PBDES, PCBs, and Dioxin-Like PCBs in Harbor Seals from the Northwestern Atlantic

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Introduction

Brominated flame retardants, especially the polybrominated diphenyl ethers (PBDEs), are persistent organic pollutants (POPs) that biomagnify and have been associated with endocrine-disrupting and neurodevelopmental effects in animals (Birnbaum and Staskal, 2003). As a result of their lipophilicity and widespread use in household products including textiles, furniture, and electronics, PBDEs are now ubiquitous and have been found in tissues of humans and wildlife, even in remote areas (de Wit et al. 2006). Temporal studies have shown that PBDEs are increasing in biota and humans, particularly in the United States, where they are still in extensive production and use (Hites 2004, Schechter et al. 2005). Marine mammals from industrialized regions accumulate relatively high PBDE levels (~1000 ng/g, lw) (She et al. 2002, Law et al. 2003, Hites 2004, Lebeuf et al. 2004, Law et al. 2005, Law et al. 2006), and these concentrations are reportedly increasing in some areas. Although ~80% of the PBDEs produced globally consist of DecaBDE, the presence of BDE 209 has scarcely been detected in marine mammals. At present, it is not known whether marine mammals can debrominate BDE 209 to lower brominated congeners, as was shown in fish (Stapleton et al. 2004), but recent data suggest that metabolic capacity for this congener is highly species-specific in marine animals (Johnson-Restrepo et al. 2005).

Harbor seals (*Phoca vitulina concolor*) inhabiting the northwestern Atlantic are closely associated with near-shore environments and have been studied as indicators of environmental contamination by POPs (Shaw et al. 2005, Shaw et al. 2006a, Shaw et al. 2006b). Our previous study analyzed 36 mono- through hexa-BDEs in harbor seals (n=28) from this region, and found relatively high ∑PBDE levels in blubber on a global scale (Shaw et al. 2006a). The objective of the present study was to concurrently analyze PBDE congeners including mono- through decaBDE (BDE 209), along with PCB congeners in a larger sample size to gain a better perspective on the present status of PBDE contamination and the toxicological implications of current body burdens in these animals. Here we report the results of an extended analysis of PBDEs and PCBs in northwestern Atlantic harbor seals.

Materials and Methods

Samples. Blubber samples were collected from 42 harbor seals (7 adult males, 8 adult females, 14 yearlings, 13 pups) that stranded along the northwestern Atlantic coast from the eastern coast of Maine to Long Island, New York between 1991 and 2005 (Figure 1). Seals were weighed, and standard length and axillary girth were measured. Age was estimated based on body size. Condition indices were calculated by dividing axillary girth/standard length and body weight/standard length. Blubber samples were stored in a freezer at -40°C until analysis.

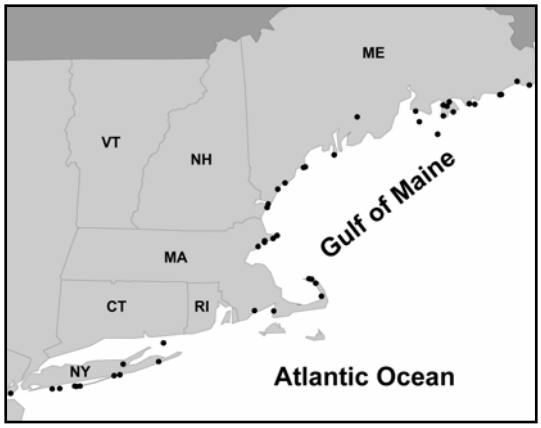

Figure 1. Map of the northwestern Atlantic showing stranding locations of harbor seals

Chemical Analysis. Harbor seal blubber samples were analyzed for 146 PCB congeners (including 8 mono- and 4 non-ortho coplanar PCBs) and 40 PBDE congeners (ranging from mono- through hepta BDEs and BDE 209) following the isotope dilution quantification method as previously described (Shaw et al. 2006). Analyses of PCBs and 36 BDE congeners were performed by HRGC-LRMS (HP 6890GC with DB-XLB column, 30 m × 0.25 mm i.d. × 0.25 µm film thickness coupled to an HP 5972 mass spectrometer) and monitored by selected ion monitoring (SIM) at the two most intensive ions in the molecular ion or or M-2Br ion cluster . Analysis of BDE 209 and hepta BDE isomers were carried out by HRGC-HRMS (HP 5890GC with Rtx-5MS column, 15 m × 0.25 mm i.d. × 0.1 µm film thickness coupled to an Autospec Q high resolution magnetic sector mass spectrometer, R~ 4000). PCB and PBDE concentrations were calculated using the internal standard method and were corrected by surrogate recoveries. In cases where congeners were reported as non-detects, concentrations were calculated by treating the result as if half the detection limit. WHO-TEQs were calculated for 4 non-ortho coplanar and 8 mono-ortho PCBs using the most recent international WHO-TEFs (Van den Berg et al. 2006).

