

POLYBROMINATED DIPHENYL ETHERS (PBDES) IN HARBOR SEALS FROM THE NORTHWESTERN ATLANTIC: ARE SEALS DEBROMINATING DECA BDE?

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Abstract

Marine mammals inhabiting industrialized regions of the world accumulate high levels of the flame retardants polybrominated diphenyl ethers (PBDEs), with blubber concentrations typically comprising tetra- through hexa-BDEs. Although ~80% of the PBDEs produced globally consist of DecaBDE, BDE 209 has rarely been found in marine mammals. Since BDE 209 is often the major congener in marine sediments, the main reason for the low concentrations in marine mammals appears to be due to relatively rapid clearance after biotransformation. Harbor seals (*Phoca vitulina concolor*) inhabiting the northwestern Atlantic are closely associated with polluted near-shore environments and are highly contaminated by PBDEs and other persistent organic pollutants (POPs). In this study, BDE 209 was detected above trace levels in blubber of four of eight harbor seals, indicating for the first time that BDE 209 is present at measurable levels in the marine food chain and can accumulate in marine mammals in the wild. This data, along with the finding of hexaBDEs among the predominant congeners in blubber, suggests selective uptake of DecaBDE through the food chain and debromination of BDE 209 to lower brominated, more persistent congeners in these seals. The accumulation/debromination of BDE 209 in marine mammals is of concern, as large amounts of DecaBDE are still in use.

Introduction

The brominated flame retardants polybrominated diphenyl ethers (PBDEs), are persistent organic pollutants (POPs) that biomagnify and have been associated with endocrine-disrupting and neurodevelopmental effects in animals.¹ As a result of their lipophilicity and widespread use in household products including textiles, furniture, and electronics, PBDEs are now ubiquitous global contaminants.² Temporal studies have shown that PBDEs are increasing in biota and humans, particularly in the United States, where the Penta- and OctaBDE formulations have only recently been phased out of commerce and the DecaBDE formulation is still in extensive production and use.³ Marine mammals inhabiting industrialized regions accumulate relatively high PBDE levels, with blubber concentrations typically dominated by tetra- through hexaBDEs.⁴⁻⁹ Although ~80% of the PBDEs produced globally consist of DecaBDE, BDE 209 has rarely been found in marine mammals.¹⁰⁻¹² Since BDE 209 is often the major congener in marine sediments, the main reason for the low concentrations is suggested to be a low bioaccumulation potential due to relatively rapid excretion after biotransformation. Debromination of BDE 209 has been demonstrated *in vivo* in rats and fish, suggesting it is metabolized.¹³⁻¹⁵ Recent experiments using fish liver microsomes¹⁵ found that BDE 209 was rapidly debrominated to form lower brominated congeners, primarily hexa-, hepta-, octa- and nonaBDEs, that have the potential to be more persistent and bioaccumulative than the parent compound. A recent study reported a short half-life (15 days) of BDE 209 in serum of exposed workers, and significant accumulation of octa- and nonaBDE congeners in serum, suggesting that debromination of BDE 209 may occur in humans.¹⁶ In a study of grey seals experimentally dosed with DecaBDE, the measured half-life of BDE 209 was 8-13 days in serum, implying that seals may possess a similar potential for rapid debromination of this congener.¹⁷

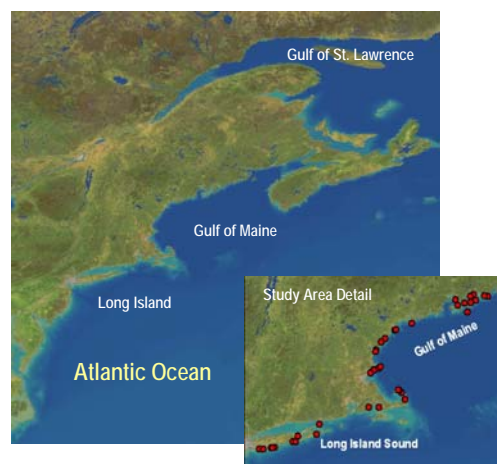


Figure 1. Map of NW Atlantic showing harbor seal stranding locations

Harbor seals (*Phoca vitulina concolor*) inhabiting the northwestern Atlantic are closely associated with polluted near-shore environments and have been shown to be highly contaminated by PBDEs and other persistent organic pollutants (POPs) on a global scale.¹⁸⁻²⁰ Moreover, the population is currently experiencing an epizootic of unknown etiology and it can be speculated that immune and endocrine-disrupting chemicals including the PBDEs may be playing a contributory role in this event. Our previous study reported on mono- through hexaBDEs in blubber of harbor seals from this region. Here we report on the extended analysis of PBDEs including BDE 209 in a larger sample size.

Materials and Methods

Samples. Blubber samples were collected between 1991 and 2005 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 (Figure 1). Seals were weighed, and standard length and axillary girth were measured. Age was estimated based on body size. Blubber samples were stored in a freezer at -40°C until analysis.

Chemical Analysis. Harbor seal blubber samples were analyzed for 41 PBDE congeners (mono- through heptaBDEs and BDE 209) following the isotope dilution quantification method previously described.²¹ Analyses of 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 M-2Br ion cluster. Analysis of BDE 209 was 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). PBDE concentrations were calculated using the internal standard method and were corrected by surrogate recoveries. Concentrations are reported on a lipid weight (lw) basis.

Statistics. Variables were log-transformed prior to statistical analysis using SPSS 14.0. Concentrations below the level of detection were calculated by treating the result as if half the detection limit.

