,  $R^2Y=0.58$ ,  $Q^2=0.39$ . 3 components.

$Q^2=0.217$  meaning that the egg concentration of HBCDD and PBDE-100 have the lowest predictive values of the BFRs.

When looking at the respective BFRs separately the variables that co-variate most with the BFRs are different (fig 2). For the three PBDEs (-47, -99 and -100) the pattern is similar, with a high positive correlation between variation in the PBDE concentrations and that of PCB-180, PCB-153, PCBsum, PCB-138 and the fat content of the egg (F%). A completely different pattern is shown by the variables correlating to varying concentrations of HBCDD with a high positive correlation between variation in the HBCDD concentration and that of  $\beta$ -HCH, PCB 52, HCB and the length of the egg. There are also indications that HBCDD concentrations are positively correlated to other size parameters than the length of the egg. This differs from the correlation-pattern the PBDEs display. Also, when the modelling was performed in the same way but using the respective substance's concentrations expressed on a fresh weight basis instead of on a lipid weight basis, the same pattern emerged (data not shown).

This difference in co-variation between various HOCs and biology/morphology of the egg might be related to differences in the metabolism and pathway of studied HOCs from food via the female to the egg. The findings are promising for the work started, which aims to model biomagnification processes in the Baltic food web

#### Acknowledgements

MISTRA for financially supporting Katrin Lundstedt-Enkel within the NewS programme. The data for BFRs in guillemot eggs was produced within the Swedish Environmental Monitoring Programme, Swedish Environmental Protection Agency. Umetrics for the software<sup>6</sup>.

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- <sup>6</sup>Simca 8.1 by Umetrics, [www.Umetrics.com](http://www.Umetrics.com)

## Spatial and Temporal Distribution of Polybrominated Diphenyl Ethers and Polybrominated Biphenyls in Lake Trout from the Great Lakes

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The focus of this study was to investigate the presence of the brominated flame-retardants (BFRs), polybrominated diphenyl ethers (PBDEs), and polybrominated biphenyls (PBBs) in lake trout from the Laurentian Great Lakes.

PBDEs and PBBs are two types of brominated flame-retardants used in a variety of commercial products to prevent fires. Both of these flame-retardants are additive and therefore have the potential to leach from their host material into air, water and sediment. This activity could be harmful to the environment, since these toxic compounds are persistent, lipophilic and bioaccumulate.

In order to describe the spatial and temporal distribution of brominated flame-retardants in the Great Lakes, lake trout (*Salvelinus namaycush*) (n=10 per lake) were analysed for PBDEs and PBBs using high-resolution mass spectrometry. For the spatial analysis, six-year-old lake trout, collected in 1997, from Lake Superior, Lake Huron, Lake Erie, and Lake Ontario were used, while the temporal trend focused on five-year-old lake trout collected from Lake Ontario sites between 1978 and 1998.

Mean levels of PBDEs (Figure 1 (a)) were significantly higher in fish from Lake Ontario in comparison to Lake Superior, Lake Huron, and Lake Erie lake trout (p<0.05). In all samples, the predominant PBDE congeners detected were 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), and 2,2',4,4',6-pentabromodiphenyl ether (BDE-100). These are the most prevalent components of the commonly used flame-retardant, Bromkal 70-5DE<sup>®</sup>. Figure 1(b) shows lake trout from Lake Huron had significantly higher concentrations of PBBs than all other lakes tested (p<0.05). In

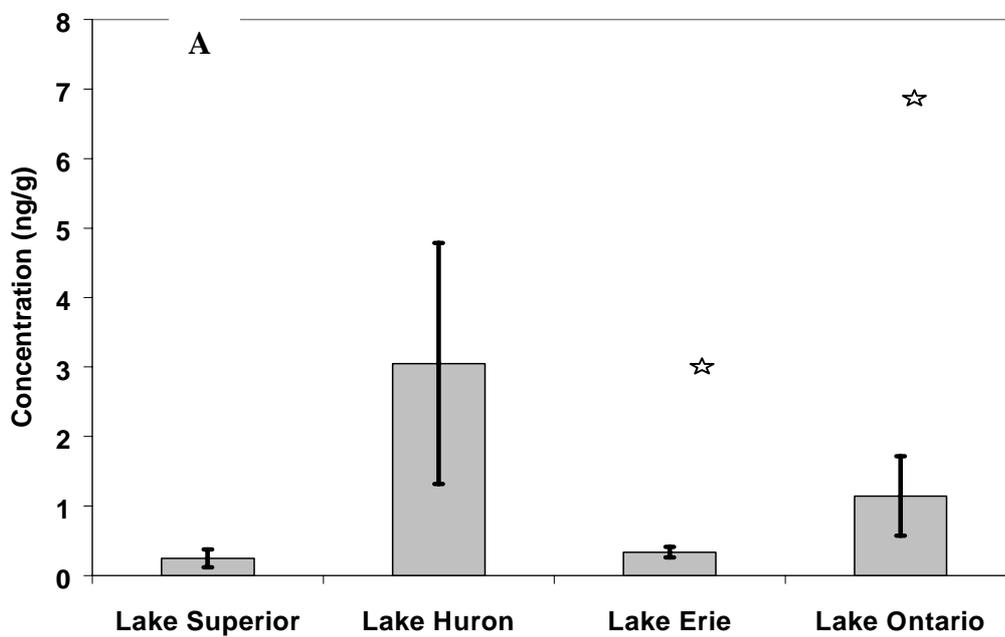
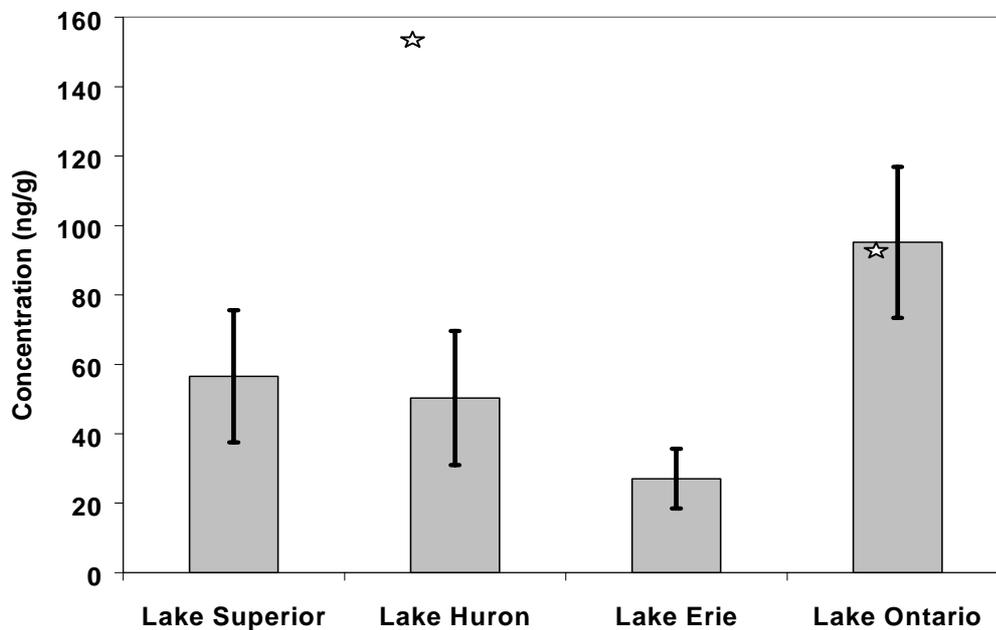
all lake trout samples analysed, the major constituent of the flame-retardant FireMaster BP-6<sup>®</sup>, 2,2',4,4',5,5'-hexabromobiphenyl (BB-153), was consistently identified as the PBB congener with the highest concentration.

The significantly higher levels of PBDEs in Lake Ontario lake trout combined with the high-density of surrounding human habitation prompted an historical study of BFR accumulation. A significant increase ( $p < 0.05$ ) in the mean concentrations of PBDEs shown in Figure 2 (a) correlates with the increased use of PBDEs as flame-retardants in manufacturing. In contrast, the mean concentrations of PBBs in lake trout decreased over the twenty-year time-period (Figure 2 (b)). The observed decline in levels of PBBs coincides with its ban following the 1973 Michigan, U.S.A. incident, in which cattle feed was contaminated with BB-153.

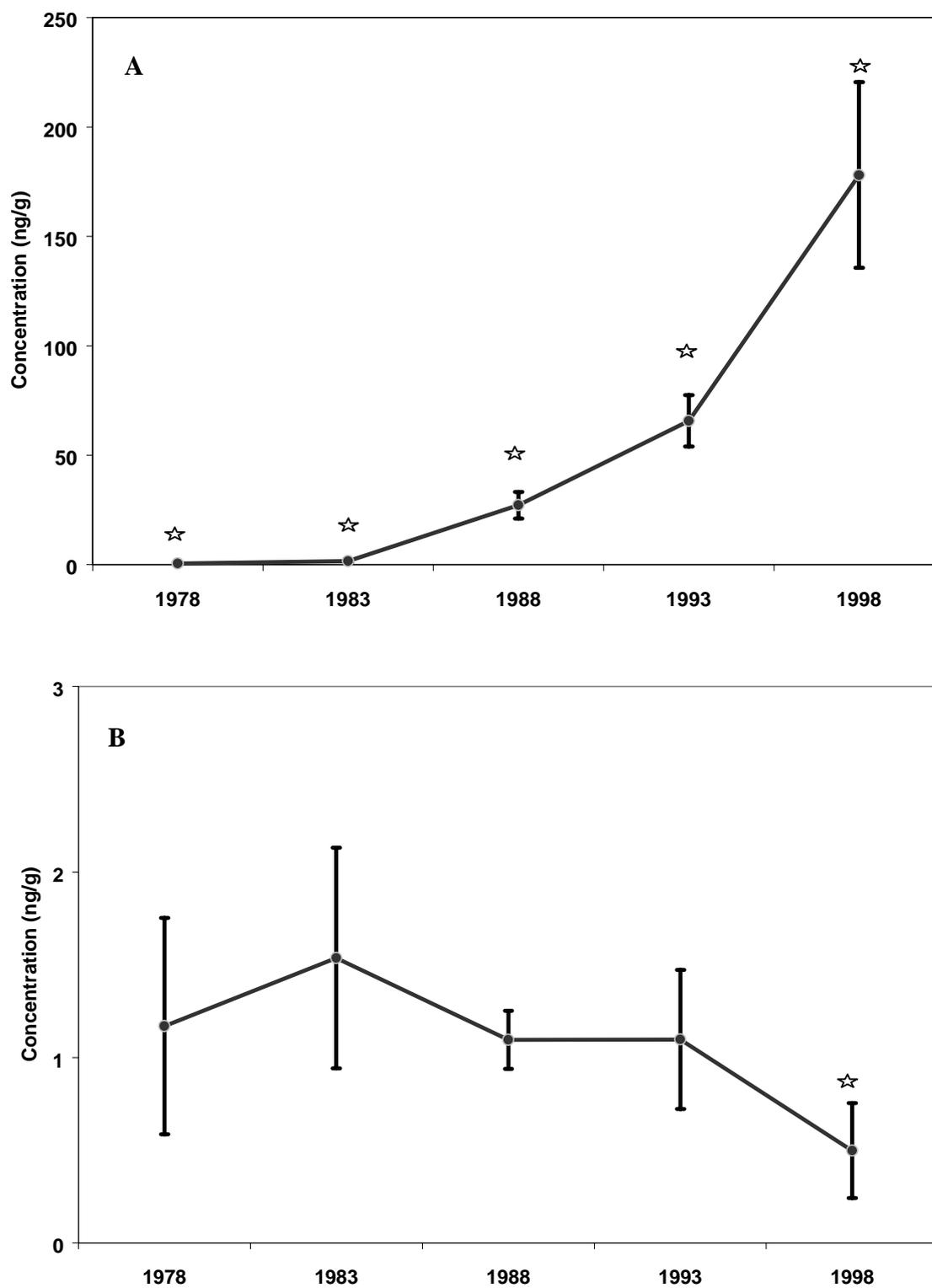
Together, these data demonstrate that PBDEs and PBBs are ubiquitous pollutants and appear to be bioaccumulating in the Laurentian Great Lakes.

Figure 1: Total concentrations of PBDEs (a) and PBBs (b) in lake trout from Lake Superior, Lake Huron, Lake Erie, and Lake Ontario (ng/g ww) (+/- standard deviation).

☆ = (p<0.05, in comparison to all other lakes studied)



**Figure 2:** The average concentration (ng/g ww) (+/- standard deviation) of total PBDEs (a) and PBBs (b) in Lake Ontario lake trout from 1978 to 1998. The error bars for both 1978 and 1983 are small (<1%) and can not be viewed on the graph. ☆ = (p<0.05, in comparison to all other lakes studied)



## Spatial Distribution of some Polybrominated Diphenyl Ethers and Hexabromocyclododecane in Herring (*Clupea harengus*) along the Swedish Coast

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### Summary

The spatial distributions of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) were studied in herring from the Swedish coast as a part of the Swedish Environmental Monitoring Programme on Contaminants in Biota (SEMPC). The highest concentrations for all investigated compounds were found in the southern Baltic Proper.

