PBDE Profiles in Aquatic Species at Different Levels of the Food Chain

M.G. Ikonomou[†], M.P. Fernandez[†], R.F. Addison[†], and W.T. Stobo[‡]

[†]*Institute of Ocean Sciences, 9860 West Saanich Road, Sidney, BC, Canada, V8L-4B2 ;*
[‡]*Bedford Institute of Oceanography, 1 Challenger Dr., Dartmouth, NS, Canada, B2Y-4A2*

Introduction

Polybrominated diphenyl ethers (PBDEs) are globally distributed contaminants which have been shown to be present in many marine and terrestrial species and numerous temporal studies have indicated that PBDE levels are rapidly increasing worldwide. Documented adverse effects of PBDE exposure in mammals and related experimental systems include impact on neurobehavioural development, thyroid hormone levels and fetal toxicity/teratogenicity at doses in the low mg/kg body weight[1]. 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[2]. 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[3].

PBDE analysis was conducted using a GC-HRMS isotope dilution method using either a 15 m DB-5HT or a standard 30 m DB-5 column[3]. Criteria for identification and quantification of congener peaks, along with quality control measures undertaken during GC-HRMS analysis, were based on procedures established in the Environment Canada "River Road" protocol[4] for PCDD/PCDF analysis. A total of 31 individual mono- to hepta- PBDE congener peaks and three co-eluting bands (each composed of two congeners) were identified and quantified, establishing the initial data set of 37 congeners overall: BDE-1, -2, -3, -7, -8/11, -10, -12, -13, -15, -17, -25, -28/33, -30, -32, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -119, -138/166, -140, -153, -154, -155, -181, -190.

Results and Discussion

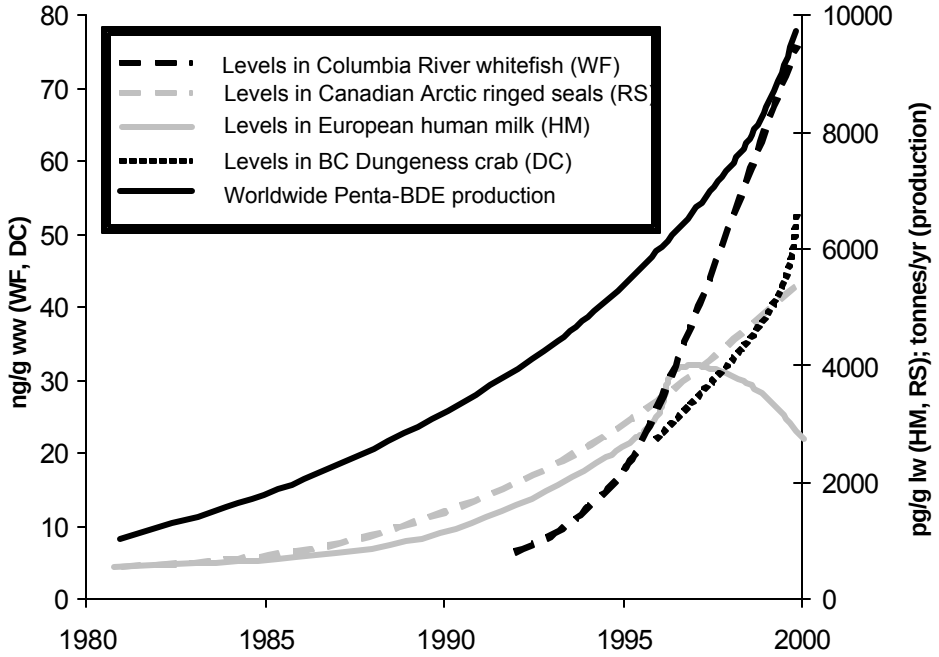

Fig. 1. Temporal trends for PBDE occurrence in wildlife and humans along with the worldwide production trend.

