Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in a Canadian Arctic Marine Food Web

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Residues of hydroxylated (OH-) and methoxylated (MeO-) polybrominated diphenyl ethers (PBDEs) have been previously detected in precipitation, surface waters, wildlife, and humans. We report measured concentrations of OH-PBDEs, MeO-PBDEs, and Br_3−Br_7 PBDEs in sediments and biota from a Canadian Arctic marine food web. PBDEs exhibited very low trophic magnification factors (TMFs between 0.1−1.6), compared to recalcitrant PCBs (TMFs between 3 and 11), indicating biotransformation via debromination and/or cytochrome P450 mediated metabolism. OH-PBDEs were not detectable in samples of blood, muscle, and/or liver of fish and marine wildlife. Five OH-PBDEs were detected at very low concentrations (range: 0.01−0.1 ng·g^{-1} lipid equivalent) in beluga whale blubber and milk. The data indicate negligible formation/retention of OH-PBDEs in these Arctic marine organisms. Appreciable levels of several MeO-PBDEs were observed in bivalves, Arctic cod, sculpin, seaducks, and beluga whales (mean range 0.1−130 ng·g^{-1} lipid equivalent). 2′-MeO-BDE-68 and 6-MeO-BDE-47 exhibited the highest concentrations among the brominated compounds studied (including BDE-47 and BDE-99) and biomagnified slightly in the food web, with TMFs of 2.3 and 2.6, respectively. OH- and MeO-PBDEs in this Arctic marine food web may occur via metabolic transformation of PBDEs or bioaccumulation of PBDE degradation products and/or natural marine products. We observed no evidence of a local natural source of OH- or MeO-PBDEs, as no measurable quantities of those compounds were observed in ambient environmental media (i.e., sediments) or macroalgae. Further investigations of PBDEs and their hydroxylated and methoxylated analogues would be useful to better understand sources, fate, and mechanisms governing biotransformation and bioaccumulation behavior of these compounds.

Introduction

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants used in a variety of consumer products, including polyurethane foams, textiles, furniture, appliances, and computers. The occurrence of structural analogues to PBDEs, namely hydroxylated (OH-) and methoxylated (MeO-) PBDEs, have been recently investigated in field studies (*1*−*9*) and controlled animal exposure experiments (*10*−*16*) (Table S1, Supporting Information). Analyses of field collected samples have shown the presence of several OH- and/or MeO-PBDEs in abiotic media such as surface water and rainfall and snow (*3*) as well as blood/tissues of fish (*1, 4, 5*), birds (*2, 5, 6*), and marine mammals (*2, 7*). OH- and MeO-PBDEs have also been detected in human plasma and breast milk (*8, 9*).

Laboratory studies tracking PBDE metabolism (mainly BDE-47, -99, and -209) in exposed rats have shown the formation of several OH-PBDEs in tissues and/or feces (*10*−*16*). Similar to cytochrome P450 mediated metabolism of PCBs to OH-PCBs, OH-PBDE metabolites are retained in organisms mainly via protein binding as a protective mechanism against phase II conjugation (*17*). One study in fish demonstrated retention of OH-PBDEs in pike (*Esox lucius*) following exposure to BDE-47 (*13*). Nine OH-PBDEs have been structurally identified (by comparison with authentic reference standards) as probable PBDE metabolites. These include the following: 4′-OH-BDE-17, 2′-OH-BDE-28, 3′-OH-BDE-28, 4-OH-BDE-42, 6-OH-BDE-47, 3-OH-BDE-47, 5-OH-BDE-47, 4′-OH-BDE-49, and 2′-OH-BDE-66. Additionally, several other OH-PBDEs have been detected (but not structurally identified) *in vivo*. For example, Malmberg et al. (*10*) observed 16 Br_4−Br_7 OH-PBDEs in rats following an equimolar dose of BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209. Further, the authors estimate a total of 43 OH-PBDEs could be formed via metabolism of major PBDEs present in PentBDE mixtures (BDE-47, -99, -100, -153, -154, and -183), assuming the possibility of both direct hydroxylation and formation involving a 1,2 bromine shift (*18*). Morck et al. (*12*) observed three Br_7 OH-PBDEs in rats following exposure to BDE-209. This latter study also reported the formation of hydroxy-methoxy PBDEs (i.e., guaiacol structure) in rats following exposure to PBDE-209. In terms of biological effects, the bioformation and retention of OH-PBDEs is of particular concern as those compounds are structurally similar to the thyroid hormone thyroxin (T4) and can effectively bind to thyroxin-transporting proteins (transthyretin or TTR), thereby altering thyroid hormone homeostasis (*19, 20*).

OH-PBDEs can also occur from sources other than *in vivo* PBDE biotransformation. Ueno et al. (*3*) recently reported Br_2 to Br_6 OH-PBDEs in abiotic media from the Great Lakes region were likely byproducts of atmospheric OH radical reactions with aerial PBDE concentrations and/or the result of sewage treatment plant effluents. Also, several ortho OH substituted OH-PBDEs have been identified as naturally produced organohalogens, generated by marine organisms such as sponges, tunicates, or algae (*21*−*23*) (Table S1). These include nine OH-PBDEs (6′-OH-BDE-17, 2′-OH-BDE-28, 6-OH-BDE-47, 2′-OH-BDE-68, 6-OH-BDE-85, 6-OH-BDE-90, 6-OH-BDE-99, 2-OH-BDE-123, and 6-OH-BDE-137).