### Introduction

Brominated flame retardants, such as PBDE, are widespread environmental pollutants detected in biological samples not only from urban areas but also from remote regions. The first report of PBDE in fish was published in 1981 (Andersson and Blomkvist). The fish were caught in the Swedish River Viskan, where textile industries are located. Since then a number of reports have been published on PBDE concentrations in freshwater and marine fish (for reviews see Sellström *et al.*, 1999, de Wit., 2000) including Baltic herring (Sellström *et al.*, 1993; Haglund *et al.*, 1997; Strandman *et al.*, 1999; Bureau *et al.*, 1999). HBCD is mainly used as an additive flame retardant to polystyrene (EU Draft, 1999). Relatively few reports on environmental levels of HBCD have been published until now. The presence of HBCD has been reported in fish from the River Viskan (Sellström *et al.*, 1998) and in guillemot eggs from the Baltic Sea (Kierkegaard *et al.*, 1999).

PBDEs have previously only been studied within SEMPC in guillemot eggs from St Karlsö in the Baltic (Sellström *et al.*, 1999) and in pike from a freshwater lake (Kierkegaard *et al.*, 1999). In 1999, the programme was expanded to include PBDE and HBCD-analyses in herring from six sites. Herring from the same sites were included in a previous study (Sellström *et al.*, 1993). In

the present study, the distribution of the geometric mean concentrations for the first year of analyse are presented together with a comparison of the distribution pattern of one PCB congener, CB-153. To our knowledge this is the first report on HBCD levels in fish from the Baltic Sea.

## **Material and Methods**

*Samples:* Twelve specimens of herring (*Clupea harengus*), were collected and analysed from five different sites: Harufjärden in the Bothnian Bay, Ängskärsklubb in the Bothnian Sea, Landsort in the northern Baltic Proper Karlskrona archipelago in the southern Baltic Proper and at Fladen in the Kattegatt. At Väderöarna in the Skagerakk, twenty specimens were analysed. All sites are reference sites within SEMPC with no known local sources of pollutants and thus believed to be representative for a larger area. At all sites, sampling was conducted in the autumn. All specimens were females, 2-3 years old in the Kattegatt and the Skagerakk and 3-4 years old from the rest of the sites.

*Analysis:* The muscle samples were extracted by a method described earlier (Jensen *et al.*, 1983) and analysed according to Sellström (1999). In short the samples were analysed by GC/MS using chemical ionisation, measuring negative ions (MS-ECNI), ammonia was used as reaction gas. The mass fragments monitored were  $m/z$  79, 81 for PBDE, HBCD and 237, 239 for the internal standard, dechlorane. HBCD and the following PBDE congeners were recorded; BDE-47, BDE-99, BDE-100, BDE-153, BDE-154. Fat content and biological measurements are presented in Table 1.

*Statistics:* To study the spatial distribution and differences between regions, the geometric mean concentrations were plotted together with their corresponding 95% confidence intervals. Analysis of Variance (ANOVA) was applied to find out whether the differences were statistically significant ( $p < 0.05$ ). The ANOVA was followed by a pairwise multiple comparison test. To get a rough comparison between the spatial distribution pattern of PBDEs with PCBs, ratios of the various PBDEs were formed with the PCB-congener CB-153.

## **Results and Discussion**

For all PBDE congeners and HBCD, a similar geographical pattern was encountered (Figure 1 and Table 2). In general significantly higher concentrations were found for all the investigated PBDEs and for HBCD in the samples from the southern Baltic Proper compared to the other sites..

The higher concentrations found in the samples from the Karlskrona archipelago can not be explained by an extremely low fat content or by any deviant biological variables such as age, size etc. There are no known local sources in this area. Hence, a fair assumption so far would be that the pollution loads of PBDEs and in particular HBCD are higher to the southern Baltic Proper than to rest of the Baltic and to the Swedish west coast. Similar results were indicated by Sellström *et al.* (1993, 1999), in herring collected in 1987 at the same sampling sites. However, the PBDE concentrations found in this study are lower than the earlier reported concentrations (BDE-47, -99, -100), which may indicate decreased PBDE concentrations in Baltic herring during the period (1987–1999). A decreasing temporal trend covering the same time period has been reported for guillemot eggs collected in the central Baltic Proper (Sellström, 1999, *paper V*). However, no estimates of unexplained between-year variation are yet available for the Baltic herring, thus these differences may not remain if several years of samples will be analysed.

Earlier studies in herring of the spatial PCB distribution in the Baltic area has shown significantly higher concentrations of PCB in the Baltic Proper compared to the Bothnian Bay and the Swedish west coast (Bignert *et al.*, 1998). In this study we found significantly higher concentrations of all PBDE congeners and HBCD in the southernmost location but also a more *even* concentration distribution at all other locations compared to CB-153.

### **Acknowledgement**

The Swedish Environmental Monitoring Programme on Contaminants in Biota is financed by the Swedish Environmental Protection Agency.

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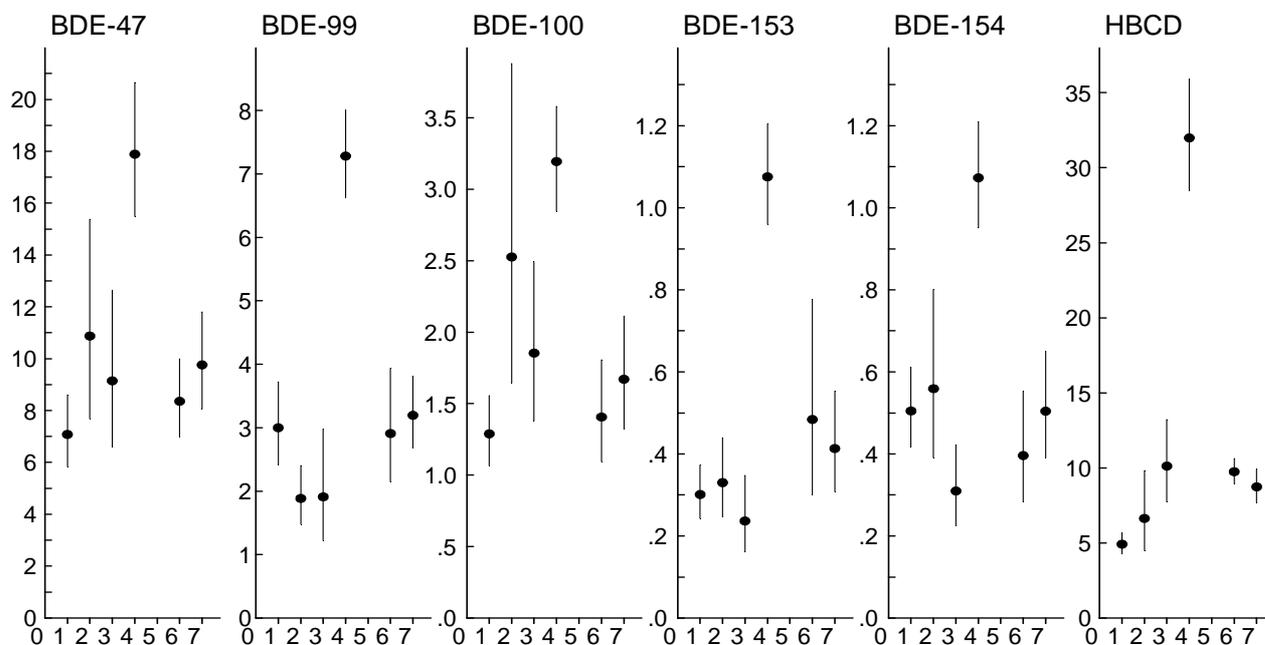
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Site	n	fat %	age	weight (g)	length (cm)
Harufjärden (1)	12	2.9 (2.5-3.3)	3	25.4 (23.9-26.9)	15.9 (15.5-16.3)
Ängskärsklubb (2)	12	1.7 (1.2-2.3)	3-4	33.3 (28.5-38.9)	17.5 (16.6-18.5)
Landsort (3)	12	3.5 (2.8-4.3)	4	34.2 (32.4-36.1)	17.3 (17.0-17.5)
Karlskrona (4)	12	2.0 (1.8-2.2)	3	40.2 (37.5-43.0)	18.9 (18.5-19.4)
Fladen (6)	12	4.3 (3.6-5.0)	2	51.0 (48.4-53.9)	19.8 (19.5-20.1)
Väderöarna (7)	20	5.3 (4.4-6.3)	2	67.9 (64.5-71.5)	21.2 (20.8-21.6)

**Table 1.** Number of samples (n), geometric mean concentrations and 95% confidence intervals of fat and various biological variables.

Site	n	BDE-47 ng/g fat	BDE-99 ng/g fat	BDE-100 ng/g fat	BDE-153 ng/g fat	BDE-154 ng/g fat	HBCD ng/g fat	CB-153 ng/g fat
Harufjärden (1)	12	7.1 (5.8-8.6)	3.0 (2.4-3.7)	1.3 (1.1-1.6)	0.30 (0.24-0.37)	0.50 (0.42-0.61)	4.9 (4.3-5.7)	35 (30-41)
Ängskärsklubb (2)	12	11 (7.7-15)	1.9 (1.5-2.4)	2.5 (1.6-3.9)	0.33 (0.25-0.44)	0.56 (0.39-0.80)	6.6 (4.5-9.8)	180 (120-270)
Landsort (3)	12	9.1 (6.6-13)	1.9 (1.2-3.0)	1.9 (1.4-2.5)	0.24 (0.16-0.35)	0.31 (0.23-0.42)	10 (7.7-13)	92 (69-120)
Karlskrona (4)	12	18 (15-21)	7.3 (6.6-8.0)	3.2 (2.8-3.6)	1.1 (0.96-1.2)	1.1 (0.95-1.2)	32 (28-36)	130 (110-150)
Fladen (6)	12	8.4 (7.0-12)	2.9 (2.1-3.9)	1.4 (1.1-1.8)	0.48 (0.30-0.78)	0.40 (0.28-0.55)	9.8 (8.9-11)	59 (50-71)
Väderöarna (7)	20	9.8 (8.1-12)	3.2 (2.7-3.8)	1.9 (1.2-3.0)	0.41 (0.31-0.55)	0.50 (0.39-0.65)	8.7 (7.7-9.9)	33 (26-42)

**Table 2.** Number of samples (n), geometric mean concentrations and 95% confidence intervals for the analysed PBDE congeners, HBCD and CB-153 from the various sites.



**Figure 1.** Concentrations of PBDEs and HBCD (ng/g lipid weight) in herring muscle from 1) Harufjärden, Bothnian Bay, 2) Ängskärsklubb, southern Bothnian Sea, 3) Landsort, northern Baltic Proper, 4) Karlskrona archipelago, southern Baltic Proper, 6) Fladen, the Kattegatt, 7) Väderöarna, the Skagerakk.

## Screening of brominated flame retardants in Danish marine and freshwater sediments

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### **Summary**

The first screening of brominated flame retardants in sediments collected in the Danish marine and freshwater environment is presented in this work. 10 marine and 6 freshwater sediments were analysed for the following brominated diphenylether congeners (PBDEs): BDE-47, BDE-85, BDE-99, BDE-100, BDE-153, and BDE-209. The sum of the 6 PBDEs is in the range of 0.06-25.2 and 0.07-10.7 µg/kg dry weight in marine and freshwater sediment, respectively.

### **Introduction**

The demand and production of flame retardants have increased during the nineties from a global consumption of 610.000 tonnes in 1992 to a global consumption of 924.000 in 1996<sup>1</sup>. Approximately 150.000 and 202.000 tons of brominated flame retardants (BFRs) were consumed in 1992 and 1996, respectively. Polybrominated diphenyl ethers (PBDEs) accounted for approximately 25% of this consumption.

PBDEs in the Danish environment are entered by long range transport and by emission from products imported to Denmark such as television and computer screens. An estimated worst case scenario of the accumulated inventory in products within Denmark is 1,300 tons of PBDEs. Until now only few measurement of the concentration of PBDEs in Danish sediment, soil and sewage sludge has been performed. For the first time a screening of the concentration of PBDEs in marine and freshwater sediments from the Danish environment have been performed. Sediment samples were analysed for tetra-deca brominated diphenyl ethers.

