CONGENER PATTERNS, SPATIAL AND TEMPORAL TRENDS OF POLYBROMINATED DIPHENYL ETHERS IN BIOTA SAMPLES FROM THE CANADIAN WEST COAST AND THE NORTHWEST TERRITORIES

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Introduction

Polybrominated diphenylethers (PBDEs) are anthropogenic chemicals used as additive flame retardants in polymeric materials. Production of PBDE was estimated at 40 000 tons/year in 1992 and is increasing.[1] PBDE are not covalently bound but only dissolved in products such as plastics, paints, textiles, machines and electronic devices and can therefore leach out into the environment. Being relatively persistent, lipophilic and bioaccumulating, they have been found in a variety of matrices and even in samples from remote areas which suggests a world-wide distribution.[1] However, data in Canada is lacking and, therefore, this study focuses on monitoring PBDE levels and congener distributions in tissue and blubber samples of several marine organisms collected off the Canadian west coast and Holman Island in the Northwest Territories.

PBDE have been detected in sediment, air, water and biota including humans at theppb to ppm of lipid levels.[1] Some studies have shown an increase in levels over several years.[1-3] Biomagnification has been reported in fish-eating biota.[1] Even though 75% of PBDE production is based on deca-BDE, only major amounts of tetra and penta congeners have been found in biota. This has been attributed to preferential uptake of lower brominated PBDE as diffusive in addition to mediated uptake through the membrane is possible for these smaller molecules.[4] The deca congener is also less bioavailable due to its low water solubility and thus strong adsorption to sediment.[1] Even when fed to rainbow trout, deca-BDE uptake was minimal.[5] However, deca-BDE has been found in airborne dust[1] and ppb levels of the hepta (BDE183) and deca congeners were shown to have been inhaled by Swedish workers.[6] The acute toxicity of PBDE is low; however, there is concern for its long term effects on the endocrine system.[1]

Most of the analyses in the past have concentrated on only a few specific PBDE congeners. However, a reliable method for the separation and ultra-trace quantification of individual congeners is required to determine the extent of environmental exposure, the risk associated with specific congeners and their fate in the environment. The purpose of this study was to a) develop a comprehensive GC/HRMS method to analyse several congeners of all homologue groups mono-deca in order to determine a more detailed congener pattern within environmental samples; b) determine and compare PBDE levels and congener patterns within Canadian environmental samples from areas affected by industrial and/or urban activity to those from an area remote from PBDE point sources; and c) determine temporal and gender trends with respect to PBDE content in ringed seals.

Methods and Materials

Samples: Several marine biota samples were collected from harbours, the Fraser River estuary and near pulp and paper mills in the Strait of Georgia, British Columbia (BC), Canada during 1991-1996. Hepatopancreas of dungeness crab (5), blubber of harbour porpoises (5 males) and a harbour seal (female, 3+ years) were analysed. Included in this study were several blubber samples of ringed seals (*Phoca hispida*) (12 males and 9 females with ages 7-15) that had been obtained from Holman Island, Northwest Territories (NWT) during 1981, 1991 and 1996.

Analysis: Tissue (10g) and blubber (0.2g) were processed for GC/HRMS (EI/SIR positive) analysis using a multiresidue method.[7] A DB-5 and a DB-5HT column was used to analyse mono-hexa and hepta-deca congeners, respectively. The parent ion was monitored for the mono,di and tetra congeners, whereas the most intense fragment $(M-2Br)^+$ for the remaining congeners. Pure standards were not available for the higher brominated congeners and, therefore, commercial mixtures were used to quantify hepta-deca congeners although the identity of the hepta and octa isomers is not known (Table 1). For the tri-hepta congeners there were several other nontarget peaks that met criteria (accurate mass, isotope ratio and within elution time range); however, their sum was only an average 3% of the total PBDE and thus they were not included in the total.

2-BDE1	2,4,4'/2',3,4-BDE28/33[+]	2,2',3,4,4'-BDE85	2,2',3,4,4',5,6-BDE181
3-BDE2	2,4,6-BDE30	2,2',4,4',5-BDE99	2,3,3',4,4',5,6-BDE190
4-BDE3	2,4',6-BDE32	2,2',4,4',6-BDE100	Hp(I)-(IV)[a]
2,4-BDE7	3,3',4-BDE35	2,3,4,5,6-BDE116	Oc(I)-(IV)[a]
2,4'-BDE8	3,4,4'-BDE37	2,3',4,4',6-BDE119	BDE206[a,b]
2,6-BDE10	2,2',4,4'-BDE47	2,2',3,4,4',5'-BDE138	BDE207[a,b]
3,3'-BDE11	2,2',4,5'-BDE49	2,2',3,4,4',6'-BDE140	BDE208[a,b]
3,4/3,4'-BDE12/13[+]	2,3',4,4'-BDE66	2,2',4,4',5,5'-BDE153	BDE209[a,b]
4,4'-BDE15	2,3',4',6-BDE71	2,2',4,4',5,6'-BDE154	
2,2',4-BDE17	2,4,4',6-BDE75	2,2',4,4',6,6'-BDE155	
2,3',4-BDE25	3,3',4,4'-BDE77	2,3,4,4',5,6-BDE166	

Table 1. Composition of standard used to quantify PBDE levels in samples.
[+] two congeners coelute; [a] from commercial mixture OCBDE; [b] from commercial mixture Dow-FR-300BA; others are from CIL produced at Cambridge Isotope Laboratories