Like OH-PBDEs, ortho MeO substituted MeO-PBDEs have previously been identified as marine natural products (*24, 25*) (Table S1). Previous studies have attributed the occurrence of methoxylated PBDE residues in wildlife and humans to accumulation of natural products rather than PBDE metabolism (*1, 5, 26*−*28*). To our knowledge, MeO-PBDEs have never been observed as metabolites following exposure to PBDE flame retardants in animal studies. 2′-MeO-BDE-68,

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which is frequently detected in wildlife, is likely of natural origin, due to the lack of a major PBDE precursor. 2′-MeO-BDE-68 and 6-MeO-BDE-47 were detected in pike from Swedish waters, and no relationship was found between temporal trends of PBDEs and MeO-PBDEs (*27*), indicating the source of the MeO-PBDEs was of natural origin. Radiocarbon measurements ($\Delta^{14}C$) of 6-MeO-BDE-47 and 2′-MeO-BDE 68 extracted from blubber of a True's beaked whale from the North Atlantic positively revealed that those compounds were of natural origin (*28*). Malmvarn et al. (*23*) identified four MeO-PBDEs (2′-MeO-BDE-68, 6-MeO-BDE-47, 6-MeO-BDE-85, and 6-MeO-BDE-137) as likely naturally produced by red algae or its associated microflora/microfauna. However, it has been suggested that MeO-PBDEs could occur by methylation of OH-PBDEs and/or PBDEs by intestinal microflora or via microbial methylation in sediments (*7*). In particular, meta and para MeO substituted MeO-PBDEs may be the result of *in vivo* methylation of those OH-PBDEs as a protective mechanism against toxicity (*2*). Thus, residue concentrations of OH-PBDEs and perhaps MeO-PBDEs in the environment and organisms may originate from marine natural products or PBDE flame retardants. The presence of multiple sources of OH- and MeO-PBDEs adds an additional layer of complexity in tracking the fate and bioaccumulation of PBDE flame retardants.

The objective of this study was to evaluate the occurrence and bioaccumulation of OH- and MeO-PBDEs in a Canadian Arctic marine food web. To assess potential sources and bioaccumulation behavior of those compounds, we compared concentrations and patterns of several OH- and MeO-PBDEs with PBDE congeners in various compartments of the food web, including bottom sediments, macroaglae, bivalves, fish, seaducks, and marine mammals. We further used combined analyses of PCBs and organochlorine pesticides (OCPs) to study the bioaccumulation of PBDEs, OH-PBDEs, and MeO-PBDEs in relation to those well characterized bioaccumulative substances. The study provides chemical concentrations as a function of trophic level (TL) and contains information on contaminant burdens in Arctic wildlife species utilized for subsistence by indigenous Inuit peoples of northern Canada.

Materials and Methods

Samples. During the months of May to September between 1999 and 2003 marine sediment and biota samples were collected from the Hudson Bay region of northeastern Canada (64° 15′N 113° 07′ W) (Figure S1): bottom sediments (using petit ponar grab at between 25−80 m depths) and biota including macroalgae (*Fucus gardneri*), bivavles (*Mytilis edulis*), Arctic cod (*Boreogadus saida*), sculpin (*Myoxocephalus scorpioides*), salmon (*Salmo sp.*), and beluga whales (*Delphinapterus leucas*). Samples of ringed seal (*Pusa hispida*) blubber and livers of seaducks, including common eider ducks (*Somateria mollissima sedentaria*) and white-winged scoters (*Melanitta fusca*), collected from Hudson Strait (Quaqtaq, Salluit), were provided by DCG Muir (Environment Canada's, National Water Research Institute, NWRI, Burlington, ON) and M. Kwan (Nunavik Research Centre, NvRC, Kuujuaq, Quebec), respectively. Details regarding sample collection and storage for these sediment and biota samples are reported elsewhere (*29, 30*). Sample sizes are given in Table 1.

Extraction and Cleanup. Contaminant analyses were conducted at the Institute of Ocean Sciences (IOS), Fisheries and Oceans Canada (DFO), Sidney, BC. Details on procedures for the simultaneous extraction, cleanup, and analysis of PBDEs, OH-PBDEs, and MeO-PBDEs using gas chromatography/high resolution mass spectrometry (GC-HRMS) are documented by Lacorte et al. (*31*). Compiled physical-chemical properties, including molecular weights (MW), octanol−water partition coefficients (K_{OW}s), and octanol-air partition coefficients (K_{OA}s) for PBDEs, OH-PBDEs, and MeO-PBDEs are shown in the Supporting Information. Briefly, samples (approximately 10 g wet wt for macroalgae and sediment, 5−15 g for fish, 2 g for liver, and 1 g for blubber (beluga whales and ringed seals)) were homogenized with hydromatrix using mortar and pestle. The homogenate powder was spiked with a ^{13}C-labeled procedural internal standard mixture (Cambridge Isotope Laboratories, Andover, MA), consisting of ∼2000−5000 pg of each ^{13}C PBDEs (^{13}C BDE-3, -15, -28, -47, -77, -118, -99, -100, -153, and -183), and extracted using pressurized liquid extraction (PLE) with an accelerated solvent extraction (ASE) apparatus, ASE 200 (DIONEX, U.S.A.), using *n*-hexanes:CH_2Cl_2 (2:1 v/v). All samples were cleaned up using Florisil chromatography. For samples with high lipid content (blubber, milk), bulk lipids were removed prior to Florisil cleanup by gel permeation chromatography (GPC) column-consisting of 70 g BioBeads S-X3 (BioRad) in 1:1 CH_2Cl_2:hexane (v/v). The lipid fraction from the GPC (180 mL) was collected and discarded, while the remaining 300 mL of eluent was collected, evaporated to near dryness, and solvent exchanged into hexane. The Florisil column consisted of a 30 cm glass column which was wet-packed with 8 g of 1.2% deactivated Florisil in hexane. Compounds were eluted with 60 mL of 1:1 CH_2Cl_2:hexane (v/v) and 20 mL of CH_2Cl_2. Lipid contents were determined gravimetrically from a parallel PLE extraction.

