Polybrominated-diphenyl-ethers in Biota Samples from Coastal British Columbia, Canada.

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Introduction

Polybrominated diphenyl ethers (PBDEs) are used as additive flame retardants in polymeric materials such as polystyrenes. They are added to plastics, paints, textiles, machines and electronic devices and many thousand tons are produced annually.[1] The penta-, octa- and decabromo substituted diphenyl ethers are the major components.[1] These additives are only dissolved within the material and, therefore, can leach out into the environment. Bioaccumulation of PBDEs is possible since they are highly lipophilic and resistant to degradation. They have been shown to be more persistant than polychorinated biphenyls (PCBs) during *in vitro* biotransformation tests with hepatic microsomes.[2] The efficiency of PBDE uptake is thought to decrease with the degree of bromination due to an increased difficulty to pass through the membrane.[3] Several studies have been completed analyzing for levels and effects of polychlorinated diphenyl ethers (PCDEs) in freshwater and marine organisms[4] but less has been reported for the PBDEs[1-3]. Since the structure of these ethers resemble that of PCBs and dioxins, they may display similar toxicity.[1] Although, in contrast to PCBs, the mono-ortho chloro-substituted PCDE are the most immunotoxic congeners.[4] PCDEs have been shown to effect, for example, the mixed-function oxidase enzymes and ultra structure of rat and trout liver.[4] Differing only by the type of halogen, PBDEs are also suspected to be toxic. In fact, PBBs have been shown to be much more potent than PCBs as inducers of the hepatic mixed-function oxidase.[5] Upon heating, PBDEs can form dioxins and furans. PBDEs have been found in samples from remote areas which suggests a world-wide distribution.[1] Therefore, more data on the levels and effects of PBDE contamination are required.

Over the past few years our interests have been: a) to develop ultra-trace analytical methods for the determination of PBDEs in environmental samples[6]; and b) to monitor the environmental levels and congener distribution of PBDEs in the aquatic environment. In this paper we report the distribution of PBDEs in tissue and blubber samples of several marine organisms collected from the coastal waters of British Columbia.

Materials and Methods

All samples examined in this study (some 25 in total) were resident species collected in the Strait of Georgia British Columbia. The same procedure was used to process tissue and blubber samples. The sample sizes used for extraction were 10 g for tissue and 0.2g for blubber. Samples were spiked with a suite of internal standards (see Table 1) and processed for GC/HRMS analysis using the methodology described in our previous publication.[6] Quantitation was based on custom standard solutions prepared by Cambridge Isotope Laboratories. The composition of the quantitation solution and the surrogate internal and performance standards used are tabulated in Table 1. Since there is limited information on the elution order of PBDEs and their fragmentation

characteristics under GC/HRMS it is difficult to calculate totals of homologue series without having a larger selection of authentic standards. In this work we report quantitative measurements only for the 23 congeners that we have standards for.

TABLE 1. Composition of Quantitation Standard

2-MoBDE (1)	2,4,6-TrBDE (30)	2,4,4',6-TeBDE (75)
3-MoBDE(2)	2,4',6-TrBDE (32)	3,3',4,4'-TeBDE (77)
2,4-DiBDE (7)	2',3,4-TrBDE (33)	2,2',3,4,4'-PeBDPE (85)
2,4'-DiBDE (8)	3,3',4-TrBDE (35)	2,2',4,4',5-PeBDPE (99)
2,6-DiBDE (10)	3,4,4'-TrBDE (37)	2,3',4,4',6-PeBDPE (119)
3,4-DiBDE (12)/	2,2',4,4'-TeBDE (47)	2,2',4,4',5,5'-HxCDE (153)
3,4'-DiBDE (13)	2,3',4,4'-TeBDE (66)	2,3,3',4,4',5,5'-HpBDE (189)
4,4'-DiBDE (15)	2,3',4',6-TeBDE (71)	

