PBDEs and their Hydroxylated and Methoxylated Derivatives in Marine Sediment and Biota from Canada's Eastern Arctic

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Introduction

The extensive use of polybrominateddiphenyl ethers (PBDEs) in commercial applications and products since the early 1980s has resulting in extremely high production volumes (HPVs) of these compounds in North America and Europe. Recent studies have focused on *in vivo* metabolic transformation products of PBDEs in laboratory animals.[1,2] Hydroxy (OH-) and methoxy (MeO-) substituted BDEs have also been detected in wild fish[3], birds[4], marine mammals [5] and humans.[6] Because OH-BDEs are structurally very similar to the thyroid hormone Thyroxine (T4), increased accumulation of OH-BDE derivatives may lead to lower Vitamin A levels and negative impacts on thyroid hormone function.[7,8] The objective of the present study is to assess the levels and bioaccumulation behaviour of OH- and MeO-BDEs in biota from an eastern Canadian Arctic marine food web.

Materials and Methods

Marine sediment and biota samples were collected from Eastern Hudson Bay during July and September 1999-2002. For determination of OH- and MeO-BDEs, tissue samples (0.5-10 g ww) of lichens, macro-algae, fish muscle (cod, sculpin, capelin), seaduck liver (common eider and scoters) and beluga whale and ringed seal blubber were homogenized with ~20g hydromatrix, spiked with 2000-5000 pg of ^{13}C BDEs procedural internal standards (Cambridge Isotope Laboratories, Andover, MA) and extracted using accelerated solvent extraction (ASE, DIONEX, USA) in 1:1 v/v Hexane:CH_2Cl_2. Further clean-up steps included gel permeation chromatography (GPC) and Florisil chromatography. OH-BDEs were derivatized (i.e., acetylated) by addition of 100 µl of pyridine and acetic anhydride, 2 min vortex mixing, and 30 min on heating block at 60^{o}C. Identification of OH- and MeO- BDEs in biota sample extracts was conducted by relative retention time (RRT) comparisons to authentic synthesized reference standards by high-resolution gas-chromatography mass spectrometry (GC-HRMS). Quantification was done by isotope dilution using a standard 30 m DB-5 column.[9] Peak confirmation and resolution of coeluting compounds was conducted by using a second polar column SP 2331 (30m x 0.25 mm i.d x 0.2 µm film thickness).

Results and Discussion

Identification of OH- and MeO-BDEs. Table 1 summarizes the suite of forty six OH- and MeO-BDE compounds we currently monitor by GC/HRMS, along with corresponding relative retention times (RRTs), i.e, relative to BDE-47, on the 30 m DB-5 column and method detection limits (MDLs) for beluga blubber. RRTs of the eleven compounds for which we have synthesized reference standards (compounds in bold) were determined by direct comparison of RTs to RT of BDE-47, present in our OH- and MeO- BDEs calibration solution. RRTs for the other OH- and MeO-BDEs, which are not currently present in our calibration solution, were determined from previously reported OH- and MeO-BDE RRTs in the literature.

Table 1: List of OH- and MeO-BDEs, RRTs (relative to BDE-47) on standard 30 m DB-5 column (relative to BDE-47) and MDLs (ng·g^{-1} ww) for GC/HRMS analysis.

OH-BDEs	RRT	MDL ng·g^{-1} (ww)	MeO-BDEs	RRT	MDL ng·g^{-1} (ww)
6' OH-BDE-17	0.983	0.0170	6' MeO-BDE-17	0.948	0.0135
4' OH-BDE-30	0.984	0.0170	4' MeO- BDE-30	0.950	0.0135
2' OH-BDE-28	0.996	0.0170	**2' MeO- BDE-28**	**0.966**	**0.0123**