### **Method**

The method is separated in two major parts, the cleanup procedure and the chemical analysis. The cleanup procedure is described in detail by Cleemann *et al*<sup>2</sup>. The chemical analysis is performed using a high resolution gas chromatography – low resolution mass selection technique. The used analytical equipment was a HP-6890 gas chromatograph interfaced with a HP-5973 mass selector. A 60 m high resolution capillary column, DB-5 (methyl + 5%

phenyl, I.D. 0.25 mm, film 0.25 µm), was applied in the analysis of the concentration of the tetra-hexa BDE congeners. A 15 metre high-resolution capillary column, DB-1 (dimethylpolysiloxane, I.D. 0.25 mm, film 0.10 µm), was applied in the analysis of the concentrations of BDE-209. J&W Scientific, Folsom, CA, USA supplied the columns. The mass selector was running in a negative chemical ionisation mode using methane as the chemical reaction gas. The mass fragments were monitored using selected ion monitoring (SIM). The quantifying ions were m/z -78.9 and -80.8 for tetra-hexa BDEs, m/z -486.4, -488.4 for BDE-209 and m/z -494.4, -495.4 for the <sup>13</sup>C labelled BDE-209. BDE-71 was used as internal standard whereas BDE-77 and <sup>13</sup>C labelled BDE-209 were used as recovery standards. The samples were analysed in batches containing approximately 10 sediments, two samples of reference sediments (LRMs) and one blank sample. Observed blank values were in all samples below the detection limit.

## Results

Obtained results are shown in Table 1. In all samples BDE-85 was under the detection limit. The results in Table 1 are corrected for the recovery values. Recovery values for tetra-hexa BDEs were 84±29 % (2 standard deviations). Matrix effects were observed for the BDE-209 congener giving typical recovery values for <sup>13</sup>C labelled BDE-209 between 150-200%.

Sample No.	Sampling area	Water (%)	BDE47	BDE99	BDE100	BDE153	Sum of four PBDEs	BDE209
M5	South of Ven	37%	< 0.1	<b>0.25</b>	< 0.05	< 0.05	<b>0.25</b>	<b>3.9</b>
M6	South East of Anholt	67%	<b>0.09</b>	<b>0.16</b>	< 0.04	< 0.04	<b>0.25</b>	<b>2.2</b>
M7	Copenhagen Harbour	64%	<b>1.12</b>	<b>2.14</b>	<b>0.38</b>	<b>0.05</b>	<b>3.69</b>	<b>21.5</b>
M8	Øresund	24%	<b>0.03</b>	<b>0.07</b>	< 0.02	< 0.02	<b>0.10</b>	<b>1.6</b>
M9	Odense Fjord	50%	< 0.04	<b>0.08</b>	< 0.04	< 0.04	<b>0.08</b>	<b>1.9</b>
M10	Limfjorden	16%	< 0.03	<b>0.06</b>	< 0.03	< 0.03	<b>0.06</b>	< 0.9
M4	Randers Fjord	81%	<b>0.23</b>	<b>0.64</b>	<b>0.12</b>	<b>0.08</b>	<b>1.07</b>	
M4	Randers Fjord	82%	<b>0.21</b>	<b>0.63</b>	<b>0.13</b>	<b>0.07</b>	<b>1.04</b>	
M3	Århus Bay	70%	<b>0.10</b>	<b>0.12</b>	<b>0.02</b>	<b>0.03</b>	<b>0.27</b>	
M3	Århus Bay	43%	<b>0.03</b>	<b>0.03</b>	< 0.1	<b>0.01</b>	<b>0.07</b>	
F1	Søgard Sø	92%	<b>0.33</b>	<b>0.44</b>	<b>0.08</b>	< 0.07	<b>0.84</b>	<b>4.4</b>
F3	Varde Å	62%	<b>0.03</b>	<b>0.04</b>	< 0.03	< 0.03	<b>0.07</b>	< 1.3
F4	Silkeborg Langsø	85%	<b>0.46</b>	<b>0.76</b>	<b>0.14</b>	<b>0.02</b>	<b>1.37</b>	<b>4.2</b>
F5	Tystrup Sø	87%	<b>0.18</b>	<b>0.56</b>	<b>0.14</b>	<b>0.04</b>	<b>0.92</b>	<b>2.1</b>
F6	Brabrand Sø	85%	<b>0.90</b>	<b>1.28</b>	<b>0.27</b>	<b>0.12</b>	<b>2.58</b>	<b>8.1</b>
F8	Søndersø	64%	<b>0.10</b>	<b>0.14</b>	<b>0.02</b>	< 0.03	<b>0.26</b>	<b>2.5</b>

**Table 2:** Measured concentrations (µg/kg dry weight) of marine and freshwater sediment collected in Denmark.

The screening show that freshwater sediment is more polluted with PBDEs than marine sediment.

The level of tetra-hexa BDEs in marine and freshwater sediments (without Copenhagen harbour) are 0,06-0,25 and 0,07-2,58 µg/kg dry weight, respectively. An exception to this is, however, observed in the Copenhagen harbour where levels of 3,69 and 21,5 µg/kg dry weight for the sum of tetra-hexa BDEs (BDE-47, BDE-85, BDE-99, BDE-100, and BDE-153) and BDE-209, respectively, were found.

In general the concentration of PBDEs in sediments close to populated areas such as sediment from harbours and lakes in urban areas, as e.g. sediment from the Copenhagen harbour and sediments from Brabrand Sø (urban lake), contains the highest contamination of PBDEs in the this screening.

For BDE-209 the level observed are somewhat higher <1,3 – 8,1 in freshwater sediment and <0,9-3,9 µg/kg dry weight for marine sediment (without Copenhagen harbour). Generally BDE-209 is the most abundant PBDE congener in sediment followed by BDE-99, BDE-47, BDE-100 and BDE-153.

Ranking the concentration of the tetra-hexa BDEs gives the following order: BDE-99>BDE-47>BDE-100>BDE153 with BDE-99 approximately a factor of 2 higher than BDE-47. This observation is inconsistent with a concentration of 35% of both BDE-47 and BDE-99 in the commonly used technical “penta” blend Bromkal 70-5DE.

## Conclusion

A screening of BDE-47, BDE-85, BDE-99, BDE-100, BDE-153 and BDE-209 in marine and freshwater sediments have been performed in this study. Found concentrations are far below an acute toxic level of these chemicals but is however observed in all collected samples.

BDE-209 is the most dominant PBDE congener in all the collected sediments

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<sup>2</sup>Cleemann, Marianne, Paulsen, Gudrun B., Storr-Hansen, E., ; Fromberg, A., *Journal of AOAC International*, **1999**, 82, 1175-1184.

<sup>3</sup>Christensen, J. H. ; Platz, J., **2001**, Dancea-AMAP report, 1-21.

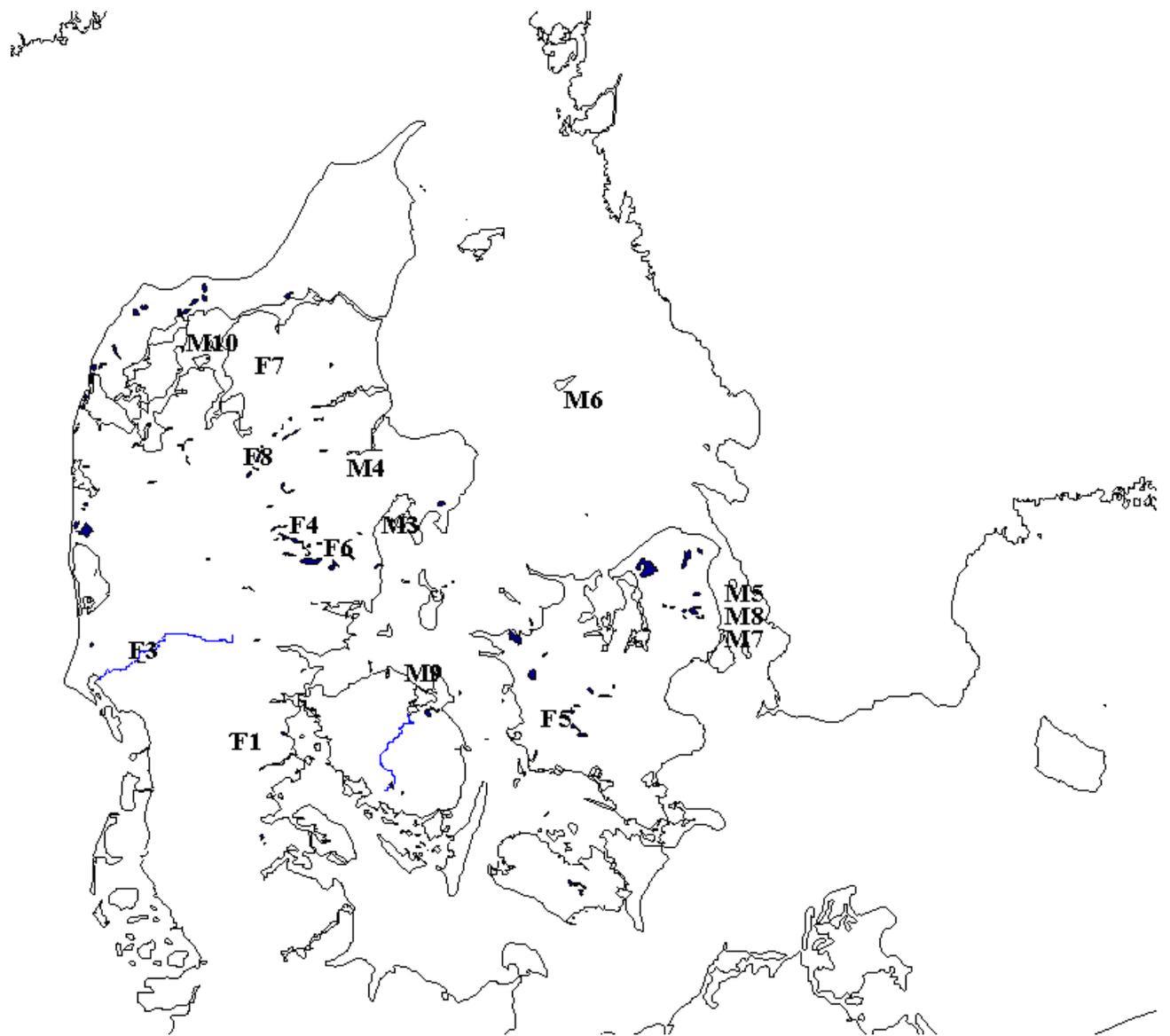


Figure 1. Map of sampling locations.

## **HBCDD in Sweden – a screening of an brominated flame retardant.**

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The main uses of HBCDD are in the polymer and textile industries. The substance has been used commercially since the 1960s. HBCDD is used as a flame retardant mainly in polystyrene, and as coating polymer dispersion in textiles.

According to industry information, 85% of HBCDD are used in polystyrene products. The main use of HBCDD in polystyrene is in insulation blocks for building construction. HBCDD is also used to a small extent in textiles, corresponds to 10 % of the total use of HBCDD. Minor amounts are used in “high impact polystyrene” (HIPS). The latter correspond to 5% of the total use.

HBCDD is not chemically bound in the products and may therefore be released to the environment. Information on exposure is important both for estimations of environmental and human exposure as well as for the risk assessment of the substance.

Only a few studies exist, considering the occurrence of HBCDD in the Scandinavian environment. Little is therefore known about the emission, distribution and long range transport of the compound. Swedish Environmental Protection Agency initiated a screening project to measuring HBCDD in ‘unaffected’ areas, and from areas affected by diffuse pollution. Furthermore, human exposure was estimated by analyzing different food samples.

HBCDD concentrations in air samples, precipitation, sediment, municipal sludge, fish and different foodstuff are now available. The different samples were collected from areas affected by, point source and diffuse exposure. These data are compared to unpolluted areas in Sweden. This is an ongoing project and some results from the project will be presented.

## PBDEs and Bromocyclen in Biota from the Pond of a Municipal Sewage Treatment Plant

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### Summary

In a total of 17 biota samples from the pond of a German municipal sewage treatment plant high PBDE and bromocyclen concentrations were analysed (PBDE 47: 320-3400 µg/kg lipid weight, bromocyclen: 120-850 µg/kg lipid weight). The results of this study elucidate the considerable contribution of sewage treatment plants as to the environmental contamination of aquatic ecosystems by these halogenated compounds.

### Introduction

Polybrominated diphenylethers (PBDEs) are used in large amounts as additive flame retardants in plastic and textile materials.<sup>1</sup> These chemicals can enter the environment during their production, shipping, processing, and during usage, incineration, recycling, or deposition of PBDE-containing products. Like other organohalogen compounds PBDEs are very lipophilic<sup>2</sup> and persistent. Therefore, several PBDE congeners were found to bioaccumulate significantly in organisms of the aquatic environment.<sup>1,3</sup> Hitherto, relatively little knowledge is available about the release of these flame retardants from industrial and municipal sewage treatment plants (STPs) and their contribution to the general environmental contamination regarding PBDEs. Only scattered sewage sludge samples from German and Swedish STPs were analysed<sup>4-6</sup>, and de Boer et al.<sup>7</sup> found relatively high PBDE concentrations in STP influents and effluents. In cooperation with the University of Hamburg we analysed synthetic musk compounds in water, sediment, and biota samples taken from a municipal STP (including its pond) in order to study in detail bioaccumulation and biotransformation of the synthetic musk fragrances in aquatic systems.<sup>8-10</sup> In the context of this study also PBDE was detected in the biota samples. Furthermore, these biota extracts were screened for other brominated xenobiotics. In this paper, we present first results of these supplementary investigations on the occurrence of brominated compounds in aquatic biota.