A worldwide increase in PBDEs has been documented in several environmental compartments, ecosystems and regions around the world. Fig. 1, illustrates a few of the exponential increases in this poly-halogenated aryl-hydrocarbon documented in Canadian wildlife from crab to fish to arctic seals, along with corresponding trends observed in human breast milk (the recent decline is thought to be due to tighter European standards regulating flame retardant chemicals). Fig. 1 also highlights the remarkable similarities between the increase in PBDE levels in humans and wildlife and the worldwide "penta" production trend. "Penta" formulations typically consist of 50-62% pentabromodiphenyl ethers and 24-38% tetrabromodiphenyl ethers. Tetra- and penta-bromodiphenyl ethers are thought to bioaccumulate and persist to an extent greater than that of higher brominated groups. However, most (~80%) PBDE formulations currently used consist of 97-98% decabromodiphenyl ether which is thought to have too large an effective cross-sectional diameter to be considered bioaccumulative and extreme hydrophobicity to be effectively transported in aquatic environments. Only relatively small amounts of larger, hydrophobic congeners have been reported in humans (i.e. BDE-183 and 209)[5] and in exposure experiments with fish (hexa-deca)[6]. Most PBDE compositions in biota are dominated by BDE-47 (tetra) and BDE-99 (penta) as illustrated in our work (Fig. 2) for a variety of species (with the exception of Dungeness crab) sampled from coastal regions of British Columbia (BC) as well as the Columbia River which originates in the Southeast corner of BC.

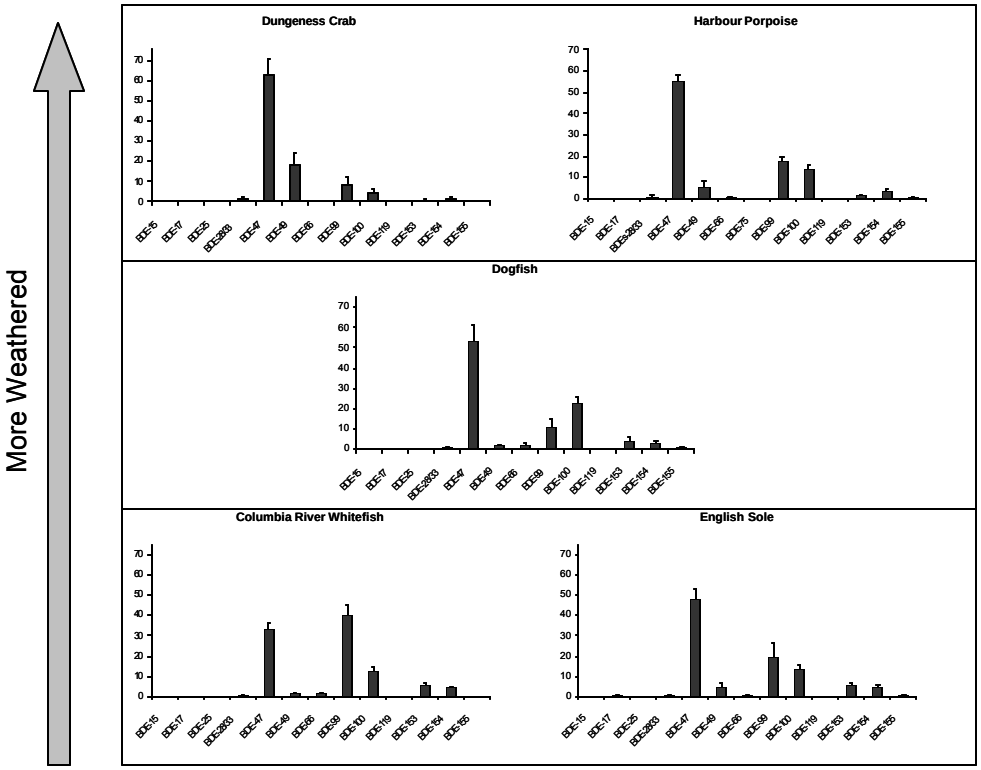

Fig. 2. 14 congener PBDE profiles in various marine biota collected off BC's West Coast (with the exception of the Whitefish which were from the Columbia River in BC).

