Levels and Bioaccumulation Patterns of PBDEs in Biota from Coastal British Columbia Waters

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Introduction

Increasing market demand for usage of polybrominated diphenyl ethers (PBDEs) in commercial applications and products has resulting in extremely high production volumes (HPVs) of these compounds in North America and Europe. PBDEs are no longer regarded as new chemicals of concern, but rather as globally distributed ubiquitous environmental contaminants, present in many marine and terrestrial organisms, including humans. Numerous temporal trend studies have indicated that PBDE levels are rapidly increasing worldwide.[1,2] PBDE *in vivo* exposures in laboratory animals indicate suggest potential adverse impacts on neurobehavioural development and fetal toxicity/teratogenicity at doses in the low mg/kg body weight.[3] In order to perform a comprehensive evaluation of their risk to various receptors, both temporal and spatial congener specific data is necessary.

Materials and Methods

Fish, crab and marine mammal samples were sampled and prepared in accordance with procedures developed in our laboratory and documented elsewhere.[4] Wherever possible, samples were homogenized tissue composites of several organisms to achieve more statistically significant results. Approximately 0.2-10 g (wet) of tissue (blubber, hepatopancreas, liver and muscle tissue samples) were spiked with a suite of ^{13}C-labeled PBDE procedural internal standards (Cambridge Isotope Laboratories, Andover, MA). Tissue samples were extracted by elution with dichloromethane:hexane (1:1 v/v). Clean-up involved a three stage process commencing with a gel permeation chromatography (GPC) column followed by Silica and Alumina chromatography.[5] PBDE quantitation was conducted using a GC-HRMS isotope dilution method using either a 15 m DB-5HT or a standard 30 m DB-5 column.[5]

Results and Discussion

Temporal trends. Figure 1 illustrates the exponential increases in ∑PBDEs in Dungeness crab and Columbia River whitefish (ng·g^{-1}lw), along with corresponding trends observed in human breast milk from Sweden and global production tonnes/years. Fig. 1 highlights the similarities between the increase in PBDE levels in humans and wildlife and the worldwide "penta" production trend during the 1980s and 90s. The recent decline (post 1995) observed in human breast milk PBDE levels from Sweden is thought to be due to tighter European standards regulating flame retardant chemicals. The exponential increase of PBDEs in Columbia river whitefish, with a doubling time of approx. 1.6 years, demonstrates the most rapid PBDE increases reported worldwide.

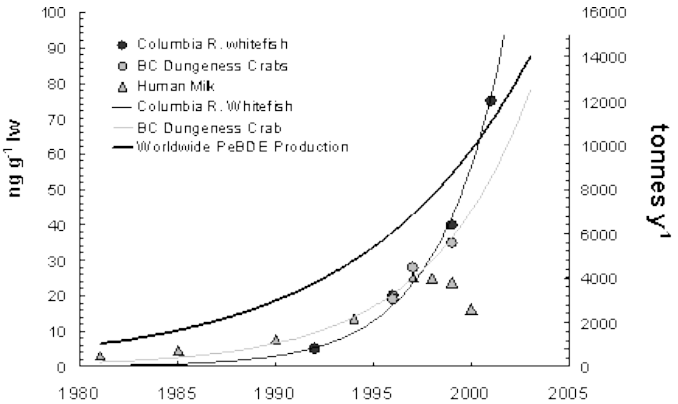

Fig. 1. Temporal trends of PBDE levels in Columbia R. whitefish and Dungeness crab from British Columbia coastal waters along with PBDE data for Swedish human breast milk and global PeBDE production trend.

Congener specific bioaccumulation patterns. BDE congener compositions in biota from coastal regions of British Columbia (BC) are dominated by lower brominated congeners such as BDE-47 and BDE-99 (Fig. 2), which is consistent with other studies of BDE patterns in marine biota.[6,7] Only relatively small amounts of larger, hydrophobic (i.e., higher brominated) congeners have been reported in humans (i.e. BDE-183 and 209)[8] and in exposure experiments with fish (hexa-deca).[9] Dungeness crab tends to exhibit an elevated contribution of BDE-49 and diminshed burdens of BDE-99. For the Columbia River system, the unusually high prevalence of BDE-99 observed in whitefish (*i.e.*, ~40% of ∑PBDEs) is likely a result of the close proximity to a "penta" source predicted in the region. The observed trend toward lower brominated congeners is not unexpected as general trends observed in substituted benzenes dictate that PBDE debromination may lead to the following congener degradation pathways: BDE-153 - BDE-99 - BDE-47 and BDE-183 - BDE-154 - BDE-100. The unique BDE pattern for Dungeness crab, *i.e.*, elevated levels of BDE-49, suggests potentially a unique metabolic conversion in this species. Higher trophic organisms such as birds and marine mammals may therefore accumulate high burdens of the lower brominated congeners (*e.g.*, Tetra BDE-47) which have been show to be more toxicologically potent than higher brominated congeners in laboratory animals.[1] Thus, marine mammal species such as killer whales, harbour seals and porpoises on the west coast of Canada are at an elevated risk to exposure and toxic effects of PBDEs.