## Materials and Methods

The sampling site of this study was a municipal STP in the German Federal State of Schleswig-Holstein. From the STP the treated waste water is directly led to a pond covering an area of 128.000 m<sup>2</sup> and having a depth of 4 m, where it is allowed to remain for some weeks, assuming an average water exchange rate of about 17,000 to 22,000 m<sup>3</sup>/d. The effluent of this pond is closed with bars so that only small fishes are able to enter the pond or escape from it. Therefore, equilibrium conditions can be assumed in fish tissues of bigger animals which are retained in the pond. No commercial or private fishing activities are allowed in the pond. For this study rudd (*Scardinius erythrophthalmus*), tench (*Tinca tinca*), crucian carp (*Carassius carassius*), and eel (*Anguilla anguilla*) samples were caught by electro-fishing on June 24th, 1997. Freshwater mussels (*Dreissena polymorpha*) from an uncontaminated lake were exposed to the pond in polypropylene nets for 7 weeks without subsequent depuration. The biological parameters of these biota samples are given in <sup>10</sup>. The tench and crucian carp samples were analysed as individuals, whereas the rudd, eel, and mussel samples were pooled before analysis. For the chemical analysis the fish fillets (without skin) were taken. After cold-extraction with water/acetone/petroleum ether using an ultraturrax, the lipid extracts were cleaned-up by GPC and subsequent silica gel column chromatography<sup>11</sup>. The final analysis was carried out by GC/ECD on a dual-column system (CP-Sil 8 for pesticides, 50 m x 0.25 mm x 0.12 µm, and CP-Sil 19 for pesticides, 50 m x 0.25 mm x 0.20 µm, carrier gas: hydrogen). Selected samples were also analysed by GC/NCI/MS (Finnigan TSQ 700, DB 5-MS, 30 m x 0.25 mm x 0.25 µm, carrier gas: helium), using methane as reagent gas. The PBDE congeners 28, 47, 85, 99, 100, 153, and 154 were determined, PCB 167 and ε-HCH were used as internal standards.

## Results and Discussion

The used analysis method was validated within the scope of the first world-wide interlaboratory study on PBDEs<sup>12</sup>. PBDE 209 was not included in this study because several investigations seem to prove that decabrominated diphenylether does not tend to bioaccumulate in fish and mussels<sup>2,7,12-14</sup> due to its super-hydrophobicity, very low uptake efficiency and metabolism in biota. The lipid-based concentrations of PBDE 47, the typical marker for PBDE contamination and major PBDE congener, are listed in Tab. 1. For comparison, this table also includes the levels of some representative organochlorine compounds. The PBDEs 99, 100, 153, and 154 were also quantified in the biota samples at

lower concentrations showing a typical PBDE congener pattern (details will be presented in the poster). High PBDE 47 concentrations were found in most of the biota samples, with a maximum of 3400  $\mu\text{g}/\text{kg}$  lipid. In 1983 we found in some carp samples from the same pond levels of about 12.000  $\mu\text{g}/\text{kg}$  lipid<sup>19</sup>. The PBDE 47 levels exceed those of 4,4'-DDE, lindane, and HCB significantly in all biota samples, they were higher than or of the same order of magnitude as the PCB 153 concentrations. PBDE 47 belongs to the major peaks in the ECD and MS/NCI chromatograms. From the analysed data a species-dependent bioaccumulation and/or biotransformation of PBDE 47 may be assumed; however, more comprehensive studies with higher numbers of samples would be necessary for confirmation. The found PBDE 47 concentrations belong to the highest values reported in literature<sup>1,3,15</sup>, similarly high levels were only found in fish samples taken from rivers polluted by industrial discharges. The presented PBDE levels in biota from a municipal STP indicate their leakage from private households, industries, traffic, and other diffuse sources, and their ineffective removal in STPs. Although considerable portions of PBDEs are adsorbed on particles (sediment, sludge)<sup>1,7</sup>, the relatively low concentrations of these chemicals in water cause high levels in biota due to their super-lipophilicity and pronounced bioaccumulation. Thus, fish is a sensitive and well-suited bioindicator which is able to integrate temporal fluctuations of PBDE contamination.

Tab. 1: Concentrations of PBDE 47, PCB 153, 4,4'-DDE, Lindane, HCB, and Bromocyclen in Biota Samples ( $\mu\text{g}/\text{kg}$  lipid weight)

Biota species	Lipid (%)	PBDE 47	PCB 153	4,4'-DDE	Lindane	HCB	Bromocyclen
Rudd	0.6	<b>3400</b>	3100	940	230	180	120
Rudd	1.1	<b>2900</b>	2400	820	230	190	150
Rudd	0.8	<b>2900</b>	2600	850	240	160	150
Tench	0.8	<b>1900</b>	1500	520	330	160	520
Tench	1.3	<b>1800</b>	1500	510	320	160	680
Tench	0.8	<b>1800</b>	1300	520	330	160	550
Tench	0.6	<b>1700</b>	2800	650	300	180	480
Crucian carp	1.1	<b>1200</b>	680	350	300	110	270
Crucian carp	1.7	<b>1100</b>	680	330	310	120	590
Crucian carp	2.0	<b>1200</b>	900	350	290	120	850
Crucian carp	2.6	<b>1400</b>	930	400	310	120	500
Crucian carp	2.5	<b>1400</b>	850	370	280	120	460
Crucian carp	1.7	<b>1300</b>	830	380	290	100	300
Crucian carp	3.5	<b>1300</b>	890	310	340	110	810
Eel	15.7	<b>470</b>	1300	360	390	130	380
Eel	18.1	<b>360</b>	730	260	350	110	320
Mussel	1.4	<b>320</b>	280	170	270	110	400

In addition, in all biota samples also the mixed-halogenated compound bromocyclen (CAS-No. 1715-40-8, Fig. 1) was unambiguously analysed, and its concentrations ranged from 120 to 850  $\mu\text{g}/\text{kg}$  lipid weight (0.7-60  $\mu\text{g}/\text{kg}$  wet weight) (Tab.1). The insecticide and acaricide bromocyclen has been widely used against ectoparasites for the treatment of domestic animals until 1994. In 1991 we found bromocyclen for the first time as pollutant in fish from several rivers and fish farms, with a maximum concentration of 440  $\mu\text{g}/\text{kg}$  lipid<sup>16,17</sup>. The origin of that contamination was then quite unknown, however, but the results already indicated its high bioaccumulating potential and persistence in the aquatic environment. Due to these

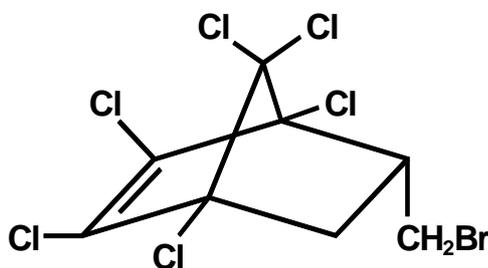


Fig. 1:  
Chemical structure of bromocyclen

characteristics and findings the only producer decided for the voluntary phase-out of this pesticide in 1994. In 1995 we started a comprehensive study to investigate the input of bromocyclen in a selected aquatic ecosystem: water and fish samples from different stations along the river Stör (a tributary of the river Elbe in Schleswig-Holstein, Germany) were analysed<sup>18</sup>. The highest bromocyclen contamination level was found downstream of some municipal STPs, so that additionally a number of influents and effluents from 3 different STPs were included in that study. Bromocyclen was found in the range of 0.76 to 19.1 ng/L in the waste water samples. Thus, STPs could be reliably identified as one important source of bromocyclen emissions for aquatic ecosystems, even after its phase-out. The exact source of this pollution is still unknown and could possibly be traced back to private households and/or industries. Also, the data presented in this paper verify that the continuous bromocyclen contamination from municipal STPs is still ongoing, as bromocyclen residues in 7 fish samples (eels and most of crucian carps) exceeded the German tolerance level of 10 µg/kg wet weight.

### Acknowledgement

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**Brominated flame retardants (BFR) in young Grey Seal Males (*Halicoerus grypus*)  
from the Baltic Sea.**

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Summary

Blubber from twenty juvenile male grey seals from the Baltic were analysed for polybrominated diphenyl ethers (PBDEs) and hexabromocyclododekane (HBCD). The seals were divided into three groups: healthy seals collected 1980-1985 and two groups from the 1990s: one having no or slight intestinal ulcers, and one having moderate, severe or fatal intestinal ulcers. No obvious differences in concentrations were found between the three groups that could be connected with the disease other than that concentrations of BDE-153, BDE-154 and HBCD were lower in the 1980s.

Introduction

Since the end of the 1950s, the Baltic has been severely polluted by DDT and PCB. A disease complex among Baltic grey (*Halichoerus grypus*) and ringed seals (*Phoca hispida*) was described including sterility among females and a connection to the high pollutant burden in their diet was made (Bergman and Olsson, 1985). Since the 1980s the health condition has improved. Most of the lesions that were found (uterine obstructions, arteriosclerosis, claw deformations etc) are not as common or severe as 10-15 years ago (Bergman, 1999). This positive tendency can be related to decreasing environmental concentrations of PCB. This pollutant was banned already in the beginning of the 1970s and since then, the PCB concentration in Baltic biota, including fish, has decreased substantially (Bignert et al., 1998).

Although the health of the grey seal has improved, some problems remain. An unexpected increase in the frequency of intestinal ulcers, often with fatal outcome, has been found (Bergman, 1999). The ulcers are found in high frequencies also in young animals, and new or unidentified environmental contaminants might be the underlying cause. The World Wide Fund for Nature (WWF) is supporting this project which aims to identify a tentative

causative contaminant. The present study presents concentration data on brominated compounds in relation to the prevalence of intestinal ulcers in young grey seals.

Polybrominated diphenyl ethers were first reported in fish from a contaminated area by Swedish scientists in the beginning of the 1980s (Andersson and Blomkvist, 1981). Jansson et al. (1987) reported on presence of PBDE also in seals and birds from the Baltic Sea and Arctic Ocean, a finding indicating that these compounds might be widely distributed environmental contaminants. Since then, PBDE have been measured in biota in a large number of studies (for an overview see de Wit, 2000). PBDE has previously been reported in grey seals from the Baltic Sea (Sellström, 1999; Haglund et al., 1997; Andersson and Wartanian, 1992). Much less data is available for HBCD, but fish from the Swedish River Viskan and guillemot eggs from St Karlsö in the Baltic Sea have been analysed (Sellström et al., 1999). To our knowledge the present study is the first report on HBCD levels in seals from the Baltic Sea.

### **Material and Methods**

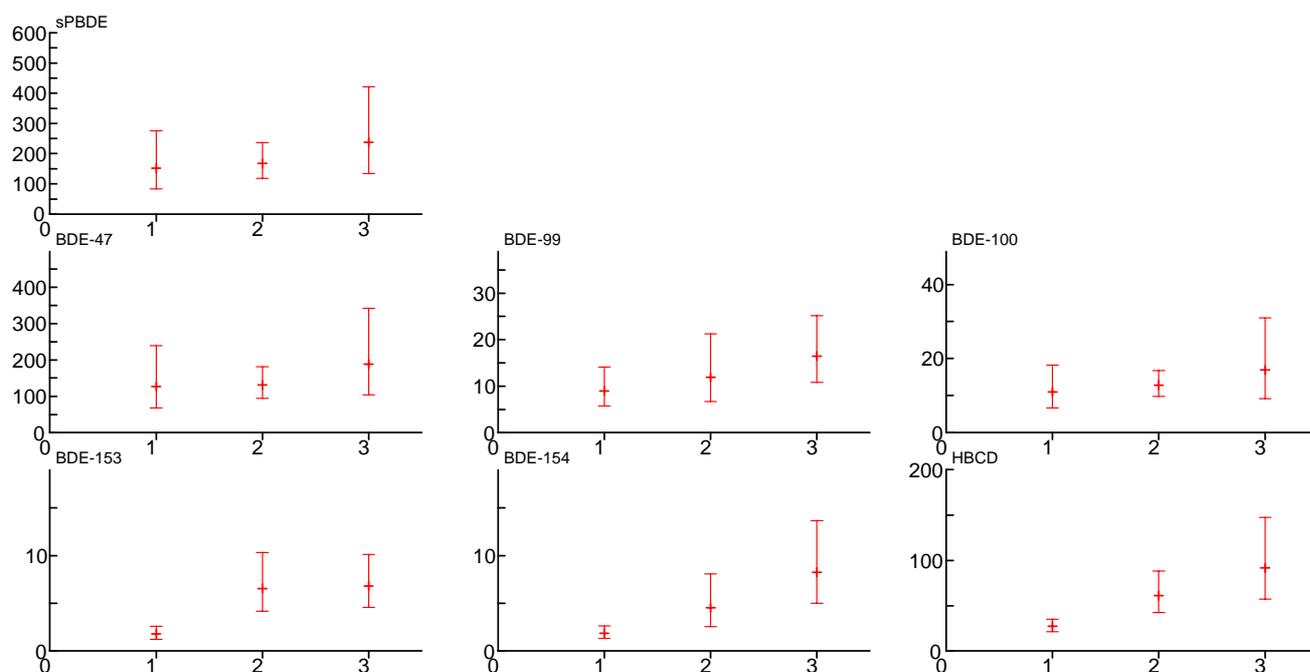
**Samples:** Blubber from 20 young male grey seals collected between 1980-2000. The seals were between 1-3 years old. The grey seals were divided into three groups: Group 1 = seals with no intestinal ulcers, collected between 1980 and 1985, Group 2 = seals with no or slight intestinal ulcers collected 1993-2000, Group 3 = seals with moderate, severe or fatal intestinal ulcers collected 1993-2000. Most of them were drowned in fishing gear, but two seals in group number 3 had fatal ulcers. An analysis of variance (ANOVA) was used in order to compare the three groups statistically.

