

Spatial and Temporal Trends of PBDEs in Biota from the Canadian Arctic Marine Environment

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Introduction

Levels of past-use persistent organic pollutants (POPs) including PCBs, DDTs and toxaphene in Arctic biota have stabilized or are in decline since regulatory actions imposed during the 1970s and 80s.¹ Conversely, “current-use” typically high production volume (HPV) chemicals such as PBDEs have exhibited exponential increases in Canadian Arctic biota.² Increasing PBDE exposure to wildlife and humans is of concern due to documented adverse effects in laboratory studies, including impacts on neurobehavioural development, thyroid hormone levels and fetal toxicity/teratogenicity at doses in the low mg/kg body weight.³ The primary aim of this paper is to present our most recent PBDE data (2001-2003 concentrations) in our 1981-present temporal trend study of PBDEs in Arctic ringed seals from Holman Island, Northwest Territories, Canada.²

Materials and Methods

Tissue samples of several marine biota species including Arctic cod, eider ducks, ringed seals and beluga whales from across the Canadian Arctic have been collected for trace analysis of multiple organohalogens in accordance with procedures developed in our laboratory and documented elsewhere.⁴ Approximately 0.2-10 g (wet) of tissue (blubber, liver and muscle tissue samples) were spiked with a suite of ¹³C-labeled PBDE procedural internal standards (Cambridge Isotope Laboratories, Andover, MA) and extracted with dichloromethane:hexane (1:1 v/v). Clean-up involved gel permeation chromatography (GPC), followed by Silica and Alumina chromatography.⁵ PBDE analysis was conducted using a GC-HRMS isotope dilution method with either a 15 m DB-5HT or a standard 30 m DB-5 column.⁵ 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.

Results and Discussion

Temporal Trends of PBDEs in Canadian Arctic Ringed Seals. Figure 1 illustrates time-series concentrations (pg·g⁻¹lw) of Σ PBDEs, and BDE congeners 47, 99 and 100 in two age-classes of male ringed seal blubber (0-15 and 16-35 years) during the period 1981-2003, along with a temporal trend of worldwide “Penta” BDE production (tonnes/year). Our past work demonstrated significant exponential increases of Σ PBDE, BDE47 and BDE-99 concentrations in ringed seals aged 0-15 years from Holman Island, NWT during the period 1981-2000, with 4-5 year doubling times.² The most recent 2002 and 2003 samples for the 0-15y male ringed seals indicate that mean PBDE have not significantly changed since 2000 (confirmed by one-way Analysis of Variance (ANOVA) $\alpha=0.05$) confirms no significant differences between mean PBDE concentrations of those animals during 2000, 2002 and 2003 samples. The determination of a statistically significant change in the 2003 time point for 0-15 y males was complicated by a low sample size ($n=2$) for those animals. Similarly, PBDE concentrations in the older 16-35 age class of male ringed seals during 2002 and 2003 were comparable and not significantly different from those concentrations observed in 2000 samples. While PBDE levels appear to be stabilizing, it will likely require another 5-10 years of sampling/tissue residue analyses to detect if any significant decline in PBDEs are occurring in Canadian Arctic ringed seals.

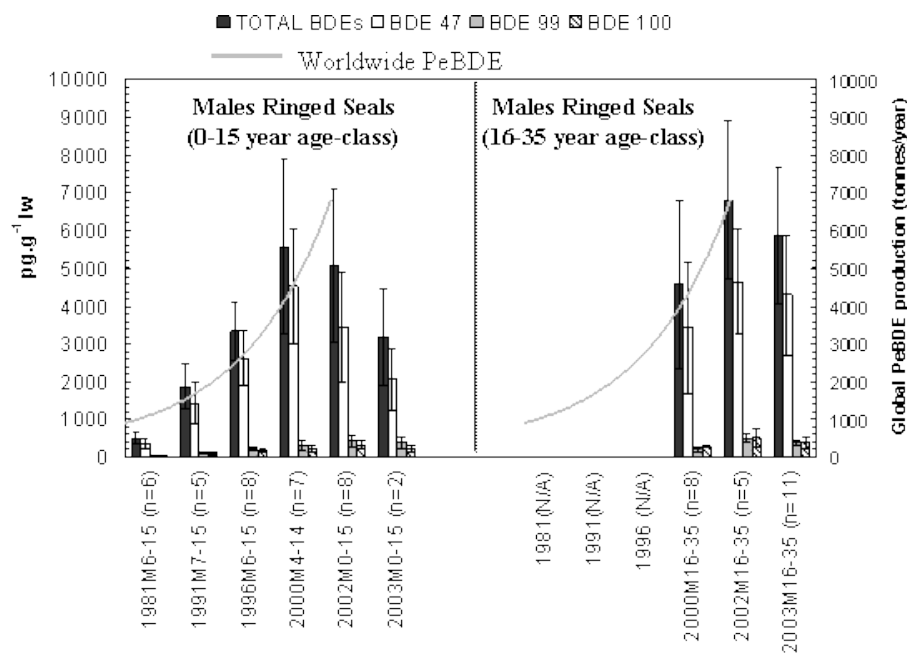


Fig. 1. Temporal trends for PBDEs in male ringed seals along with the worldwide PeBDE production trend. Bars represent arithmetic means and error bars standard deviations.