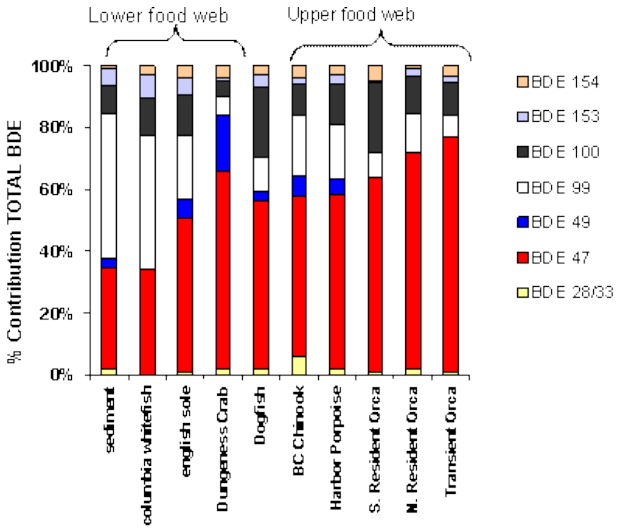

Fig. 2. Seven congener PBDE profiles (% contribution) in various organisms from the Canadian west coast marine food web

Spatial Trends. Figure 3 summarizes the spatial variation in PBDE levels among various marine species collected off Canada's coasts from 1991-2000. In general, ∑PBDE concentrations in marine animals from urbanized / industrialized regions such as the St. Lawrence Estuary (eastern Canada), and Howe Sound and Georgia Strait (Lower Mainland of BC) were typically 100 times higher than ∑PBDE concentrations observed in animals from more remote locations. For example, ∑PBDE levels in blubber of St. Lawrence beluga whales and southern resident (Georgia Strait) Killer whales[10] were approximately 700, 650 ng·g^{-1}lw, respectively, while ∑PBDEs measured in Arctic ringed seals (Holman Island), SE Baffin Bay whales and E. Hudson's Bay beluga whales all ranged between approximately 5-10 ng·g^{-1}lw.[1] Whitefish from urbanized sections of the Columbia R. exhibited ∑PBDE levels around 650 ng·g^{-1}lw and Dungeness crab's from the urbanized waters of Howe Sound demonstrated relatively high ∑PBDE levels (i.e. ~500 ng·g^{-1}lw). These relatively high levels observed in Dungeness crab and whitefish are comparable to measured ∑PBDE levels in higher trophic animals in the regions such as southern resident BC killer whales (~ 650 ng·g^{-1}lw).[10]

Conclusions

- Highest PBDE levels in coastal BC biota were found in animals near urbanized coastal waters. *.e.g.*, Columbia R. whitefish, Howe Sound Dungeness crabs.

- Extremely rapid PBDE increases in Columbia R. whitefish exhibit doubling time of 1.6 years and indicates that PBDEs are beginning to surpass PCB levels.
- In general, congener profiles indicate trend towards lower brominated congeners with increasing trophic level.
- PBDE congener pattern for Dungeness crab show increased contribution of BDE-49, which may be due to a unique

metabolic capacity by crabs.

- PBDE levels in west coast transient killer whales (~1100 ng·g^{-1}lw) are comparable to those levels measured in beluga whales (~ 750 ng·g^{-1}lw) and harbour seals (~1000 ng·g^{-1}lw) from the St. Lawrence river estuary.

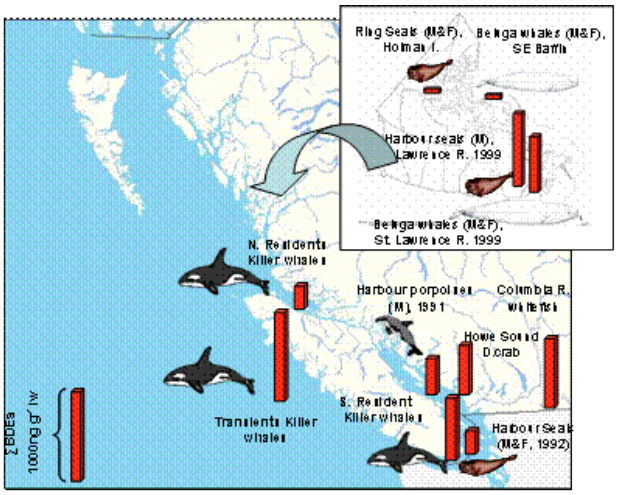

Fig. 3. PBDE levels (SUM mono-hepta congeners, ng·g^{-1} lw) in select marine mammals from Canadian waters.

Acknowledgements

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