**Analysis:** The samples were extracted by a method described earlier (Jensen et al., 1983) and analysed according to Sellström (1999). In short, the samples were analysed by GC/MS using chemical ionisation, measuring negative ions (MS-ECNI), ammonia was used as reaction gas. The mass fragments monitored were  $m/z$  79, 81 for PBDE and 237, 239 for the surrogate standard dechlorane.

### **Results and Discussions**

Differences were found for HBCD ( $p < 0.002$ ), BDE-153 ( $p < 0.003$ ) and BDE-154 ( $p < 0.003$ ) but not for sPBDE, BDE-47, -99 and -100 (Figure 1). The differences indicate higher concentrations in seals from the 1990s than in 1980-1985. The sPBDE concentrations (=sum of the congeners BDE-47, -99, -100, -153 and -154) in the juvenile grey seals ranged between 60-582 ng/g lipid weight, with a median concentration of 194 ng/g (l.w). Concentrations of HBCD

ranged from 16-177 ng/g (l.w.), with a median concentration of 59 ng/g (l.w.), with lower concentrations in seals collected during the early 1980s. The most dominating brominated diphenyl ether in this study was BDE-47 – more than 75% of sPBDE was BDE-47. This pattern is similar to that of other aquatic marine animals but different from what is found in for example the peregrine falcon (Sellström et al., 2001), which has higher concentrations of BDE-153 and BDE-99, i.e. the higher brominated congeners.



**Figure 1.** Geometric mean concentrations with 95% confidence limit of PBDEs and HBCD in juvenile grey seal males from the Baltic (ng/g l.w.). Group 1= seals with no intestinal ulcers, collected 1980-1985, Group 2 = seals with no or slight intestinal ulcers collected 1993-2000, Group 3 = seals with moderate, severe or fatal intestinal ulcers collected 1993-2000.

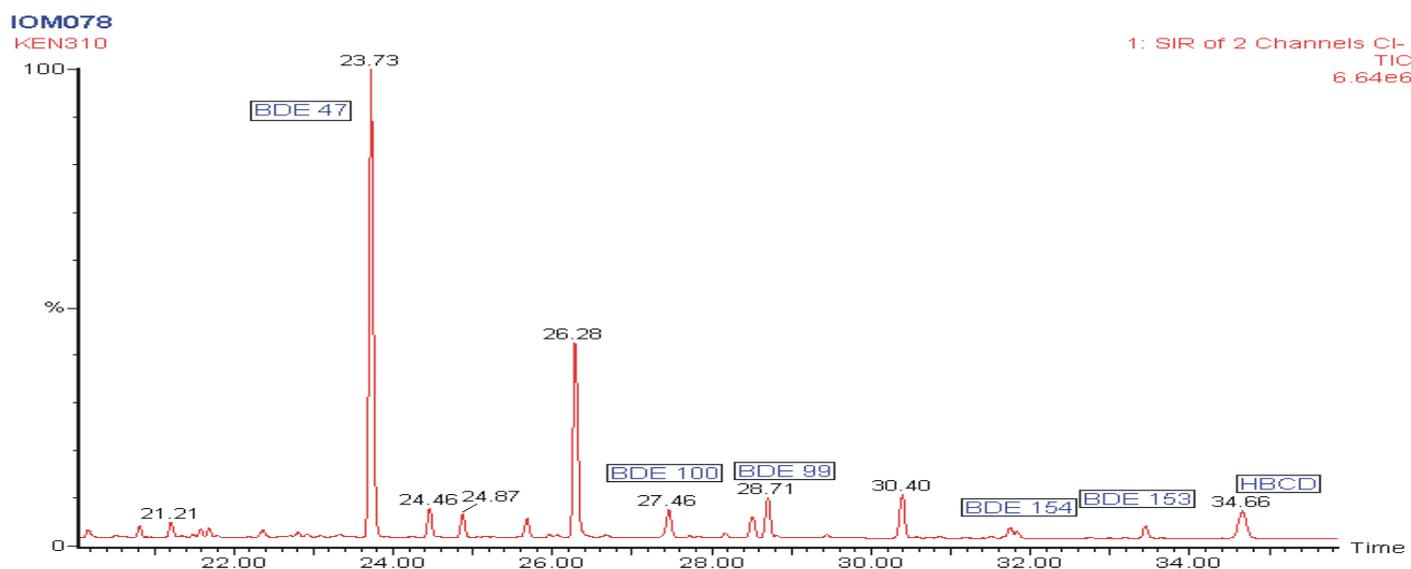
Sellström and coworkers (1999) analysed one pooled sample of blubber tissues from eight grey seals collected between 1979 and 1985 from the Baltic. The concentrations of BDE-47, BDE-99 and BDE-100 were higher (590 ng/g l.w./31 ng/g l.w. and 37 ng/g l.w. respectively) than in the seals from our study. However, no information on age nor any other biological parameters was given so a proper comparison with our results on young seals cannot be done.

Anderson and Wartanian (1992) analysed seals from Swedish waters: grey, ringed and harbour seals (*Phoca vitulina*) collected mainly during the 1980s. Altogether 109 seals were analysed in 22 pooled samples (juveniles of the three species, adult males and adult grey seal females in different health condition). The reported PBDE concentrations in the juvenile

grey seals (one year olds) were in the same order of magnitude as our results (0.30 and 0.31 mg/kg l.w. respectively).

Concentrations of PBDEs in herring (*Clupea harengus*) from six different sites in Swedish waters collected in 1999 indicate much lower concentrations in herring than in grey seal blubber for all congeners (BDE-47, -99, -100, -153, -154 and HBCD), which demonstrates that the PBDEs are bioaccumulative (Nylund et al., 2001).

In summary, the present results show that these brominated compounds are biomagnifying. The data also indicate that concentrations were higher in seals during the 1990s than during the early 1980s. However, the results do not support, nor reject, a hypothesis that brominated compounds are the causative agent to the increasing prevalence of intestinal ulcers in young grey seals during recent time.



**Figure 2.** Chromatogram of a blubber sample from a grey seal belonging to group 3 (GC/MS, ECNI, n/z 79,81).

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## **Polybrominated diphenylethers and other persistent organic pollutants in Norwegian freshwater fish**

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### ***Summary***

The concentrations of an extended range of persistent organic pollutants were studied in samples of different Norwegian freshwater fishes. High levels of polybrominated diphenylethers were found in Arctic char muscle from Ellasjøen, Bear Island and in Burbot liver from Lake Mjøsa, Southern Norway.

### ***Introduction***

During the seventies the most common persistent organic pollutants (POP) were measured in Norwegian freshwater fish as part of the OECD-program “Wildlife Sampling and Analysis for Environmental Contamination”, 1972-1977 and during the project “Sur Nedbørs virkninger på Skog og Fisk”, 1975-77. The Norwegian Pollution Control Authority (SFT) was interested to update the knowledge on contamination of the freshwater environment with POPs. Compared to the earlier measurements the compound spectrum was extended considerably. In this project we measured not only polychlorinated biphenyls (PCB) and the common chlorinated pesticides but also toxaphene, polychlorinated dibenzodioxins and furans (PCDD/PCDF), polychlorinated naphthalenes (PCN), polychlorinated alkanes (PCA) and polybrominated diphenylethers (PBDE). The following samples were used in this project: Trout muscle (*Salmo trutta*), Arctic char muscle (*Salvelinus alpinus*) and Burbot liver (*Lota lota*; a fresh water cod). The samples were collected in the whole country in order to identify local sources of pollutants in addition to the general background contamination through atmospheric long-range transport.

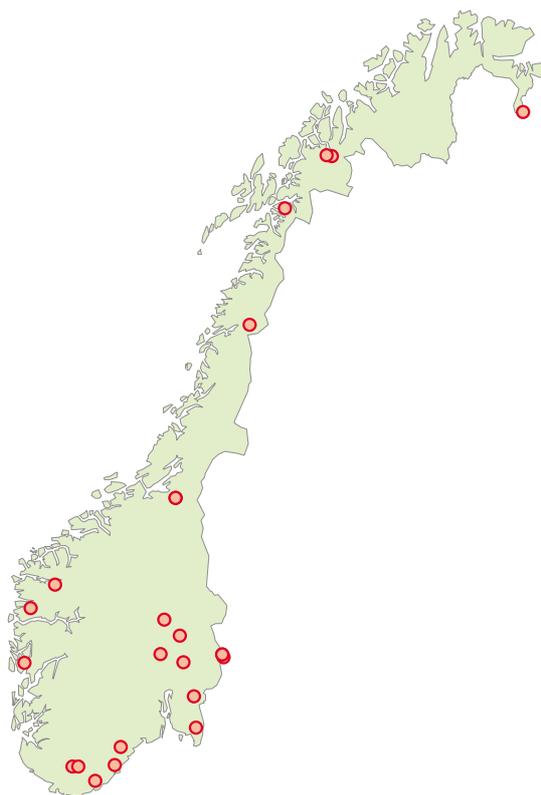


Figure 1: Sampling stations

### **Sample collection and analytical methods**

Samples were collected using gill nets or hook. For analysis of POP muscle samples were taken from the dorsal axial muscle (approximately 20 g wet weight). Specially cleaned equipment and vials were used for sample preparation and storage. Samples were frozen (-18 °C) until analysis. About 1 to 15 g of fish sample was homogenized with sodium sulfate. The mixture was filled into a glass column and an internal standard mixture containing  $^{13}\text{C}$ -labeled HCB, HCHs, DDE and PCBs was added on top of the column. The lipophilic compounds were eluted by a slow flow of cyclohexane. Lipids were removed by gel permeation chromatography (GPC) on 50 g Biobeads SX-3 with cyclohexane/ethylacetate (50/50). The POP fraction was cleaned additionally on 30 g alumina with the following mobile phase: n-hexane and n-hexane/methyl-t-butyl ether (MTBE) (50/50). Before quantification 1,2,3,4-tetrachloronaphthalene was added as recovery standard. PBDE congeners were determined by high resolution gas chromatography (HRGC) (HP Ultra-II) combined with low resolution mass spectrometry in the negative ion chemical ionisation mode (LRMS-NCI) using a HP Engine (Methane as reagent gas, detection of  $\text{Br}^-$  and  $\text{Br}_2^-$ ). A rigorous quality control concept based on the requirements in the European quality norm EN 45001 was applied.

## Results and Discussion

Table 1: Results given as pg or ng/g wet weight (fresh weight).