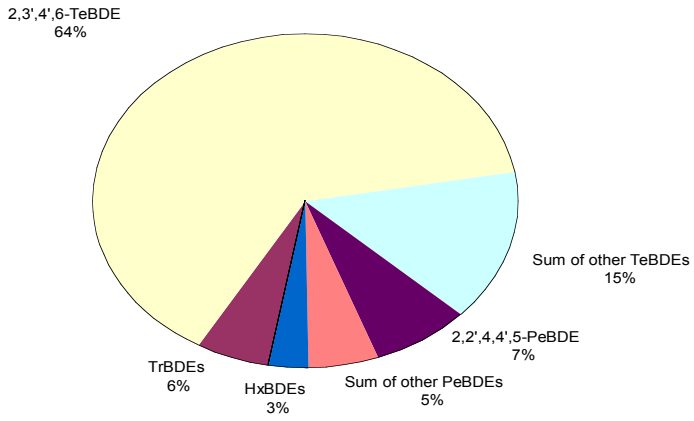
$^{13}C_{12}$-2,3,3',4,4',5-HxCDE (156)	Internal Standard
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCDE (170)	Internal Standard
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCDE (194)	Internal Standard
$^{13}C_{12}$-3,3',4,4'- TeBDE (77)	Performance Standard

Results and Discussion

The samples examined for PBDEs were tissue such as Dungeness crab hepatopancreas, muscle and liver of sturgeon and blubber of porpoises, seals and killerwhales. Pacific Sockeye salmon, Pacific herring and lake trout CRMs were also analyzed. The samples were collected in harbours, the Fraser River estuary and near pulp and paper mills.

In all samples examined no mono-BDE were detected and the di-, tri-, hexa- and hepta-BDE were ca. <10% of the total PBDE measured. In Figure 1 is shown the congener distribution of a hepatopancreas sample from Burrard in Vancouver harbour. In this particular example HpBDE was 0.03% and the total DiBDE was 0.04%. The relative contributions of the individual PBDEs measured were similar for all samples examined with 2,3',4',6-TeBDE and 2,2',4,4',5-PeBDE being the most abundant.

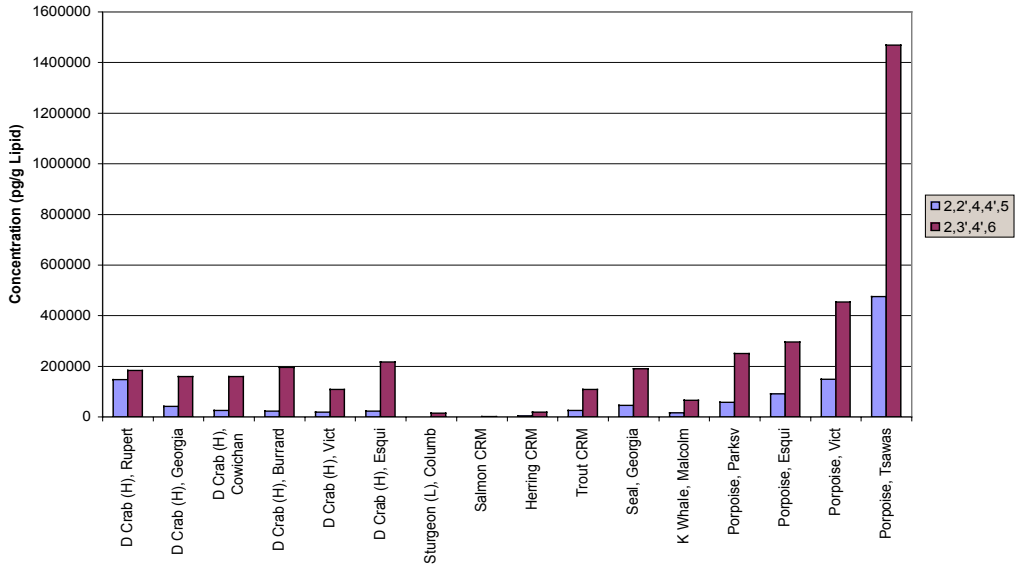
Fig. 1 PBDEs in the hepatopancreas of a Dungeness crab from Burrard



In other studies the tetra- and penta-bromodiphenyl ethers were also the major PBDEs found in biota samples.[1-3] However these studies were limited in the number of congeners measured, i.e. only the 2,2',4,4'-TeBDE and 2,2',4,4',5-PeBDE congeners were measured, as in the present study a more comprehensive number of TeBDEs and PBDEs were measured.