Extracts were evaporated to ∼0.5 mL and transferred with toluene into centrifuge tubes for the purpose of derivatization (i.e., acetylation) of OH-PBDEs. The transferred samples were dissolved in 500 μL of toluene, and then 100 μL of pyridine and acetic anhydride were added to the sample. The sample was vortexed for 2 min and heated at 60 °C for 30 min. After derivatization, 700 μL of 2× toluene washed water was added to pull out the reaction byproduct and leftover reagents. The sample was vortexed and back extracted into another centrifuge tube using 3 hexane washes. The extracted sample was passed through a Pasteur pipet filled with hydromatrix to remove remaining water. The sample was then nitrogen evaporated to 100 μL, transferred to a microvial, nitrogen evaporated to near dryness, and reconstituted in CH_2Cl_2. At this stage, 100 μL of IS BDE-77 was added giving a total amount of 1200 pg.

Quantification. Analyses of OH- and MeO-PBDEs were performed by GC-HRMS using a VG-AutoSpec-S (Micromass, Manchester, U.K.) equipped with a Hewlett-Packard model 5890 series II gas chromatogram (Agilent, Palo Alto, CA, U.S.A.) and a CTC A200S autosampler (CTC Analytics, Zurich, Switzerland). The MS was operated under positive electron ionization conditions with the filament in the trap stabilization mode at 600 μA, an electron energy of 35 eV, and perfluorokerosene as calibrant. The instrument was operated at a resolving power of 10,000, and data were acquired in the selected ion monitoring mode (SIM). The GC was operated in the splitless injection mode using 1 μL injection volumes. OH- and MeO-PBDEs were separated using a 15 m DB-5 column (0.25 mm i.d. × 0.1 μm film thickness from J&W Scientific (Folsom, CA). Following Marsh et al. (*1*), a 30 m SP2331 polar column (0.25 mm i.d. × 0.2 μm film thickness from Supelco, Bellefonte, U.S.A.) was used in a separate GC run for confirmation purposes. GC conditions for both GC columns were identical to those reported by Marsh et al. (*1*).

OH- and MeO-PBDEs were identified by comparing analyte retention times to those of authentic standards, under identical GC conditions. The calibration standards used in the present study contained 11 previously synthesized OH- and MeO-PBDEs and included 2′-MeO-2,4,4′-BDE-28 (2′-MeO-BDE-28), 4′-MeO-2,2′,4-BDE-17 (4′-MeO-BDE-17), 4′-OH-2,2′,4-BDE-17 (4′-OH-BDE-17), 2′-MeO-2,4,4′,6-BDE-75 (2′-MeO-BDE-75), 6-MeO-2,2′,4,4′-BDE-47 (6-MeO-BDE-47),

TABLE 1. Concentrations of Hydroxylated (OH-) and Methoxylated (MeO-) PBDEs in Marine Sediments (ng·g^{-1} dry wt) and Biota (ng·g^{-1} lipid equivalent wt) Collected from E. Hudson Bay and Hudson Strait between 1999 and 2003 and Concentrations of Total PBDEs (ΣPBDE), PCBs (ΣPCBs), and Organochlorine Pesticides (ΣDDTs, ΣHCHs, ΣCBz, and ΣCyclodienes)[a,b,c]