Lake	Northern	Eastern	Sample	PCDD/F pg TE/g	no-PCB pg TE/g	Sum PCN pg/g	PCB7 ng/g	PBDE-47 ng/g	PBDE-99 ng/g	PBDE(47+99) ng/g	PCA ng/g	Fat %
Takvatn	69,1	19,1	Trout	0,11	0,20	16,0	2,04	<b>0,10</b>	<b>0,06</b>	<b>0,15</b>		1,80
Fjellfrøsvatnet 99	69,1	19,3	Trout	0,09	0,12	9,89	0,87	<b>0,08</b>	<b>0,07</b>	<b>0,14</b>	3,30	1,10
Grunnvatnet	68,3	16,7	Trout	0,11	0,06	8,64	0,23	<b>0,06</b>	<b>0,04</b>	<b>0,10</b>		1,30
Store Raudvannet	66,3	14,5	Trout	0,31	0,55	12,1	3,20	<b>0,21</b>	<b>0,16</b>	<b>0,36</b>		2,50
Selbusjøen 99	63,3	11,0	Trout	0,12	0,10	8,97	1,19	<b>0,22</b>	<b>0,27</b>	<b>0,49</b>	3,10	1,40
Breimsvatn	61,7	6,4	Trout	0,10	0,13	9,93	2,32	<b>0,32</b>	<b>0,24</b>	<b>0,57</b>		1,30
Bogevatnet 99	61,3	5,5	Trout	0,12	0,07	6,59	1,68	<b>0,23</b>	<b>0,40</b>	<b>0,62</b>	3,60	0,70
Kalsjøen 99	60,4	12,5	Trout	0,34	0,29	25,6	2,92	<b>0,17</b>	<b>0,15</b>	<b>0,31</b>		1,80
Kalandsvatn	60,3	5,4	Trout	0,17	0,12	18,6	4,27	<b>0,49</b>	<b>0,42</b>	<b>0,91</b>		2,60
Vegår	58,8	8,9	Trout	0,55	0,45	24,5	4,23	<b>0,81</b>	<b>1,55</b>	<b>2,36</b>		1,90
Mårvann	58,5	8,7	Trout	1,91	0,66	57,5	6,23	<b>0,65</b>	<b>0,76</b>	<b>1,41</b>		1,60
Grindheimsvt. 99	58,4	7,4	Trout	0,25	0,22	21,3	4,23	<b>0,39</b>	<b>0,04</b>	<b>0,43</b>		0,90
Lygne	58,4	7,2	Trout	0,23	0,11	10,3	2,07	<b>0,34</b>	<b>0,46</b>	<b>0,81</b>		1,30
Grovatnet 99	58,2	8,0	Trout	0,54	0,37	31,6	9,94					1,30
Ellasjøen	74,4	19,1	Char	0,20	7,16	12,9		<b>8,27</b>	<b>8,02</b>	<b>16,3</b>	6,90	1,30
Velmunden 00	60,5	10,3	Char	0,20	0,19	9,28	5,55	<b>0,52</b>	<b>0,62</b>	<b>1,14</b>		1,00
Grensefoss (Pasvikelva)	69,0	29,0	Burbot	3,25	9,50	643	205	<b>9,69</b>	<b>10,6</b>	<b>20,3</b>	38,0	11,6
Selbusjøen 99	63,3	11,0	Burbot	18,5	21,3	1 081	308	<b>62,4</b>	<b>72,4</b>	<b>135</b>	53,0	38,5
Mjøsa/Lilleh B3	61,1	10,4	Burbot				1 385	<b>324</b>	<b>332</b>	<b>656</b>		42,7
Mjøsa/ Furn. B2	60,8	11,0	Burbot				5 816	<b>1 044</b>	<b>911</b>	<b>1 955</b>		49,7
Røgden	60,4	12,5	Burbot	11,8	13,6	785	152	<b>31,5</b>	<b>11,4</b>	<b>42,9</b>	143	34,8
Røgden 348	60,4	12,5	Burbot	20,5	30,9	1 387	152	<b>136</b>	<b>27,9</b>	<b>164</b>	113	34,3
HurdalsjøenB1	60,3	11,1	Burbot				1 125	<b>149</b>	<b>43,0</b>	<b>192</b>		45,7
Øgderen 98	59,7	11,4	Burbot	13,9	14,3	982	316	<b>52,2</b>	<b>40,0</b>	<b>92,2</b>	85,0	22,0
Femsjøen	59,1	11,5	Burbot	55,4	64,9	3 423	799	<b>89,7</b>	<b>17,5</b>	<b>107</b>	608	40,0

The lowest levels of PBDE were found in samples of trout muscle from Northern Norway. However, the sample of Arctic char muscle taken at Lake Ellasjøen, Bear Island, located halfway between the Norwegian mainland and Spitsbergen, showed a very high level of PBDE (1 253 ng/g f.w.).

Table 2: Results given as pg or ng/g fat weight.

Lake	Northern	Eastern	Sample	PCDD/F pg TE/g	no-PCB pg TE/g	Sum PCN pg/g	PCB7 ng/g	PBDE-47 ng/g	PBDE-99 ng/g	PBDE(47+99) ng/g	PCA ng/g	Fat %
Takvatn	69,1	19,1	Trout	6,11	11,1	889	113	<b>5,51</b>	<b>3,07</b>	<b>8,58</b>		1,80
Fjellfrøsvatnet 99	69,1	19,3	Trout	8,18	10,9	899	79,1	<b>6,82</b>	<b>6,27</b>	<b>13,1</b>	300	1,10
Grunnvatnet	68,3	16,7	Trout	8,46	4,62	665	17,7	<b>4,92</b>	<b>2,92</b>	<b>7,85</b>		1,30
Store Raudvannet	66,3	14,5	Trout	12,4	22,0	484	128	<b>8,32</b>	<b>6,20</b>	<b>14,5</b>		2,50
Selbusjøen 99	63,3	11,0	Trout	8,57	7,14	641	85,0	<b>15,5</b>	<b>19,2</b>	<b>34,7</b>	221	1,40
Breimsvatn	61,7	6,4	Trout	7,69	10,0	764	178	<b>24,8</b>	<b>18,6</b>	<b>43,5</b>		1,30
Bogevatnet 99	61,3	5,5	Trout	17,1	10,0	941	240	<b>32,3</b>	<b>56,7</b>	<b>89,0</b>	514	0,70
Kalsjøen 99	60,4	12,5	Trout	18,9	16,1	1 422	162	<b>9,17</b>	<b>8,06</b>	<b>17,2</b>		1,80
Kalandsvatn	60,3	5,4	Trout	6,54	4,62	715	164	<b>18,8</b>	<b>16,0</b>	<b>34,8</b>		2,60
Vegår	58,8	8,9	Trout	28,9	23,7	1 289	223	<b>42,4</b>	<b>81,7</b>	<b>124</b>		1,90
Mårvann	58,5	8,7	Trout	119	41,3	3 594	389	<b>40,8</b>	<b>47,6</b>	<b>88,4</b>		1,60
Grindheimsvt. 99	58,4	7,4	Trout	27,8	24,4	2 367	470	<b>43,3</b>	<b>4,89</b>	<b>48,2</b>		0,90
Lygne	58,4	7,2	Trout	17,7	8,46	792	159	<b>26,3</b>	<b>35,7</b>	<b>62,0</b>		1,30
Grovatnet 99	58,2	8,0	Trout	41,5	28,5	2 431	765					1,30
Ellasjøen	74,4	19,1	Char	15,4	551	992		<b>636</b>	<b>617</b>	<b>1 253</b>	531	1,30
Velmunden 00	60,5	10,3	Char	20,0	19,0	928	555	<b>51,5</b>	<b>62,1</b>	<b>114</b>		1,00
Grensefoss (Pasvikelva)	69,0	29,0	Burbot	28,0	81,9	5 543	1 767	<b>83,5</b>	<b>91,4</b>	<b>175</b>	328	11,6
Selbusjøen 99	63,3	11,0	Burbot	48,1	55,3	2 808	800	<b>162</b>	<b>188</b>	<b>350</b>	138	38,5
Mjøsa/Lilleh B3	61,1	10,4	Burbot				3 244	<b>758</b>	<b>778</b>	<b>1 536</b>		42,7
Mjøsa/ Furn. B2	60,8	11,0	Burbot				11 702	<b>2 101</b>	<b>1 832</b>	<b>3 934</b>		49,7
Røgden	60,4	12,5	Burbot	33,9	39,1	2 256	437	<b>90,5</b>	<b>32,8</b>	<b>123</b>	411	34,8
Røgden 348	60,4	12,5	Burbot	59,8	90,1	4 044	443	<b>397</b>	<b>81,3</b>	<b>478</b>	329	34,3
HurdalsjøenB1	60,3	11,1	Burbot				2 463	<b>327</b>	<b>94,1</b>	<b>421</b>		45,7
Øgderen 98	59,7	11,4	Burbot	63,2	65,0	4 464	1 436	<b>237</b>	<b>182</b>	<b>419</b>	386	22,0
Femsjøen	59,1	11,5	Burbot	139	162	8 558	1 998	<b>224</b>	<b>43,8</b>	<b>268</b>	1 520	40,0

The highest PBDE concentrations in this study were found in samples of Burbot liver from Lake Mjøsa, the biggest lake in Norway. The fat weight concentration of PBDE 47 + 99 with nearly 4 000 ng/g is comparable to levels measured in Steelhead trout from Lake Michigan, USA<sup>1)</sup> (2 300 ng/g) and much higher than in Arctic char muscle from Lake Vättern, Sweden<sup>2)</sup> (464 ng/g) or Baltic salmon muscle from River Dalälven, Sweden<sup>1)</sup> (145 ng/g).

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## Atmospheric deposition of polybrominated diphenylethers (PBDEs)

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Levels of 7 PBDE congeners were assessed in bulk deposition in southern Sweden. A total of 5.2 ng  $\Sigma$ PBDE m<sup>-2</sup> was deposited by the particulate phase and 2.8 ng  $\Sigma$ PBDE m<sup>-2</sup> by the dissolved phase, over a 14 days period of sampling. Our findings point out that PBDEs in atmospheric deposition are primarily particle-associated and that temperature and the vapour pressure are important factors for the fate of PBDEs in the environment.

For many persistent organic pollutants (POPs) the atmosphere is the major transport route. The key factor in the concentration ratios of pollutants between the gaseous, particle, and dissolved phase is the vapour pressure. However the type and amount of particles also play an important role<sup>1</sup>. Gaseous and particle associated semivolatile organic compounds (SOCs), such as polybrominated diphenyl ethers (PBDEs), can be deposited via wet- and dry deposition. Up to date there is a substantial amount of research done regarding airborne SOC, such as PCBs and polycyclic aromatic hydrocarbons (PAHs), in ambient air and atmospheric deposition. However, until now there are few data on atmospheric levels of brominated flame retardants, and to our knowledge no work has been done regarding PBDEs in atmospheric deposition.

The objective of this study was to assess the dissolved and particle associated PBDE levels in total deposition in an urban area. Concentrations were used to calculate filter/adsorbent ratios (F/A), and were compared with their predicted aerosol associated fractions (FR<sub>AEROSOL</sub>). Additionally, the relationship between precipitation volume and particle associated PBDE concentrations was assessed.

The geometrical mean ( $\pm$  standard deviation) concentration of  $\Sigma$ PBDE in rain was 127 $\pm$ 57 pg L<sup>-1</sup>. Compared to recent PCB deposition studies<sup>2,3</sup> carried out in the same region, total PBDE deposition levels are about 10 times lower than reported  $\Sigma$ PCB concentrations in bulk deposition in Southern Sweden. Congeners BDE47, 99 and 183 dominated the composition of PBDEs in the total deposition. The observed patterns seem consistent with the results of other studies<sup>4-8</sup> and suggests that the atmosphere is an important transport route for PBDEs in the environment.

The F/A-ratios were significantly different ( $p < 0.001$ ) from the predicted values for the aerosol fractions. This was attributed to particle size distribution, the use of time-integrated PBDE concentrations, average daily temperatures for the entire sampling period and sampling artefacts. There was a negative relationship between PBDE concentration and rain volume. The similarity of the relationship compared with other POPs suggests the importance of particle scavenging for wet deposition of PBDEs

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## Polybrominated Diphenyl Ethers (PBDEs) in Lake Michigan Salmonids

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**Summary:** Six PBDE congeners were observed in 21 salmon taken from Lake Michigan tributaries. The average concentration across all samples of the sum of PBDE congeners was 2440 ng/g of lipid. The concentrations of PBDEs and PCBs are highly correlated in individual fish. Data suggest that PBDEs have been a part of the Lake Michigan environment for many years and are distributed throughout the lake similar to PCBs.

While chlorinated compounds have been the topic of much Great Lakes toxics research, brominated compounds have been studied very little. One class of brominated compounds, the polybrominated diphenyl ethers (PBDEs), has been used extensively over the past two decades as flame-retardants. Data from Sweden, Holland, and Japan indicate PBDEs are accumulating in the environment, but few measurements are available for the North American Great Lakes. We measured PBDEs in 21 coho and chinook salmon taken from Lake Michigan tributaries in 1996. Six PBDE congeners were observed in all twenty-one samples, and the rank order of concentration of these congeners was similar to that in commercial mixtures of PBDEs. The average concentration of the sum of PBDE congeners was 80.1 ng/g wet weight. This is much less than the average sum PCB concentration (1450 ng/g wet weight) in these samples. However, the average concentration of the most abundant PBDE congener (IUPAC BDE-49: 52.1 ng/g wet weight) was about one-third of the average concentration of the most abundant PCB congener (IUPAC CB-153: 149 ng/g wet weight). The concentrations of PBDEs reported here are among the highest in the world for an environmental matrix.

Of the PBDE congeners, congener BDE-47 was the most abundant (consistent with PBDE congener distributions reported for other environmental samples). Also, the proportions of each of the six detected congeners were very uniform among samples. The distribution of the PBDE congeners was also similar to that found in several Steelhead trout taken from Lake Michigan by a colleague and analyzed by researchers in the Environmental Chemistry

Department at Stockholm University. The muscle tissue of the Steelhead contained about half the average total PBDE found in the salmon reported here.

The concentrations of PCBs measured in the sample salmon from Lake Michigan provide interesting comparisons to the PBDEs. Both PCBs and PBDEs are positively correlated with fish length and fish mass (although the coefficients of determination are only moderate). Length is better correlated than mass and PCB is more strongly correlated than is PBDE. PBDE and PCB concentrations within each fish were highly correlated ( $r^2 = 0.81$ ). Such covariance suggests that the brominated and chlorinated contaminants are being acquired from the same source (i.e., Lake Michigan). It also suggests an uptake rate that is similar. PCBs have probably been part of the Lake Michigan environment for many years. Like PCBs, they are likely distributed throughout the lake. Initial results from other matrices in Wisconsin suggests that PBDEs are also widely distributed in inland Wisconsin waters. Levels of PBDEs in sewage sludge may be particularly high at certain locations.