Results and Discussion

Mean ∑PBDE concentrations in harbor seal blubber were highest in the younger seals, (3645 and 2945 ng/g, lw in pups and yearlings, respectively), followed by the adult males (1385 ng/g, lw), and adult females (326 ng/g, lw). Age differences were significant between the yearlings and adult females ($p=0.001$), while gender differences were only observed among the adults ($p=0.01$). PCB concentrations were an order of magnitude higher in these seals and were highly correlated with PBDE concentrations in blubber ($R^2=0.68$, $p<0.001$ lipid basis, $R^2=0.53$, $p<0.001$ wet weight basis), indicating parallel accumulation of these compounds through the marine food chain. Similar to the accumulation pattern for PBDEs, mean ∑PCB concentrations were highest in the younger seals (60479 and 56799 ng/g, lw in yearlings and pups, respectively) followed by the adult males (36685 ng/g, lw) and females (14047 ng/g, lw). WHO-TEQ concentrations of 4 non-ortho coplanar and 8 mono-ortho PCBs were highest in the pups (188 pg/g, lw), followed by the yearlings (126 pg/g, lw), adult males (54 pg/g, lw) and females (25 pg/g, lw). This pattern is consistent with that observed for most lipophilic compounds in which females transfer a large proportion of their body burden to the pups while an age-dependent accumulation is observed in male seals.

BDE Congener Profiles and BDE 209. The predominant BDE congeners in harbor seal blubber were BDE 47, 99, 100, 153, 154, and 155, accounting for 98% of the total PBDE content (Figure 2). BDE 47 dominated the congener profiles, contributing 60-75% of the total. For most marine mammals, the BDE profiles are in the descending order: BDE 47>99>100>154>153 (Hites 2004). The profile in our adult male seals differs in that the hexaBDE 153 is the second most abundant congener after BDE 47, and BDE 155 contributes more to the total than BDE 154. The adult females and yearlings exhibit a similar profile in which BDE 153 predominates over BDE 100, while the pups appear to preferentially retain the lower brominated congeners (BDE 47, BDE 99, and BDE 100) followed by BDE 153>BDE 154>BDE 155.

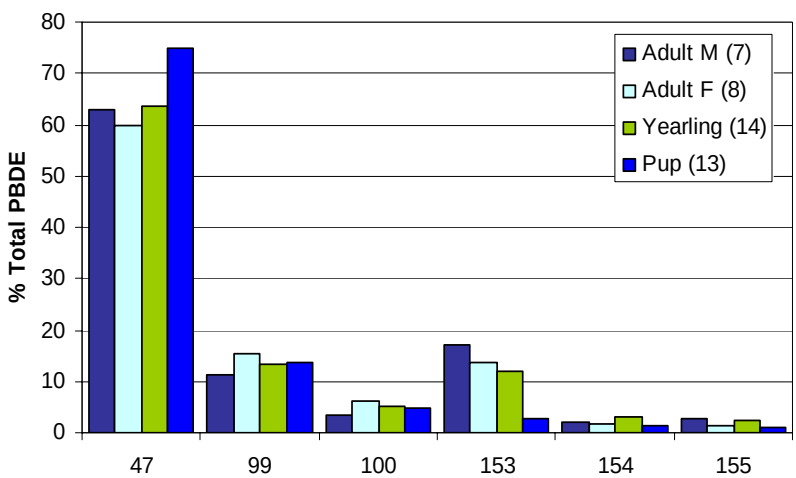

Figure 2. BDE congener profile in harbor seal blubber

The presence of the hexaBDE 155 as a major congener in these seals is an interesting finding, as this congener has rarely been detected in marine mammals (Stapleton et al. 2006). In a recent study, BDE 155 was positively identified, along with BDE 154, as one of as one of several possible break-down products of BDE 209, presumably as a result of metabolic debromination in fish (Stapleton et al. 2004). In this study, decaBDE (BDE 209) was analyzed in a subset of harbor seals (n=4) and detected in two animals with concentrations ranging from 1.4 to 7.6 ng/g, lw in a female pup and male yearling, respectively. While preliminary, this data, along with the finding of BDE 155 among the predominant congeners in blubber, suggests possible selective uptake of DecaBDE through the food chain or debromination of BDE 209 in these seals. A recent feeding study (Thomas et al. 2005) demonstrated that BDE 209 can be stored in blubber of captive seals and may accumulate, although the environmental significance of this finding is not clear. We are currently analyzing hepta- through decaBDE in a larger sample size (n=42) in order to further explore the possible accumulation of these congeners in wild seals.