3' OH-BDE-28	1.010	0.0170	3' MeO- BDE-28	0.986	0.0123
4' OH-BDE-17	**1.010**	**0.0170**	**4' MeO- BDE-17**	**0.986**	**0.0149**
6' OH-BDE-49	1.039	0.0064	6' MeO- BDE-49	1.024	0.0184
2' OH-BDE-68	1.050	0.0064	2' MeO- BDE-68	1.038	0.0184
2'-OH-BDE-75	**1.057**	**0.0051**	**2'-OMe-BDE-75**	**1.041**	**0.0184**
6 OH-BDE-47	**1.061**	**0.0077**	**6 MeO-BDE-47**	**1.054**	**0.0137**
4' OH-BDE-69	1.064	0.0064	4' MeO- BDE-69	1.058	0.0155
3 OH-BDE-47	1.074	0.0064	**2'-OMe-BDE 74**	**1.063**	**0.0490**
2' OH-BDE-66	1.075	0.0064	3 MeO-BDE-47	1.072	0.0184
5' OH-BDE-47	1.078	0.0064	2' MeO-BDE-66	1.073	0.0184
4' OH-BDE-49	1.080	0.0064	5' MeO-BDE-47	1.077	0.0184
2'-OH-BDE 74	**1.081**	**0.0065**	**6' MeO-BDE-66**	**1.079**	**0.0169**
6' OH-BDE 66	**1.089**	**0.0068**	4' MeO-BDE-49	1.079	0.0184
4' OH-BDE-121	1.109	0.0062	4' MeO-BDE-121	1.118	0.0059
4 OH-BDE-42	1.111	0.0064	4 MeO-BDE-42	1.121	0.0184
6 OH-BDE-90	1.122	0.0062	6 MeO-BDE-90	1.136	0.0059
6 OH-BDE-99	1.125	0.0062	6 MeO-BDE-99	1.140	0.0059
4 OH-BDE-90	1.150	0.0062	4 MeO-BDE-90	1.173	0.0059
2 OH-BDE-123	1.156	0.0062	2 MeO-BDE-123	1.181	0.0059
6 OH-BDE-85	1.167	0.0062	6 MeO-BDE-85	1.197	0.0059

Levels and patterns of PBDEs, OH-BDEs and MeO-BDEs in biota. Relatively high levels of MeO Tetra BDEs were observed in beluga whales from the eastern Canadian Arctic, e.g., 6 MeO- BDE-47 levels approx. 200 ng·g^{-1}lw (Figure 1). MeO-BDE levels were equivalent or greater than parent PBDE congeners. OH-BDEs were detected at low concentrations (i.e., ~ 0.01 ng·g^{-1} lw) in beluga whale blubber. OH- BDEs were only detected in marine mammals (beluga whales and ringed seals). MeO-BDEs were detected in fish, seaducks and marine mammals, but were not found in ambient samples of sediments, lichens and macro-algae. Relative contribution of Tetra methoxyBDEs (e.g., 6 MeO-BDE-47) increased while BDE-47 amounts diminished with trophic position of the Arctic food web (Figure 2).

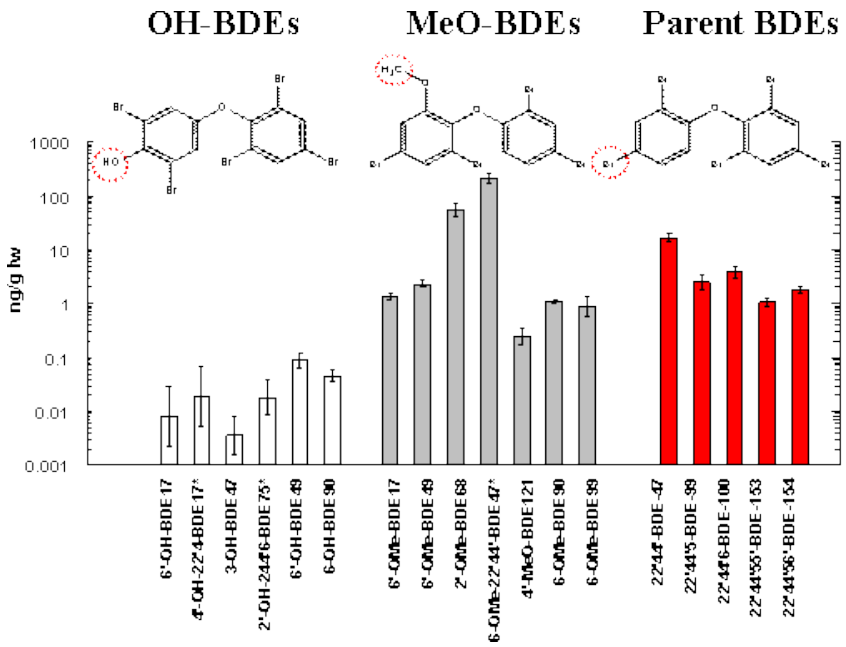
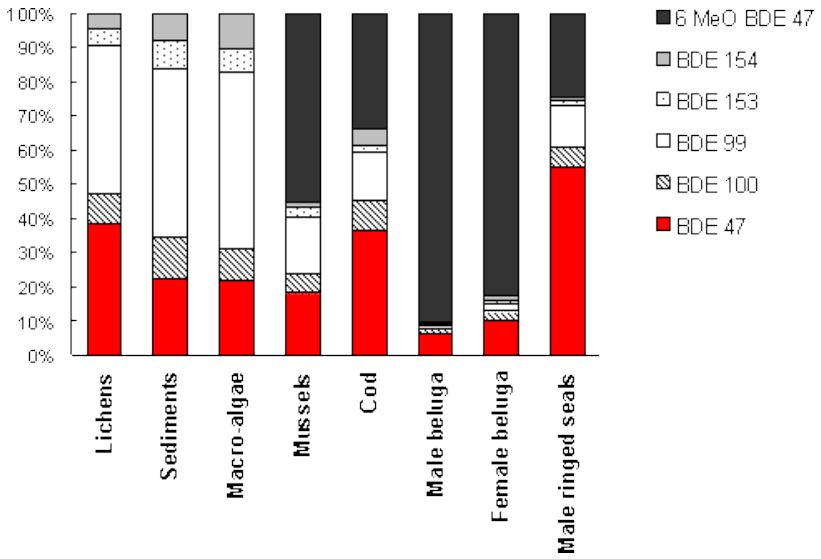