	sediment	macro-algae (*F. gardneri*)	bivalves (*M. edulis*)	cod (*B. saida*)	sculpin (*M. scorpioides*)	salmon (*Salmo sp.*)	eider ducks (*S. mollissima sedentaria*)	white winged scoters (*M. fusca*)	male ringed seals (*P.hispida*)
tissue/matrix	–	–	muscle	muscle	muscle	muscle	liver	liver	blubber
age (years)[d]	–	–	–	–	–	–	–	–	–
OH- and MeO-PBDE analyses	(*n* = 6)	(*n* = 6)	(*n* = 6)	(*n* = 5)	(*n* = 4)	(*n* = 3)	(*n* = 6)	(*n* = 5)	(*n* = 9)
PBDE, organochlorine analyses	(*n* = 12)	(*n* = 11)	(*n* = 12)	(*n* = 12)	(*n* = 12)	(*n* = 7)	(*n* = 6)	(*n* = 5)	(*n* = 11)
% OC ± SD	0.18 ± 0.1	–	–	–	–	–	–	–	–
% lipid equivalent (L_{Eq}) ± SD	–	1.6 ± 0.2	1.8 ± 0.12	1.1 ± 0.05	1.2 ± 0.16	5.4 ± 0.3	3.5 ± 0.8	5.7 ± 1.3	71.2 ± 2.8
PBDEs, OH-, and MeO-PBDEs									
ΣPBDEs	0.1 (*0.01–1.6*)	324 (*34–3,100*)	5.4 (*0.86–33*)	9.8 (*2.6–36*)	73 (*6.4–820*)	9.3 (*3.0–28*)	20 (*4.9–78*)	71 (*29–177*)	11 (*1.5–73*)
5-OH-BDE-47	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]
6′-OH-BDE-49	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]
2′-OH-BDE-68	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]
2′-OH-BDE-75	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]
6-OH-BDE-90	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]
ΣOH-PBDE	–	–	–	–	–	–	–	–	–
ΣOH-PBDE/ΣPBDE	–	–	–	–	–	–	–	–	–
6-MeO-BDE-17	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]
2′-MeO-BDE-28	ND[e]	ND[e]	0.17 (*0.05–0.5*)	ND[e]	ND[e]	0.17 (*0.07–0.4*)	ND[e]	ND[e]	0.03 (*0.006–0.2*)
4-MeO-BDE-42	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	0.02 (*0.007–0.07*)
5-MeO-BDE-47	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	0.01 (*0.002–0.1*)
6-MeO-BDE-47	ND[e]	ND[e]	8.8 (*2.3–34*)	4.9 (*1.5–16*)	1.4 (*0.4–5.1*)	34 (*9.8–120*)	0.86 (*0.19–3.9*)	2.0 (*0.34–12*)	4.5 (*1–19*)
6′-MeO-BDE-49	ND[e]	ND[e]	0.42 (*0.1–1.4*)	ND[e]	ND[e]	0.5 (*0.1–1.8*)	ND[e]	0.11 (*0.04–0.3*)	0.05 (*0.01–0.2*)
6′-MeO-BDE-66	ND[e]	ND[e]	0.26 (*0.1–0.5*)	0.22 (*0.09–0.5*)	ND[e]	0.36 (*0.09–1.5*)	ND[e]	ND[e]	ND[e]
2′-MeO-BDE-68	ND[e]	ND[e]	2.8 (*0.8–10*)	2.3 (*0.7–7*)	0.63 (*0.3–1.4*)	6.1 (*1.7–23*)	0.29 (*0.05–1.6*)	0.22 (*0.09–0.55*)	1.8 (*0.5–6.1*)
6-MeO-BDE-90	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	0.27 (*0.06–1.3*)	ND[e]	0.013 (*0.003–0.06*)
6-MeO-BDE-99	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	ND[e]	0.012 (*0.002–0.06*)
ΣMeO-PBDE	–	–	14 (*3.4–54*)	9.9 (*3.3–30*)	3.0 (*0.7–12*)	42 (*12–150*)	1.3 (*0.3–5.1*	2.1 (*0.34–13*)	6.7 (*1.7–26*)
ΣMeO-PBDE/ΣPBDE	–	–	1.3 (*0.3–6*)	0.6 (*0.2–2.6*)	0.02 (*0.003–0.2*)	5.2 (*2–13*)	0.07 (*0.02–0.29*)	0.02 (*0.003–0.12*)	0.64 (*0.2–1.8*)
organochlorines									
ΣPCBs	0.08 (*0.01–0.57*)	6 (*1–37*)	15 (*3.3–67*)	60 (*19–190*)	46 (*13–158*)	129 (*32–508*)	287 (*78–1,056*)	2,500 (*440–14,100*)	602 (*252 –1,440*)
ΣDDTs	0.006 (*0.01–0.04*)	0.7 (*0.1–5*)	1.1 (*0.5–2.7*)	50 (*12 –206*)	17 (*2.5–113*)	74 (*24–223*)	179 (*45–708*)	565 (*116–2,750*)	413 (*174 –981*)
ΣHCHs	0.02 (*0.005–0.05*)	19 (*5.5–69*)	6.1 (*2.4–16*)	10 (*1.5–65*)	13 (*2.0–85*)	19 (*5.9–58*)	15 (*3.8–56*)	8.6 (*3.1–24*)	145 (*24–864*)
ΣCBz	0.2 (*0.05–0.6*)	4.7 (*1.3–17*)	7.1 (*3–18*)	27 (*11–68*)	23 (*8.5–61*)	39 (*13 –117*)	48 (*9.0–252*)	71 (*27–183*)	78 (*17- 354*)
ΣCyclodienes	0.01 (*0.002–0.06*)	0.9 (*0.18–5.5*)	4.5 (*1.9–11*)	33 (*11 –103*)	34 (*7.6–155*)	51 (*13 –193*)	192 (*69–536*)	119 (*51–273*)	157 (*41 –606*)