**PATTERN OF BROMINATED COMPOUNDS IN TOP PREDATIONS  
OF MARINE FOOD WEBS FROM FOUR CONTINENTS**

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**ABSTRACT**

GC/ECNI-MS was used to study the pattern of brominated compounds in the blubber of marine mammals and a polar bear from different locations in the world. Next to PBDE 47 and 99, several other, often more abundant brominated compounds were detected in the samples. Most of these components were unknown or have been described only qualitatively. Monitoring of additional ion traces helped to distinguish different classes of brominated compounds.

Detection of brominated components attracts increasing interests in environmental science. ECNI-MS detection in the SIM mode using  $m/z$  79 and  $m/z$  81 is a highly sensitive and selective method for the determination of brominated compounds in environmental samples<sup>1</sup>. Such studies confirmed that concentrations of brominated flame-retardants (BFRs) are on the rise in several compartments of the world<sup>2</sup>. However, exclusive monitoring of  $m/z$  79 [ $^{79}\text{Br}$ ]<sup>-</sup> and 81 [ $^{81}\text{Br}$ ]<sup>-</sup> allows no further identification of the hydrocarbon backbone of a brominated compound. In the full scan mode it was found that several brominated components form [ $\text{Br}_2$ ]<sup>-</sup>, and/or [ $\text{HBr}_2$ ]<sup>-</sup> fragment ions, or none of them, in addition to the [ $\text{Br}$ ]<sup>-</sup> fragment ions (Table 1)<sup>3,4</sup>. The mixed halogenated compound MHC-1 also formed an ion corresponding with [ $\text{BrCl}$ ]<sup>-</sup> ( $m/z$  114)<sup>5</sup>.

Therefore, fragment ions in addition to  $m/z$  79 and 81 were selected to monitor organobromine compounds by GC/ECNI-MS in the SIM mode. The fragment ions were  $m/z$  158 ([ $^{79}\text{Br}^{79}\text{Br}$ ]<sup>-</sup>),  $m/z$  160 ([ $^{79}\text{Br}^{81}\text{Br}$ ]<sup>-</sup>),  $m/z$  159 ([ $^1\text{H}^{79}\text{Br}^{79}\text{Br}$ ]<sup>-</sup>),  $m/z$  161 ([ $^1\text{H}^{79}\text{Br}^{81}\text{Br}$ ]<sup>-</sup>),  $m/z$  114 ([ $^{79}\text{Br}^{35}\text{Cl}$ ]<sup>-</sup>),  $m/z$  116 ([ $^{79}\text{Br}^{37}\text{Cl}$ ]<sup>-</sup> and [ $^{81}\text{Br}^{35}\text{Cl}$ ]<sup>-</sup>), as well as  $m/z$  115 [ $^1\text{H}^{79}\text{Br}^{35}\text{Cl}$ ]<sup>-</sup> and  $m/z$  117 ([ $^1\text{H}^{79}\text{Br}^{37}\text{Cl}$ ]<sup>-</sup> and [ $^1\text{H}^{81}\text{Br}^{35}\text{Cl}$ ]<sup>-</sup>).

The ratio of areas of the fragment ions was constant for one component but different from compound to compound (Table 1).

By checking these ratios in GC/ECNI-MS-SIM chromatograms, a highly sensitive and selective method was obtained for confirmation of a certain brominated compound in sample extracts. This SIM method was adapted for the evaluation of the organobromine pattern in blubber extracts of top predators of marine food webs from four continents.

The major anthropogenic components investigated this time were the brominated diphenyl ethers PBDE 47 and PBDE 99, which have been used in high quantities as BFRs<sup>1</sup>. In addition, the mixed halogenated monoterpene MHC-1 (molecular formula: C<sub>10</sub>H<sub>13</sub>Br<sub>2</sub>Cl<sub>3</sub>)<sup>4</sup> and BC-1 to BC-11<sup>3,4</sup> were part of the present study. In contrast to BFRs, MHC-1 and BC-1 to BC-11 were identified as non-anthropogenic (natural) organobromines. Note, however, that BC's comprise compounds with different hydrocarbon backbone<sup>3,4</sup>. The GC/ECNI-MS chromatograms (Figure 1) demonstrate that there are several other brominated compounds we could not identify this time. Furthermore, the composition of organobromine residues differed significantly from region to region.

*Table 1: Major brominated compounds detected in various samples of marine mammals. Retention times and areas (%) of suggested ECNI-MS-SIM fragment ions relative to m/z 79.*

Compound	t <sub>R</sub> [min] *	m/z 160**	m/z 161**	m/z 116**	m/z 117**
<b><u>MHC-1</u></b>	27:35	96.3 %	6.0 %	50.8 %	-
<b>PBB 52</b>	34:20	-	-	-	-
<b>UBC-1</b>	43:00	66.2 %	-	-	-
<b>PBDE 47</b>	45:68	6.5 %	56.1 %	-	-
<b><u>BC-1</u></b>	48:20	-	-	-	-
<b>BC-2</b>	48:41	3.2 %	23.5 %	-	-
<b><u>BC-10</u></b>	50:20	-	-	-	-
<b><u>BC-3</u></b>	51:00	8.1 %	41.3 %	-	-
<b><u>UBC-2</u></b>	53:66	7.8 %	47.6 %	-	-
<b><u>BC-11</u></b>	55:04	9.3 %	68.1 %	-	-
<b>PBDE 99</b>	57:93	3.1 %	55.0 %	-	-

\* GC conditions see Figure 1

\*\* area of the fragment ion relative to m/z 79 (in %); “-“ stands for <3%

PBDE 47 and 99 were major brominated contaminants in adipose tissue of a polar bear collected at the pack ice close to Iceland (data not shown) and grey seals from the German coast at the Baltic Sea (**Figure 1a**). High abundance of PBDE 47 was also found in the blubber of harp and hooded seals from Northern Europe (**Figure 1b**) as well as grey seals

from Western Iceland. The latter samples accumulated virtually the same bromine pattern, which was dominated by the intense signal of an unknown brominated component labelled UBC-1 (**Figure 1b**).

The component labelled UBC-2 in chromatograms obtained from grey seals and hooded seals (**Figure 1a,b**) is most likely another PBDE congener, because UBC-2 showed a similar ratio of  $m/z$  79 to  $m/z$  161 than PBDE 47 and 99. Another grey seal sample from the Baltic Sea showed additional unknown brominated compounds in the retention time range of 40 – 44 min.

The blubber extract of pygmy sperm whale from Australia showed high abundance for several natural brominated compounds that were recently identified in common and bottlenose dolphins from the same region<sup>4</sup>. In addition to the major congeners in dolphins (BC-1, BC-2, and BC-3), the pygmy sperm whale showed high abundance of BC-10 and BC-11<sup>3</sup>. In contrast, major PBDE congeners were below the limit of detection in melon-headed and pygmy sperm whales (**Figure 1c**).

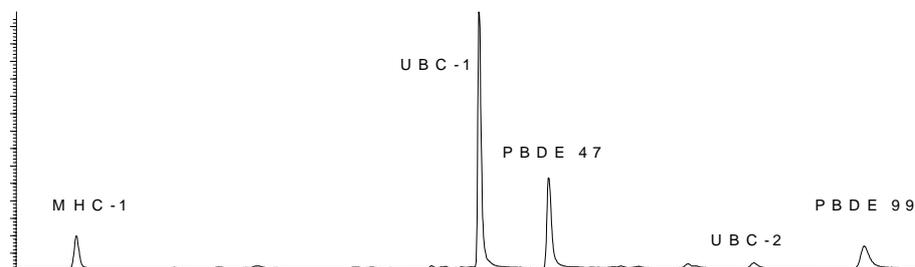
Monk seals from Mauretania (Africa) showed high abundance of PBDE 47, but also BC-2 and BC-3. Furthermore, the samples showed an abundant signal for MHC-1 (**Figure 1d**). MHC-1 was identified as a natural monoterpene which carries two bromine and three chlorine atoms<sup>5</sup>.

Most likely natural producers of MHC-1 are marine algae<sup>5</sup>. MHC-1 was also detected in blubber of hooded seals (**Figure 1a**) and harp seals from northern Europe, grey seals from Western Iceland, as well as our samples of Antarctic Weddell seals (**Figure 1e**). The Weddell seal samples also showed intense signals for BC-1, BC-2, and BC-3. The present work demonstrates for the first time that BC's are not restricted to samples from Australia. However, only blubber extracts of monk seals and not Weddell seals contained PBDE 47.

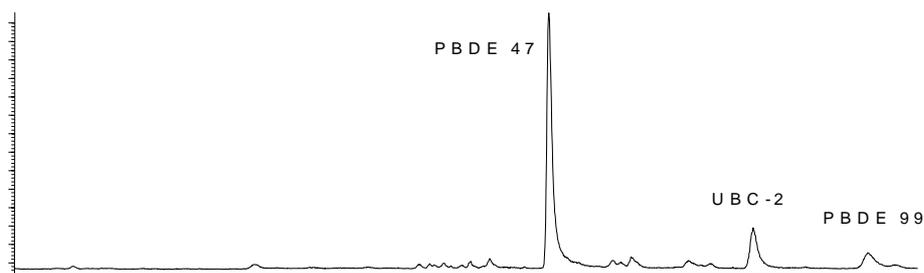
Screening samples for  $m/z$  114 - 117 (i. e. identification of selected mixed halogenated compounds) gave clear response for MHC-1 (see above). Additional peaks for  $m/z$  114/116 (next to  $m/z$  79/81) close to the detection limits were recorded at 38.2 min in the hooded seal samples.

This presentation focused on major brominated compounds. Additional lower abundant anthropogenic and natural organobromines were identified in the samples but not discussed.

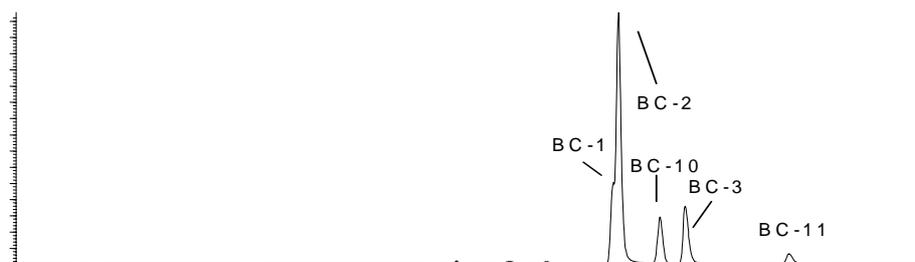
**a) Hooded Seal,  
Northern Sea,  
Europe**



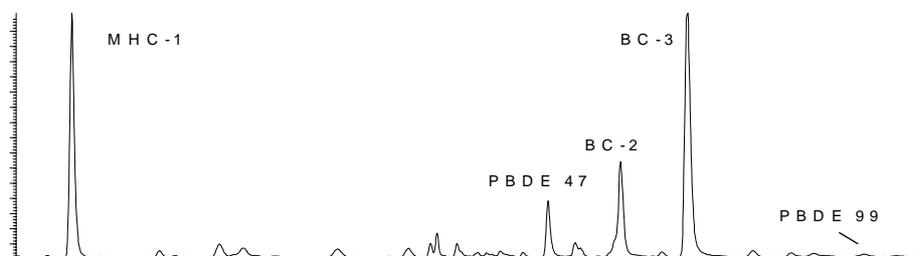
**b) Grey Seal,  
Baltic Sea,  
Europe**



**c) Pygmy Sperm  
Whale,  
Queensland,  
Australia**



**d) Monk Seal  
Mauretania,  
Africa**



**e) Weddell Seal  
Weddell Sea,  
Antarctic**

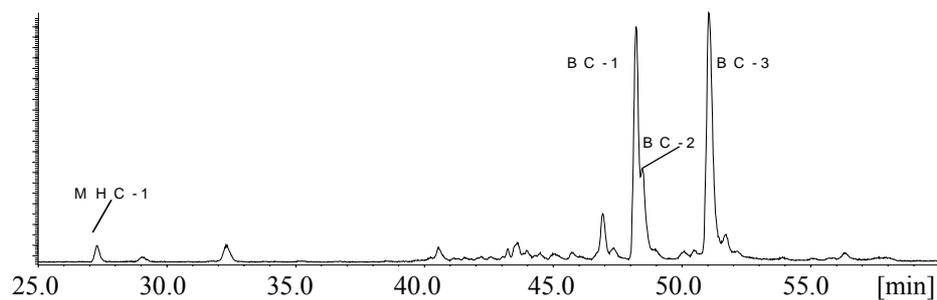


Figure 1: Bromine-selective pattern ( $m/z$  79) in different top predators of marine food webs. Analyses were performed with a chiral stationary  $\beta$ -BSCD phase diluted in 25% PS086<sup>6</sup>. The oven was programmed from 80°C to 150°C (hold time 2 min), 195°C (hold time 1 min), and 230°C (hold time 40 min) with 20°C/min in each case.