Although the prevalence of BDE-99 in the Columbia river whitefish is likely a result of the close proximity to a "penta" source predicted in the region, the greater tendency towards lower brominated congeners in higher trophic level organisms follows an expected trend. General trends observed in substituted benzenes dictate that PBDE debromination whether mediated via metabolic, photolytic, or other abiotic processes may lead to the following congener degradation pathways: BDE-153 → BDE-99 → BDE-47 and BDE-183 → BDE-154 → BDE-100. However, Dungeness crab shows an elevated level of BDE-49 with diminished amounts of BDE-99, which may suggest a unique metabolic conversion in this species.

Due to the combined effects of biomagnification and bioconversion/biodegredation of PBDE congeners with increasing trophic level, marine mammals may have a high PBDE burden made up predominantly of lower brominated congeners which are known to have lower toxicological thresholds than higher brominated congeners[1]. Thus marine mammals are at an elevated risk to exposure and toxic effects of PBDEs. Fig. 3 summarizes the spatial variation in PBDE levels among various marine mammals collected off Canada's coasts from 1991-2000. The most contaminated animals were found in heavily urbanized / industrialized regions, namely, St. Lawrence Estuary (eastern Canada), and Georgia Strait (Lower Mainland of BC).

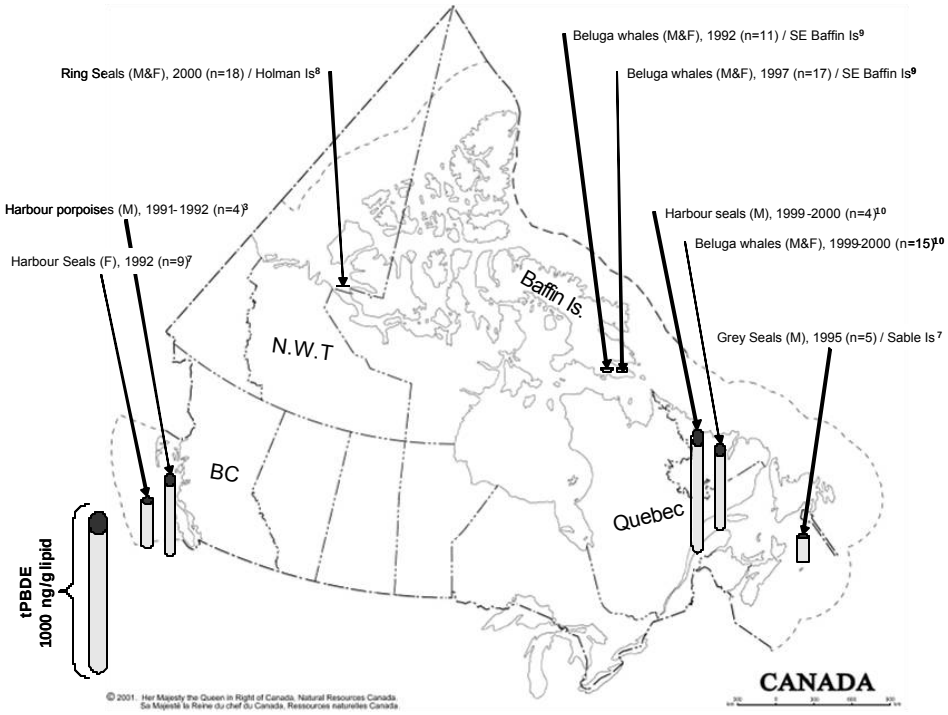

Fig. 3. Average PBDE levels in select marine mammals from Canada's coasts.

Conclusions

- Exponential increase in PBDE levels in several marine organism in Canada
- Congeners profiles indicate trend towards lower brominated congeners with increasing trophic level (D. Crab's pattern shows unique metabolic features)
- Marine mammals show elevated levels of PBDEs (particularly of tetra and penta) particularly in urbanized / industrialized zones in Canada.

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