	beluga whales (*D. leucas*)						
	calves	females			males		
tissue/matrix	blubber	whole blood	milk	blubber	whole blood	liver	blubber
age (years)	<1 year	5–35	5–35	5–35	16–35	16–35	16–35
OH- and MeO-PBDE analyses	(*n* = 5)	(*n* = 7)	(*n* = 6)	(*n* = 6)	(*n* = 6)	(*n* = 14)	(*n* = 6)
PBDE, organochlorine analyses	(*n* = 9)	(*n* = 7)	(*n* = 8)	(*n* = 14)	(*n* = 7)	(*n* = 17)	(*n* = 21)
% OC ± SD	–	–	–	–	–	–	–
% lipid equivalent (L_{Eq}) ± SD	89 ± 1.6	1.5 ± 0.1	38.1 ± 8.5	89.7 ± 0.2	1.6 ± 0.1	3.2 ± 0.3	89.4 ± 0.5
PBDEs, OH- and MeO-PBDEs							
ΣPBDEs	27 (*5.5–130*)	3.9 (*0.7–24*)	9.6 (*3.1–30*)	16 (*4.4–59*)	6.8 (*1–43*)	18 (*5.7–58*)	34 (*13–96*)
5-OH-BDE-47	ND[e]	ND[e]	ND[e]	0.02 (*0.01–0.04*)	ND[e]	ND[e]	0.01 (*0.003–0.05*)
6′-OH-BDE-49	0.11 (*0.02–0.5*)	ND[e]	0.023 (*0.01–0.08*)	0.02 (*0.01–0.06*)	ND[e]	ND[e]	0.09 (*0.03–0.28*)
2′-OH-BDE-68	0.12 (*0.03–0.5*)	ND[e]	0.020 (*0.01–0.08*)	0.02 (*0.01–0.05*)	ND[e]	ND[e]	0.04 (*0.01–0.2*)
2′-OH-BDE-75	ND[e]	ND[e]	0.01 (*0.002–0.04*)	ND[e]	ND[e]	ND[e]	0.01 (*0.002–0.02*)

TABLE 1. Continued

	beluga whales (*D. leucas*)						
	calves	females			males		
6-OH-BDE-90	ND[e]	ND[e]	ND[e]	0.02 (*0.01–0.04*)	ND[e]	ND[e]	0.02 (*0.01–0.07*)
ΣOH-PBDE	0.23 (*0.05–1*)	–	0.05 (*0.02–0.2*)	0.06 (*0.02–0.1*)	–	–	0.1 (*0.1–0.6*)
ΣOH-PBDE/ΣPBDE	0.01 (*0.002–0.02*)	–	0.003 (*0.001–0.012*)	0.01 (*0.002–0.02*)	–	–	0.004 (*0.001–0.01*)
6-MeO-BDE-17	ND[e]	0.20 (*0.08–0.5*)	ND[e]	ND[e]	0.31 (*0.08–1*)	0.29 (*0.06–1.5*)	0.16 (*0.07–0.3*)
2′-MeO-BDE-28	0.32 (*0.1–1*)	0.15 (*0.08–0.3*)	0.25 (*0.09–0.7*)	0.28 (*0.1–0.6*)	ND[e]	0.48 (*0.1–2.3*)	0.27 (*0.09–0.78*)
4-MeO-BDE-42	0.12 (*0.04–0.4*)	ND[e]	ND[e]	0.16 (*0.06–0.4*)	ND[e]	ND[e]	0.27 (*0.09–0.8*)
5-MeO-BDE-47	0.15 (*0.05–0.5*)	ND[e]	0.07 (*0.02–0.2*)	0.06 (*0.02–0.3*)	ND[e]	ND[e]	0.1 (*0.03–0.3*)
6-MeO-BDE-47	250 (*44–1,400*)	8.7 (*2.4–31*)	50 (*16–150*)	48 (*20–120*)	25 (*3.8–160*)	250 (*42–1,500*)	240 (*72–800*)
6′-MeO-BDE-49	2.8 (*0.5–17*)	ND[e]	0.53 (*0.2–1.6*)	0.58 (*0.2–1.5*)	0.52 (*0.06–4.3*)	2.9 (*0.6–15*)	2.9 (*0.9–9.8*)
6′-MeO-BDE-66	0.26 (*0.08–0.9*)	ND[e]	0.12 (*0.04–0.4*)	0.10 (*0.04–0.2*)	0.17 (*0.08–0.4*)	0.37 (*0.1–1.2*)	0.18 (*0.07–0.5*)
2′-MeO-BDE-68	53 (*9.7–280*)	2.4 (*0.8–6.7*)	12 (*3.7–38*)	12 (*4.8–31*)	4.8 *0.8–30*)	52 (*9.5 280*)	58 (*18–180*)
6-MeO-BDE-90	0.74 (*0.06–9.7*)	ND[e]	0.13 (*0.03–0.5*)	0.14 (*0.05–0.4*)	ND[e]	0.39 (*0.1–1*)	1.6 (*0.5–5.8*)
6-MeO-BDE-99	0.65 (*0.05–9.4*)	ND[e]	0.07 (*0.02–0.2*)	0.14 (*0.05–0.4*)	ND[e]	0.29 (*0.1–0.9*)	1.1 (*0.3–4.6*)
ΣMeO-PBDE	310 (*54–1,700*)	10 (*2.6–41*)	63 (*20–190*)	62 (*26–150*)	31 (*4.7–200*)	310 (*52–1,800*)	300 (*93–980*)
ΣMeO-PBDE/ΣPBDE	7.6 (*2.6–22*)	4.1 (*0.8–20*)	6.6 (*2.7–16*)	6.4 (*2.5–16*)	5.9 (*1.9–19*)	17 (*2.7–104*)	7.6 (*2.8–21*)
organochlorines							
ΣPCBs	670 (*105 –4,280*)	175 (*16 –1,870*	278 (*80–972*)	661 (*134–3,260*)	2,280 (*1,100–4,890*)	1570 (*330–7,400*)	3,690 (*1,250–10,900*)
ΣDDTs	1,030 (*138 –7,730*)	60 (*14–257*)	274 (*72 –1,040*)	520 (*120 –2,250*)	464 (*118–1,830*)	985 (*203–4,780*)	2,521 (*695–9,150*)
ΣHCHs	307 (*79 –1,200*)	19 (*5.9–64*)	103 (*33–322*)	95 (*33 –272*)	35 (*4.6–268*)	112 (*41–310*)	119 (*32–440*)
ΣCBz	487 (*90 –2,630*)	67 (*16 –277*)	138 (*48 –395*)	112 (*30–414*	285 (*723 –1,120*)	411 (*143–1,180*)	377 (*149–957*)
ΣCyclodienes	510 (*143 –1,820*)	36 (*6.8–191*)	316 (*96 –1,040*)	497 (*133 –1,860*	206 (*42–1,010*)	618 (*51–7,480*)	473 (*48–4,690*)