Figure 1. Concentrations (ng·g^{-1} lw) of OH-BDEs, MeO-BDEs and parent BDE congeners in E. Hudson Bay beluga whales. Error bars represent 1 SD of the arithmetic mean.

Figure 2. Relative patterns



(% contribution) for several BDE congeners and 6 MeO-BDE-47 in E. Hudson Bay sediment and biota samples.

Biomagnification potential and Sources of OH- and MeO-BDEs. Figure 3 shows concentrations of BDE 47 and 6 MeO-BDE-47 in selected organisms of the E. Hudson Bay marine food web. 6 MeO- BDE-47 (ng·g^{-1}lw) increased with each step-wise increase in trophic position, exhibiting similar biomagnification potential as recalcitrant PCBs (e.g., PCB 153). Other MeO- Tetra BDEs (e.g., 6' MeO-BDE-49 and 6 MeO-BDE-99) demonstrated similarly high biomagnification potential. Conversely, BDE-47 appears toexhibit similar concentrations across trophic positions, indicating potential biotransformation and trophic dilution of BDE-47. Other prevalent PBDE congeners such as BDE-99, 100 and 153 also exhibited no biomagnification in the food web. Previous studies of OH- and MeO-BDEs in fish and wildlife have suggested sources of dominant hydroxy and methoxy BDEs (e.g., 6 MeO-BDE-47) are biogenic organohalogens, originating from marine sponges and/or cyanobacteria.[3,4,5] However, the fact we observed (i) no biomagnfication of parent PBDEs and (ii) no measurable quantities of OH- or MeO-BDEs in ambient environmental samples (i.e., sediments and macro-algae) suggests that the detected OH- and MeO-BDEs are *in vivo* biotransformation products of PBDEs.

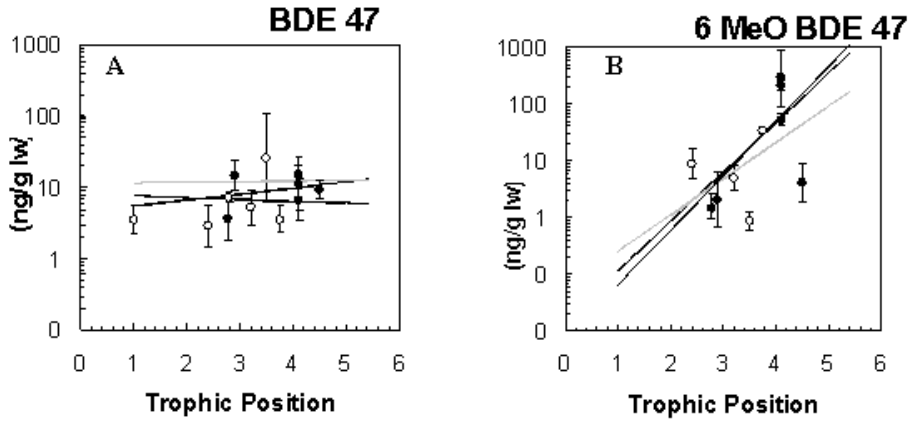


Figure 3. Plots of concentrations (ng g^{-1}lw) versus trophic position (TP) for (A) BDE-47 and (B) 6 MeO-BDE-47 in the E. Hudson Bay marine food web.

Acknowledgements

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