PBDE congener profiles in Arctic biota. Figure 2 illustrates PBDE compositions (i.e., % congener contributions) observed in Eastern Hudson Bay (EHB) biota, which represents the species and trophic positioning of a typical Canadian Arctic marine food web. Also shown in Figure 2 is the composition of the commercial pentabromodiphenyl ether formulation Bromkal®. PeBDE formulations traditionally consist of 50-62% PeBDEs and 24-38% TeBDEs. The bromodiphenyl ether congeners in Arctic biota predominate in the order TeBDE-47 > PeBDE-99 > PeBDE-100, which is consistent with congener specific bioaccumulation patterns observed in other food webs.^{6,7} The observed BDE congener pattern profile of lower brominated congeners in higher trophic level organisms follows an expected trend as PBDE debromination 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. Thus, due to the combined effects of biomagnification and bioconversion/biodegradation of PBDE congeners with increasing trophic level, birds and 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

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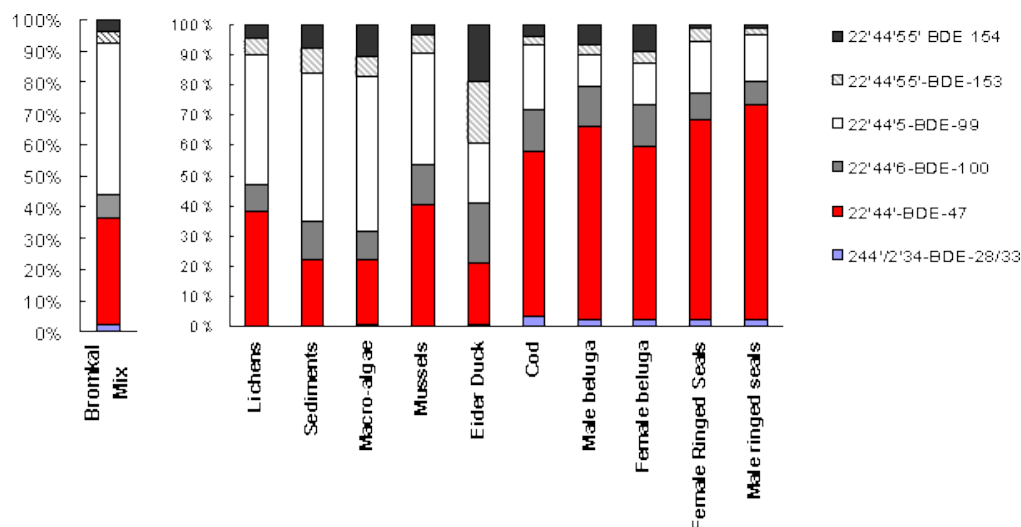


Fig. 2. Six congener PBDE profiles (% congener contribution) in various organisms from the Arctic marine food web in comparison to the technical Bromkal formulation.

Canadian Marine Mammals. Figure 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). For example, Σ PBDE levels in

blubber of St. Lawrence beluga whales and southern resident (Georgia Strait) Killer whales were approximately 700 and 650 $\text{ng}\cdot\text{g}^{-1}\text{lw}$, respectively.⁸ Σ PBDE concentrations in Canadian Arctic marine mammals, typically in the low $\text{ng}\cdot\text{g}^{-1}\text{lw}$ range, are about 100 times lower than Σ PBDE concentrations observed in marine mammals inhabiting more southern/urbanized Canadian waters. For example, SE Baffin Bay whales, E. Hudson's Bay beluga whales and Holman Island Ringed seals are all range between 5-10 $\text{ng}\cdot\text{g}^{-1}\text{lw}$.

Conclusions

- Exponential increase in PBDE levels in Canadian Arctic Ringed seals during 1981-2000 appears to be stabilizing and no significant change has been observed between 2000 and 2003 time points.
- Congener profiles indicate trend towards lower brominated congeners with increasing trophic level.
- PBDE levels in Arctic marine mammals are approximately 100 times lower than marine mammals from southern/urbanized Canadian marine systems.

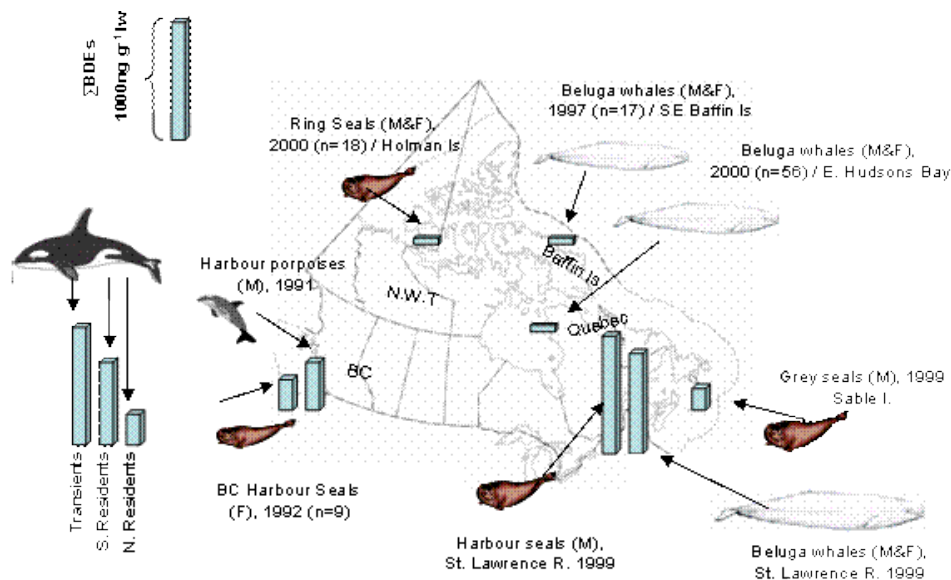


Fig. 3. Average PBDE (SUM mono-hepta) levels in select marine mammals from Canadian coastal waters.

Acknowledgements

We acknowledge DFO-ESSRF, TSRI and NCP for financial support and RDL staff for sample analysis and technical assistance.

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