[a] Organic carbon content (% OC) and lipid equivalent content (% L_{Eq}) are arithmetic means ± standard deviation. [b] Chemical concentration data are geometric means, along with 95% confidence intervals (CI) in brackets. Concentration means were calculated only if the frequency of detection was ≥60% [c] MDLs in sediments ranged between 0.001–0.004 ng·g^{-1} dry wt. For biota samples, ranges of those MDLs (in units of ng·g^{-1} lipid equivalent) were as follows: macroalgae (0.06–0.2), bivalves (0.05–0.3), cod (0.09–0.5), sculpin (0.08–0.4), salmon (0.02–0.09), eider duck liver (0.03–0.1), white winged scoter liver (0.02–0.09), ringed seal blubber (0.001–0.007), beluga blubber (0.001–0.005), beluga liver (0.03–0.1), beluga milk (0.003–0.01), and beluga blood (0.3–1.3). [d] E. Hudson Bay beluga whale age determined by analysis of extracted tooth sample. [e] ND = nondetectable concentration.

2′-MeO-2,4,4′,5-BDE-74 (2′-MeO-BDE-74), 6′-MeO-2,3′,4,4′-BDE-66 (6′-MeO-BDE-66), 2′-OH-2,4,4,6-BDE-75 (2′-OH-BDE-75), 6-OH-2,2′,4,4′-BDE-47 (6-OH-BDE-47), 2′-OH-2,4,4′,5-BDE-74 (2′ OH-BDE-74), and 6′-OH-2,3′,4,4′-BDE-66 (6′-OH-BDE-66) (*9, 31*). Additional OH- and MeO-PBDEs, which are not currently present in our calibration standards, were included in our analyses using relative retention times (RRTs) previously reported by Marsh et al. (*18*). Because we used identical GC columns and conditions as Marsh et al. (*18*), we were able to use linear regression analysis to establish RRTs of those additional OH- and MeO-PBDEs. See Table S2 for a complete compound list and corresponding RRTs (relative to BDE-47). Quantification and corresponding confirmation ions monitored for OH- and MeO-PBDEs included m/z and 437.8113 and 435.8133 for MeO-Br_3-PBDEs; m/z 423.7956 and 421.7976 for OH-Br_3-PBDEs; m/z 515.7217 and 513.7237 for MeO-Br_4-PBDEs; m/z 503.7041 and 501.7061 for OH-Br_4-PBDEs; m/z 595.6303 and 593.6323 for MeO-Br_5-PBDEs; and m/z 581.6146 and 579.6166 for OH-Br_5-PBDEs. Quantification of OH- and MeO-PBDEs was performed using the isotope dilution method using ^{13}C BDE-47 and ^{13}C BDE-100 to quantify individual Br_3 to Br_4 OH- and MeO-PBDEs and ^{13}C BDE-153 to quantify Br_5 OH- and MeO-PBDEs.

Recoveries of individual internal standards were between 40% and 120% for all analyses. The instrument detection limit (IDL) was calculated as a mean of the noise plus three times the standard deviation. Method blanks, consisting of hydromatrix, were extracted according to the same procedure as samples and analyzed with every batch of 12 samples. Because OH- and MeO-PBDEs were not detected in procedural blanks, method detection limits (MDLs) were set to the IDL. MDLs of individual OH- and MeO-PBDEs in the various samples ranged from 0.001−0.02 ng·g^{-1} wet wt. The frequency of detection (%) in OH- and MeO-PBDEs for the various matrices are summarized in Table S3.

Data Analysis. Concentrations of PCBs, organochlorine pesticides, and PBDEs in this food web have been reported elsewhere (*29, 30*). Following those previous analyses, measured concentrations of OH- and MeO-PBDEs in sediments were expressed on a dry weight (ng·g^{-1} dry wt) as well as organic carbon corrected basis (ng·g^{-1} OC wt), while concentrations in biota were normalized to a common unit, i.e. ng·g^{-1} lipid equivalent. Concentration data are reported as geometric means (GM), with asymmetric errors calculated as 1 standard deviation (SD) and 95% confidence intervals (CI). Linear regression was used to assess correlation of concentrations of individual compounds (e.g., BDE-47 vs 6 MeO-BDE-47). One-way Analysis of Variance (ANOVA) tests were used to assess concentration differences between different tissues/organs.