Results and Discussion

The PBDE levels in marine biota from the BC coast and in ringed seals from Holman Island, NWT were analysed using the GC/HRMS based analytical method. The number of identifiable congeners was increased by incorporating more CIL standards and commercial mixtures (Table 1). The crab and seals were chosen as samples since they remain local and thus reflect contaminant levels within a limited area. Also, being at a higher trophic level, they should contain detectable amounts of PBDE if present in the foodchain. The total amount of PBDE found in the BC samples ranged from 200-2269ng/g lipid (Figure 1). These values are within the ppb toppm range of other marine biota depending on species and site.[1] The porpoise from the Tsawassan area was particularly contaminated due to its location near a Vancouver municipal sewage outlet. The sum of the hepta-deca congener levels was ≤1% of the PBDE total. This is consistent with other studies not observing higher brominated congeners in biota.[1]

Even though the ringed seals were collected from a remote area, PBDE was found in the blubber

although at much lower levels than those in the BC samples. The total amount of PBDE in the 1996 seals was 2.4-4.9 and 1.2-3.4 ng/g lipid for the males and females, respectively (Figure 2). A PBDE total of ca. 400 ng/g lipid has been reported in ringed seals from the more contaminated Baltic Sea.[8] The total PBDE levels in the ringed seals collected from Holman Island have increased from 1981 to 1996 (Figure 2). For the male seals, the total PBDE increased linearly with age as has been observed for male beluga whales[9]. The levels are higher in the males than females which is consistent with another study showing more PBDE in male and young long-finned pilot whales than in the females[3]. It is a well-recognised trend in marine mammals that females unload contaminants to their young via lactation.

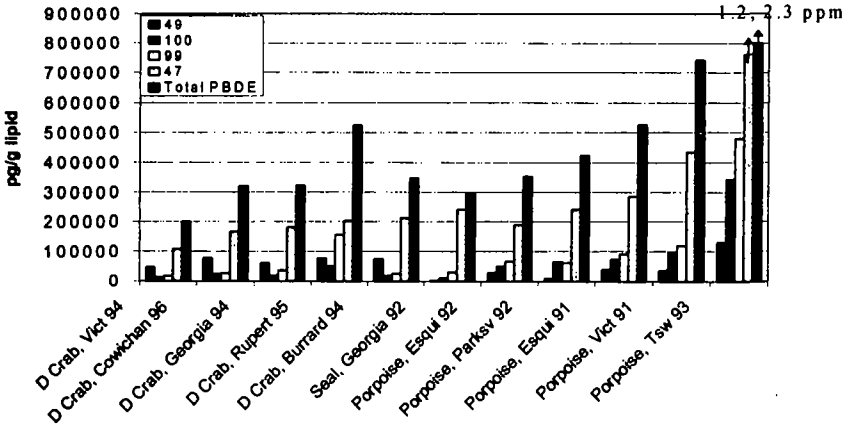

Figure 1. Levels of total PBDE and the major congeners in BC marine biota. (For the porpoise from Tsawassan, BDE47 and the total PBDE are offscale – the values are given above.)

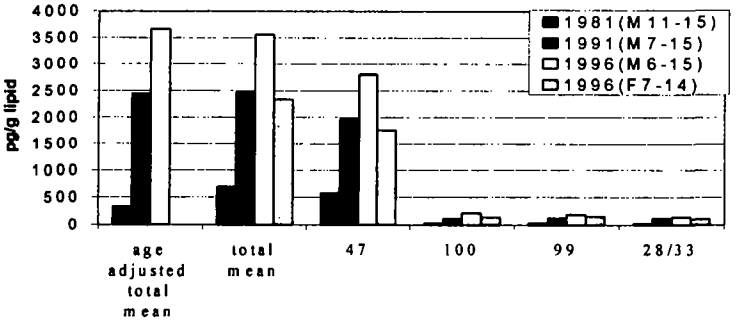

Figure 2. Levels of total PBDE and the major congeners in the Holman ringed seals collected in 1981, 1991 and 1996. (Age adjusted total mean was obtained using ANCOVA of SYSTAT8.0.)

The BC samples and the Holman ringed seal blubber contained similar congener distributions. From all the congeners monitored, BDE47, 99, 100, 49, 28/33, 153, 154 and 66 were the major contributors; their sum representing 97-99% of the total PBDE. For all samples, BDE47 was the major component: ca. 50% for the crab and porpoises, and ca. 80% for the harbour and ringed seals. This is consistent with other studies; for example, BDE47 content was 49-51% in long-finned pilot whales from the Atlantic[3] and ca. 70% in ringed seals from the Baltic Sea[8]. BDE99

and 153 were also found in those studies as well as several unidentified tetra-hexa congeners. For the porpoises and seals in our study, BDE99 and 100 were the next major congeners; whereas, for the crab BDE49 (Table 2). The congener distribution was similar among male and female ringed seals as well as among all the years sampled. The congener pattern determined in our samples differs from that of most commercial mixtures which tend to contain a large proportion of hepta-deca congeners. However, this pattern is comparable to that in the PeBDE commercial mixtures (50-60% penta and 24-38% tetra with BDE99 and 47 as the major components).[1] A water study using semi-permeable membrane devices (SPMD)[10] within the Fraser River region showed a similar congener distribution as found in the marine biota (Table 2). This suggests that major degradation from higher to lower brominated congeners has not occurred within the organism.

Congener	H. Porpoise	D. Crab	R. Seal 96M	R. Seal 96F	SPMD
BDE47	55	52	78	74	53
BDE99	17	13	6	7	26
BDE100	14	7	6	6	7
BDE49	6	20	1	2	3
BDE154	3	3	1	1	2
BDE153	2	1	1	2	2
BDE28/33	1	1	4	4	2
BDE66	1	<1	1	1	1

Table 2. Congener distribution: average % contribution of the major congeners to the total PBDE.

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