Condition. Condition indices calculated for harbor seals in this study increased significantly with age ($p<0.001$), but were not significantly correlated with PBDE or PCB concentrations. Lipid content (% lipid) was highly variable in our harbor seal blubber samples and lipids were positively correlated with condition but not significantly correlated with PBDE or PCB concentrations. This variance in lipids is typical of stranded animals and indicates that some of the animals were in poor nutritive condition. In samples from two pups and one yearling, the lipids were <20%, and PBDE and PCB concentrations in these seals were elevated compared with levels in the remaining samples. However, when these animals were removed from the analysis, concentrations in the younger animals still remained relatively high.

Temporal and Spatial Trends. In contrast with most studies examining temporal trends of PBDEs in marine mammals, we found no significant temporal trend for ∑PBDE concentrations in harbor seals between 1991 and 2005. A similar lack of a time trend was found for ∑PCB concentrations over this period, which is consistent with our previous finding for organochlorines (PCBs and DDTs) in harbor seals from this region (Shaw et al. 2005). Tuerk et al. (2004) also reported the lack of a temporal trend for PBDEs in stranded white-sided dolphins from the northwestern Atlantic between 1993 and 2000. A recent study (Stapleton et al. 2006) found no significant time trend for PBDEs in California sea lions, although the levels of hexabromocyclododecane (HBCD) were increasing over the period 1993 to 2003.

PBDE congener patterns in our harbor seals tended to shift over time. BDE 47 concentrations were increasing and BDE 153 concentrations were decreasing between 1991 and 2000; these trends leveled off between 2000 and 2005. BDE 99 concentrations increased only slightly from 2000 to 2005. Similarly, Ikonomou et al. (2002) reported that concentrations of BDEs 47, 99, and 100 were increasing in male ringed seals from the Canadian Arctic between 1981 and 1996, but increases in the levels of BDE 99 were slowing considerably between 1996 and 2000. Similar changes were reported in gull egg samples from the Great Lakes between 1981 and 2000 (Hites 2004). The meaning of these changes is not clear, but may reflect changes in the use or the composition of the commercial PBDE products over the years.

There was no significant spatial trend in PBDE or PCB concentrations in our harbor seal samples, which is similar to our previous finding for organochlorines (PCBs, DDTs, chlordanes) (Shaw et al. 2005), and undoubtedly relates, in part, to the heterogeneity of the data.

Global Comparisons and Toxicological Implications. Compared with other studies of stranded marine mammals, PBDE concentrations found in northwestern Atlantic harbor seals are approximately at the middle of the contamination spectrum on a global scale. PBDE concentrations detected in the pups and yearlings (~3000-4000 ng/g, lw) are higher than those reported in harbor seals from the North Sea and the St. Lawrence Estuary (Law et al. 2003), and similar to the levels reported in harbor seals from San Francisco Bay in the mid- to late 1990s (She et al. 2002). Levels in our younger seals are lower than the very high levels found in dolphins from UK waters (Law et al. 2003, Law et al. 2005) but are an order of

magnitude higher than levels reported in St. Lawrence beluga whales (Lebeuf et al. 2004) and cetaceans from Asian waters (Kajiwara et al. 2006). While possible differences in species-specific metabolic capacity, nutritive state, and other factors necessarily limit the utility of comparisons between studies of stranded and free-ranging seals, the PBDE concentrations detected in the harbor seal pups and yearlings in this study exceed the concentration range of 61 – 1500 ng/g, lw, associated with elevated thyroid hormone levels in live-captured gray seal pups and juveniles from UK waters (Hall et al. 2003). Concentrations in the younger seals in this study are an order of magnitude higher than the levels of PBDEs and PCBs associated with lymphoid depletion in stranded and bycaught harbor porpoises from the North and Baltic Seas (Beineke et al. 2005).

To our knowledge, this is the first report of a concurrent analysis of PBDEs and PCBs in pinnipeds from the US northwestern Atlantic. To place the PBDE results in perspective, it should be noted that body burdens of PCBs and dioxin-like PCBs in these harbor seals are relatively high, similar to those reported in seals from polluted areas of Europe and Asia (Shaw et al. 2005). PCB concentrations in the younger seals (~50-60 µg/g lw) and adult males (~37 µg/g lw) exceed the estimated threshold level of 17 µg PCB/g lw for adverse effects in the species, including immune and endocrine-disrupting effects (Kannan et al. 2000), suggesting that this population is already at risk for such effects. In view of the ongoing production and use of PBDEs in the US, further research is urgently needed to elucidate accumulation patterns, trends, and potential health effects of PBDEs in the context of the complex mixtures of POPs to which these seals are exposed.

Acknowledgments
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