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## BIOACCUMULATIVE NATURAL BROMINATED COMPOUNDS IN MARINE MAMMALS

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### **ABSTRACT**

A series of 12 natural brominated compounds (BC-1 to BC-11 and MHC-1) were detected in blubber extracts of marine mammals from different locations. Some of these compounds may be misinterpreted as anthropogenic brominated compounds. Evidence for the natural production of these secondary metabolites and their bioaccumulation in higher organisms as well as analytical protocols for their detection in the environment are presented.

Brominated flame-retardants (BFRs) have been reported in several environmental compartments and with a tendency of increasing concentrations around the world<sup>1</sup>. These trends have suggested that the brominated trace chemicals observed in tissue of higher organisms in the environment originate from the use of BFRs. Major BFR pollutants are polybrominated diphenyl ethers (PBDEs) which have been detected in numerous environmental samples using GC/ECNI-MS (SIM mode) and  $m/z$  79 and  $m/z$  81 as Br-selective fragment ions<sup>2</sup>. However, regional differences in the Br-selective residue pattern have been reported and the structure of a number of brominated compounds that are found in environmental samples is still unknown<sup>3</sup>.

During the last years, we have detected 12 natural brominated compounds in the blubber of marine mammals. These compounds would have been misinterpreted as BFRs and their presumed metabolites if detection had relied only on  $m/z$  79 and 81<sup>4,5</sup>. Nine of these compounds (BC-1 to BC-9) were recently identified in the blubber of dolphins from Australia<sup>4</sup>. The natural organohalogens Q1, BC-1, BC-2, and BC-3 were more abundant in common dolphins than any anthropogenic organohalogen contaminant detected<sup>4</sup>. Analysis of blubber extracts of a melon-headed whale (*Peponocelphala electra*) and two pygmy sperm whales (*Kogia breviceps*) from Queensland (Australia) in the SIM and full scan mode

confirmed these results and led to the detection of two new brominated compounds BC-10 and BC-11 (**Figure 1**).

Recently, Cameron *et al.* isolated a number of brominated secondary metabolites from the sponge *Dysidea sp.* collected in the same broad geographical region as our marine mammal samples<sup>6</sup>. Some of these isolated compounds may be identical with the compounds found in the mammal's tissues. E. g., BC-2 (molecular ion is formed at  $m/z$  512<sup>4</sup>) is likely identical with 1-methoxy,4,6,2',4'-tetrabromo-2,1'-diphenyl ether or 1-methoxy,3,5,2',4'-tetrabromo-2,1'-diphenyl ether which were both identified in sponges<sup>6</sup>. Note the different nomenclature in diphenyl ether (1,1') and methoxy metabolite (1',2) backbones as a result of IUPAC rules in organic chemistry.

BC-2 may be misinterpreted as a methoxy metabolite of a BFR, namely of 2,3',4,5'-tetrabromo diphenyl ether (PBDE 68) or 2,2',4,4'-PBDE (PBDE 47). The latter is a well-known major BFR compound<sup>2</sup>. However, major PBDE congeners were below the limit of detection in our samples whereas the dominating natural compounds of interest (BC-1, BC-2, BC-3, BC-10) were at least two orders of magnitude more abundant than anthropogenic brominated compounds. The lack of expected parent PBDEs and detection of BC's that clearly have different hydrocarbon backbones (see below) vote out this interpretation. Furthermore, high levels of the natural heptachlorobipyrrole derivative Q1<sup>7</sup> was found at >1 mg/kg in blubber of the marine mammals from Australia.

The molecular weight of BC-3 was determined to be 512 u on the assumption that  $m/z$  433 represents the [M-Br]<sup>-</sup> fragment ion (**Figure 1b**). The molecular ion of BC-1 starts at  $m/z$  526 (4 bromine atoms)<sup>4</sup>. This suggests an additional methylene unit on BC-1 relative to BC-2. BC-10 showed an intense molecular ion at  $m/z$  540 (**Figure 1c**). The pattern of the molecular ion corresponded with either 5 bromine atoms or 4 bromine and two chlorine atoms. In the first case, BC-10 must contain less than 12 carbons, in the second case, BC-10 may be identical with a heterocyclic compound found in eggs of sea birds<sup>8</sup>. The ECNI-MS spectra of both compounds were comparable. The example of BC-10 demonstrates that not only natural brominated diphenyl ether derivatives such as BC-2 and BC-3 may be accumulated in high organisms. In addition to samples from Australia, several BC's were also detected in marine mammals from Africa and the Antarctic.

Recently, a mixed halogenated compound (MHC-1) was detected in fish and seal from Northern Europe, the Antarctic, and Northern Africa<sup>5</sup>. MHC-1 levels in the samples reached up to 0.7 mg/kg lipid<sup>5</sup>. High resolution EI-MS analysis determined the molecular formula of MHC-1 to be C<sub>10</sub>H<sub>13</sub>Br<sub>2</sub>Cl<sub>3</sub>. MHC-1 is likely one of the two monoterpenes that were isolated

from the marine algae *Plocamium cartilagineum*<sup>9</sup>. The retention time ( $t_R$ ) of MHC-1 on DB-5-like columns was similar to the  $t_R$  of trans-chlordane. MHC-1 also gave intense GC/ECNI-MS response at  $m/z$  79/81.

Due to the low selectivity of  $m/z$  79 and 81 for an unequivocal identification of PBDEs and other brominated compounds, it is likely that natural brominated compounds may be interpreted as residues or metabolites of BFRs, particularly when the natural organobromines are less abundant than BFRs. To obtain more information on the identity of organobromines in environmental samples we suggest to record additional GC/ECNI-MS-SIM masses<sup>3</sup>. Several brominated compounds, natural and anthropogenic, also form ion clusters starting at  $m/z$  158 (corresponding with  $[\text{Br}_2]^-$ ) or at  $m/z$  159 ( $[\text{HBr}_2]^-$ ). E. g.  $m/z$  158 is formed by MHC-1<sup>5</sup> and other, unknown brominated compounds<sup>3</sup>, while  $m/z$  159 was found for PBDE 47 (moderating gas: methane), BC-2, BC-3 (**Figure 1b**), and BC-11. In contrast, other brominated compounds (BC-1 and BC-10) do not form  $[\text{Br}_2]^-$  or  $[\text{HBr}_2]^-$  fragment ions (**Figure 1c**)<sup>4</sup>. Additionally, the GC/ECNI-MS of MHC-1 is characterized by an intense ion at  $m/z$  114 ( $[\text{BrCl}]^-$ ). The  $[\text{HBrCl}]^-$  analogue was not detected, yet. This resulted in a method consisting of the SIM masses  $m/z$  79, 81, 114-117, and 158-161<sup>3</sup>.

Next to the described natural brominated compounds and well-known BFRs, we have detected various other brominated compounds in marine mammals sampled from a variety of different locations around the world<sup>3</sup>. Some of them may also represent natural components. Our data to date confirm that a range of natural halogenated compounds are present in higher organisms that inhabit the marine environment. Note that these organobromines will not be observed during studies of anthropogenic organobromines using GC/EI-MS-SIM mode since they do not form the  $[\text{M}]^+$  and  $[\text{M}-2\text{Br}]^+$  fragment ions used in PBDEs analysis.

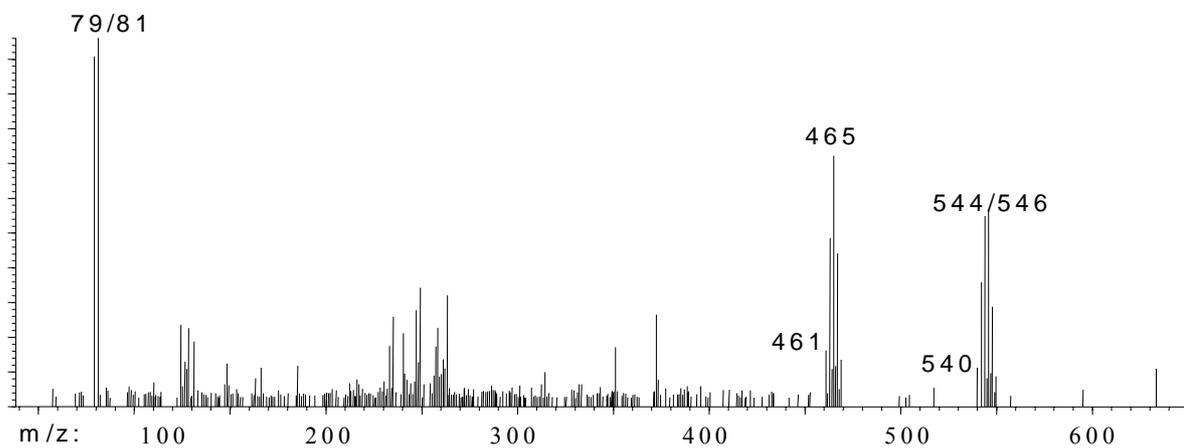
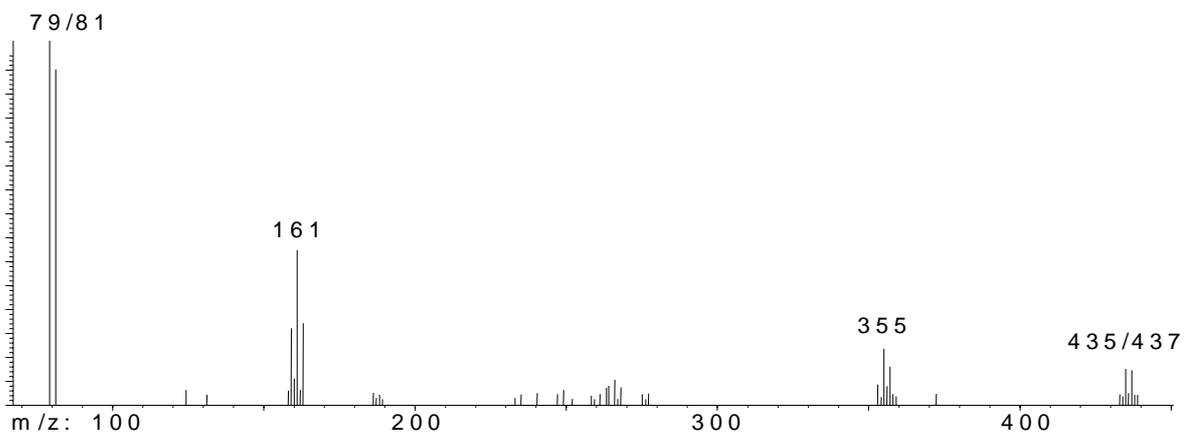
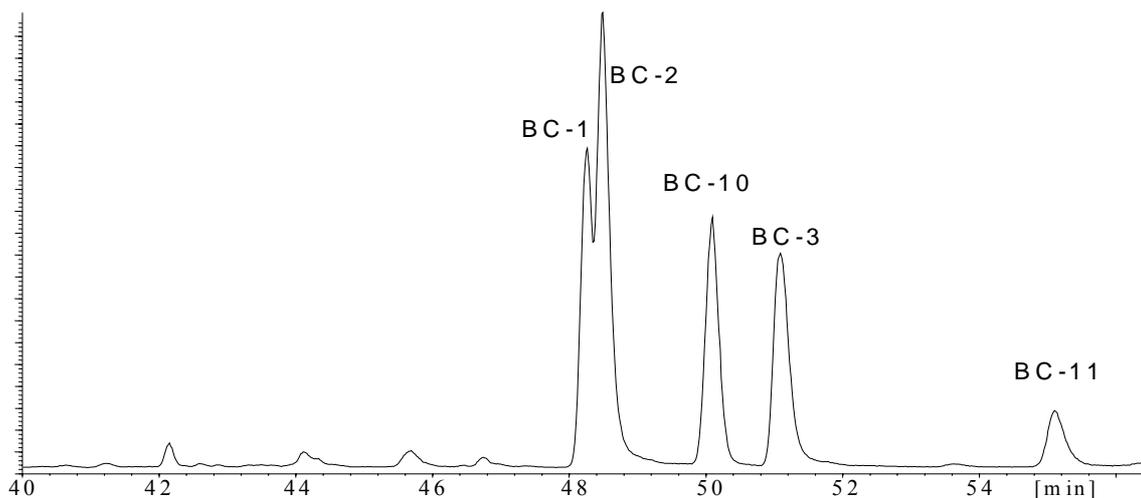


Figure 1: GC/ECNI-MS data of potential natural bromine compounds (BC's) in samples from Queensland, Australia.

- a) SIM-chromatogram ( $m/z$  79) of the blubber extract of a pygmy sperm whale (*Kogia breviceps*). BC-10 and BC-11 were previously not detected in dolphins from the same region.
- b) Full scan ECNI-MS spectrum of BC-3 recorded in a subsequent run. MS full scan data of this component were previously not available.
- c) Full scan ECNI-MS spectrum of BC-10 recorded in a subsequent run.

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