In all our data the following trends were observed among the congeners measured: 2,3',4',6-TeBDE followed by 2,2',4,4',5-PeBDE (Fig. 2) were present at significantly higher levels (ca. 100 fold) than 2,4,4',6-TeBDE and 2,2',3,4,4'-PeBDE (Fig. 3), and (ca. 1000 fold) than 2,3',4,4'-TeBDE, 2,2',4,4'-TeBDE and 3,3',4,4'-TeBDE (Fig. 3). The previous studies[1-3] generally observed more 2,2',4,4'-TeBDE than 2,2',4,4',5-PeBDE which is contra to our findings. The congener 2,3',4,4',6-PeBDE was not detected in all samples, except in the blubber of the porpoise from Tsawassan. Generally, higher concentrations of the 4 major congeners were found in the blubber samples than in the tissue samples (Fig. 2 and Fig. 3). The blubber samples originate from organisms higher up the food chain and, therefore, the larger values obtained are consistent with bioaccumulation of PBDEs.

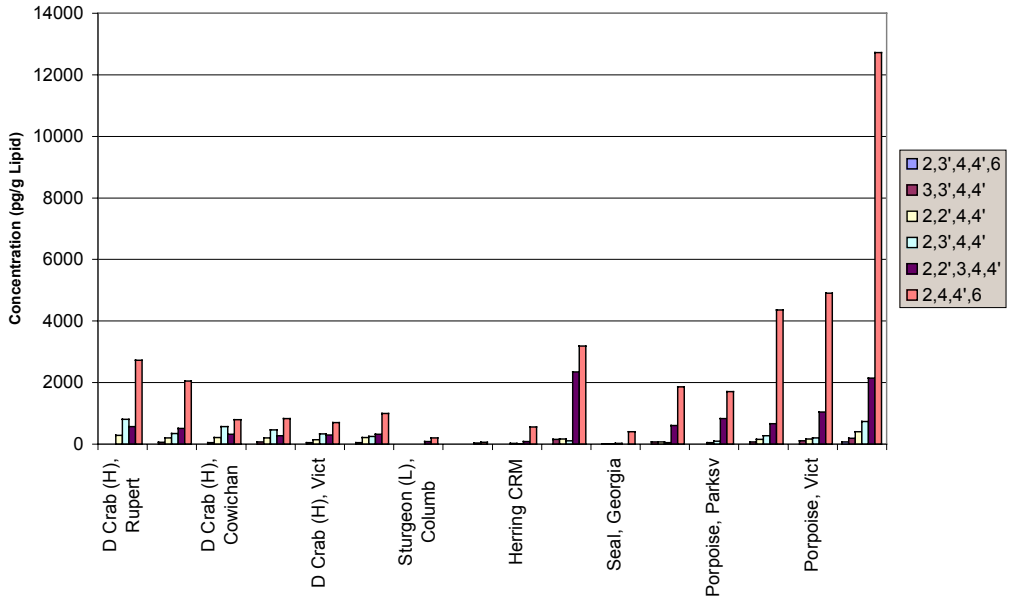
Fig. 2 2,3',4',6-TeBDE and 2,2',4,4',5-PeBDE in tissue and blubber samples



However, the Dungeness crab showed higher levels of 2,3',4,4'-TeBDE and 2,2',4,4'-TeBDE than the blubber samples (Fig. 3). Except for the trout CRM, the fish samples (sturgeon, salmon and herring) contained very low amounts of TeBDE and PeBDE. Similarly, low levels were detected in tissues (liver, red and white muscle) of other sturgeon species captured in the Fraser river. The differences in PBDE levels among the biota sampled suggest that uptake and excretion of PBDE vary among species.

The congener distribution observed in biota samples is substantially different from what is observed in commercial products that are known to contain PBDEs. Also, as discussed above, there is a major difference in the congener patterns detected among similar biota samples, i.e. marine samples collected in the West Coast of Canada versus European samples[1-3].

Fig. 3 TeBDE and PeBDE in tissue and blubber samples



Acknowledgement

The contribution of those who assisted with the analytical work at IOS's regional dioxin laboratory and those who provided the samples is gratefully acknowledged. This research has been funded under the Department of Fisheries and Oceans Toxic Chemical Program.

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