Results and Discussion

ΣPBDE concentrations (mono- through hexaBDEs) in harbor seal blubber (n=42) ranged from 80-25720, mean 2403 ± 5406 ng/g, lw. Mean concentrations 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). 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.

PBDE Congener Profiles. BDE 47 dominated the congener profiles, contributing 60-75% of the total PBDE, followed by the pentaBDEs 99 and 100 (14-21%) and the hexaBDEs 153, 154, and 155 (5-22%). In adult male seals, the hexaBDEs contributed more than the pentaBDEs to the total, whereas in pups the hexaBDEs contributed much less (5%) to the total compared to the pentaBDEs (19%) and the tetraBDEs (75%), indicating that the pups are preferentially retaining the lower BDE congeners. The hexaBDE 155 has rarely been detected in marine mammals²¹ and was recently identified, along with BDE 154, as a specific metabolic debromination product of BDE 209 in fish.¹⁵

Temporal Trends. In contrast with other studies examining temporal trends of PBDEs in marine mammals, we found no significant time trend in ΣPBDE concentrations in harbor seals between 1991 and 2005, although congener patterns 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. The meaning of these changes is

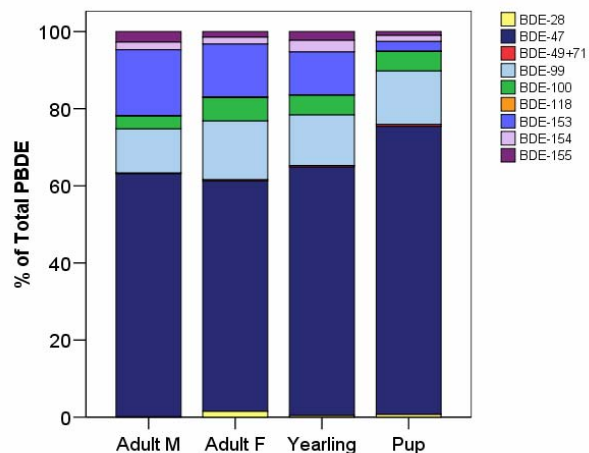


Fig. 2. BDE congener profiles in seal blubber

not clear, but may reflect changes in the use or the composition of the various commercial PBDE products over the years.

Global Comparisons and Toxicological Implications. 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,⁶ and similar to the levels reported in harbor seals from San Francisco Bay in the mid- to late 1990s.⁵ Levels in our younger seals are lower than the very high levels found in dolphins from UK waters^{8,9} but are an order of magnitude higher than levels reported in St. Lawrence beluga whales.⁶

The toxic effects of PBDEs in marine mammals in the wild are not understood. Hall et al.²³ recently reported an association between thyroid hormone alterations and PBDEs in the concentration range of 61 – 1500 ng/g, lw, in blubber of live-captured gray seal pups and juveniles from UK waters. Another recent study found an association between low levels of PBDEs and PCBs in blubber and lymphoid depletion in stranded and bycaught harbor porpoises from the North and Baltic Seas.²⁴ The harbor seal pups and yearlings in this study have much higher concentrations of PBDEs, implying that they may be at risk for similar effects. At present, the population is experiencing an epizootic of unknown etiology which has resulted in the deaths of more than 400 animals along the southern Maine coast. This is the fourth mass mortality recorded in these seals since 1980, and it can be speculated that their high body burdens of immune- and endocrine-disrupting chemicals including the PBDEs may be playing a contributory role in these events.

DecaBDE (BDE 209). BDE 209 was analyzed in eight harbor seals and detected in the blubber of four at low concentrations ranging from 1 to 8 ng/g, lw (Fig. 3). This finding is significant as it indicates that BDE 209 is present at measurable levels in the marine food chain and can be accumulated in marine mammals in the wild. Moreover, this data, along with the finding of BDE 155 among the predominant congeners in blubber, suggests selective uptake of DecaBDE through the food chain and debromination of BDE 209 via metabolism in these seals. A recent experiment in captive grey seals¹⁷ demonstrated that BDE 209 can be stored in blubber of seals and may accumulate at low levels after constant exposure for 3 to 29 days. Interestingly the levels in the grey seals (3 to 7 ng/g, lw) continuously dosed with DecaBDE is quite similar to the levels detected in our wild harbor seals. Given the evidence of rapid clearance of BDE 209 in blood¹⁷, this observation implies that these seals are exposed to DecaBDE more or less continuously to maintain the concentrations observed.

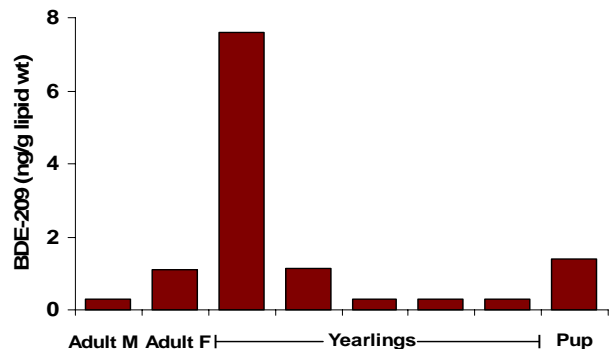


Fig. 3. BDE 209 concentrations in harbor seals

To our knowledge, this is the first report of BDE 209 concentrations above trace levels in a wild marine mammal species. The accumulation of BDE 209 in marine mammals is of special concern, as large amounts of DecaBDE are still in use. Further research is needed to elucidate the accumulation, kinetics, and toxicity of higher BDEs in the context of the complex mixtures of POPs to which these seals are exposed.

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