Log-linear regression between the base-10 logarithm ($\log_{10}$) of the lipid equivalent concentration in biota (C_B) and TL were used to assess trophic magnification

$$\text{Log } C_B = (m \times \text{TL}) + b \quad (1)$$

where m and b are the empirical slope and y-intercept, respectively. Trophic magnification factors (TMFs), which are markers of cumulative bioaccumulation across the food web, were calculated as the antilog of the slope (m) (i.e., TMF $=10^m$).

We used δ^{15}N measurements to calculate TL of the various organisms in the food web (*30*). Stable nitrogen isotope (δ^{15}N) analysis is a well established technique for assessing predator−prey interactions and organism TL of complex food webs (*32*). Previous studies have used δ^{15}N measurements to assess trophodynamics and predator−prey interactions of Arctic marine biota (*33*−*35*). Observed δ^{15}N values and TL estimates for E. Hudson Bay biota are comparable to previous reports in Canadian Arctic marine biota (*33*−*35*). The selected species (macroalgae, bivalves, fish, seaducks, ringed seals, and beluga whales) exhibit a wide range of δ^{15}N values (6.1 to 21.1 ‰), representing a TL range of approximately 1 to 5 (*30, 33*−*35*). It is important to note that selection of different tissues/compartments between predator and prey organisms, which occurs in some cases (e.g., bivalve muscle versus seaduck liver; fish muscle versus beluga liver, blood, milk, and blubber), may affect the degree of observed biomagnification. We believe that the tissues/species chosen as part of the present study adequately represent dietary exposure and tissue residue burdens of hydrophobic organic contaminants for the animals studied. Furthermore, the observed amplification of lipid equivalent corrected PCB concentrations in this food web (*29*) implies that the tissues/species selected is sufficient to detect the biomagnification of hydrophobic organic contaminants.

Results and Discussion

Concentrations of OH-PBDEs and MeO-PBDEs in the Arctic Marine Food Web. Measured concentrations of OH-PBDEs and MeO-PBDEs in samples of marine sediments, macroalgae, bivalves, fish, seaduck liver, beluga whales, and ringed seals are shown in Table 1. Concentrations of ΣPBDE (*30*) and various organochlorines (*29*) previously measured in those samples are shown for comparison.

Of the 23 OH-PBDEs monitored, we observed five compounds (5-OH-BDE-47, 6′- OH-BDE-49, 2′-OH-BDE-68, 2′-OH-BDE-75, and 6-OH-BDE-90) at low concentrations (range: 0.01−0.2 ng·g^{-1} lipid) in beluga blubber and milk samples. Of the 23 MeO-PBDEs, 10 compounds (6′-MeO-BDE-17, 2′-MeO-BDE-28, 4-MeO-BDE-42, 5-MeO-BDE-47, 6-MeO-BDE-47, 6′-MeO-BDE-49, 6′- MeO-BDE-66, 2′-MeO-BDE-68, 6-MeO-BDE-90, and 6-MeO-BDE-99) were observed. Four of the MeO-PBDEs were only observed in ringed seal (blubber) and beluga (blubber and milk) samples (6′-MeO-BDE-17, 4-MeO-BDE-42, 5-MeO-BDE-47, and 6-MeO-BDE-99). MeO-PBDEs were detected in various tissues, including blood, liver, blubber, and milk of beluga whales. In some cases, concentrations of MeO-PBDEs varied between different tissues/compartments. For example, lipid equivalent corrected concentrations of 6-MeO-BDE-47 and 2′-MeO-BDE-68 observed in male beluga whale blood were significantly lower ($P < 0.05$) compared to concentrations in liver and blubber (Table 1). Also, contaminant concentrations observed in female beluga whales were generally lower compared to concentrations in male animals and young calves (Table 1).

Mean ΣOH-PBDEs in beluga whale blubber were relatively low (0.1 ng.g^{-1} lipid, CI = 0.02−0.5). Mean ΣMeO-PBDEs ranged from approximately 1.3 ng.g^{-1} lipid equivalent in eider duck liver to 300 ng.g^{-1} lipid equivalent in beluga whale tissues. Concentrations of individual MeO-PBDEs ranged between 0.1 and 200 ng·g^{-1} lipid equivalent in biota samples (bivalves, fish, seaducks, and marine mammals). 6-MeO-BDE-47 exhibited the highest concentration among MeO-PBDEs, followed by 2′-MeO-BDE-68 and 6′-MeO-BDE-49. MeO-PBDEs were not detected in any samples of marine sediment (<0.1 ng·g^{-1} dry wt) or macroalgae (<0.1 ng·g^{-1} lipid equivalent) (Table 1).

Concentrations of individual MeO-PBDEs were generally equivalent or greater than concentrations of individual PBDE congeners (Figure S2). For example, the mean concentration of 6-MeO-BDE-47 in male beluga whale blubber was approximately 14 times higher than BDE-47 concentrations. 6-MeO-BDE-47 and 2′ MeO-BDE-68 concentrations in beluga whales were comparable to concentrations of organochlorine contaminants such as mirex, β-HCH, hexachlorobenzene, and PCB-153 in those animals (Figure S2). An evaluation of all organohalogen contaminants (i.e, ΣOH-PBDEs, ΣMeO-PBDEs, ΣPBDEs, ΣPCBs, ΣDDTs, ΣHCHs, CBz, and ΣCyclodienes) monitored in seaducks and marine mammals revealed that the total brominated diphenyl ether burden

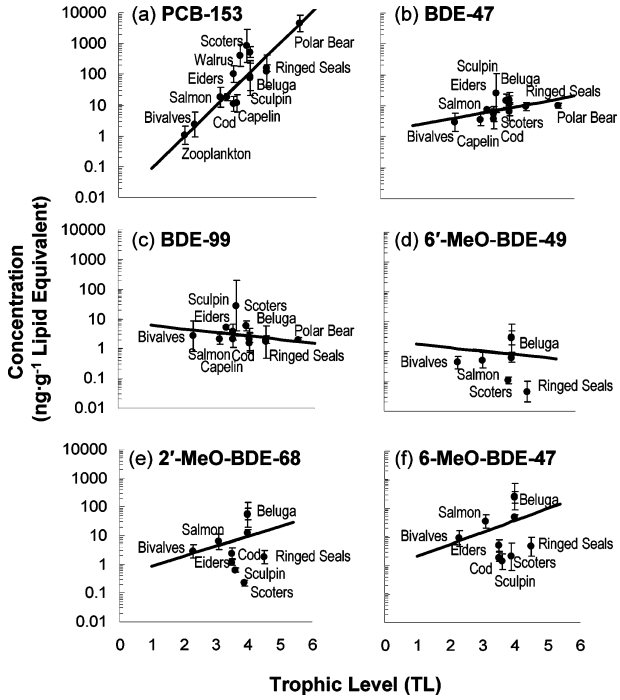

FIGURE 1. Chemical concentrations in organisms of the Arctic marine food web (ng·g^{-1} lipid equivalent) versus trophic level (TL) for (a) PCB-153, (b) BDE-47, (c) BDE-99, (d) 6 MeO-BDE-49, (e) 2′-MeO-BDE-68, and (f) 6-MeO-BDE-47. The solid line represents log-linear regression of the C_B-TL relationship over the entire food web. Data points are geometric means, and error bars represent the range of 1 standard deviation. PCB-153 concentrations shown for polar bears are for E. Hudson Bay animals (Belcher Islands) (*40*). PBDE concentrations shown for polar bears are for Western Hudson Bay animals (*41*).

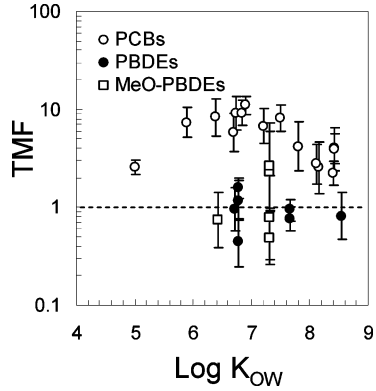

FIGURE 2. Observed TMFs for individual PCBs, PBDE, and MeO-PBDEs in the Arctic marine food web versus log K_{OW}. Error bars represent 95% confidence limits. See the Supporting Information for details regarding K_{OW} value estimates.

(i.e., PBDEs and their OH- and MeO- analogues) was a relatively small percentage of the total organohalogen burden (<10%) in those organisms (Figure S3). Conversely, PBDEs and MeO-PBDEs contributed substantially (>10%) to the overall organohalogen burden in sediments and other marine organisms such as bivalves and fish.

Trophic Magnification Factors. Strong positive relationships between chemical concentration and TL were observed for recalcitrant PCB congeners (Figure 1, Table S5). Concentrations of PCB-153 in biota increased significantly ($P < 0.05$, $R^2 = 0.76$) with increasing TL, with a TMF of 11 (Figure 1a). The majority of PBDEs did not show significant increases ($P > 0.05$) with TL (Table S5). BDE-47 exhibited slight concentration increases with increasing TL ($P < 0.05$), with

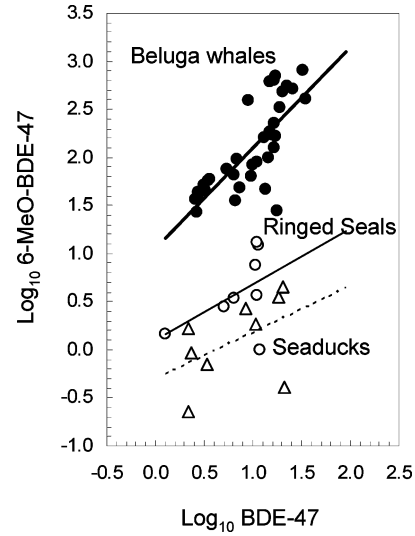

FIGURE 3. Relationship between log transformed concentrations of 6-MeO-BDE-47 versus BDE-47 in beluga whale blubber, ringed seal blubber, and seaduck (common eiders and white winged scoter) liver.

a TMF of 1.6 (CI = 1.2−2.0) (Figure 1b). Concentrations of MeO-PBDEs (2′-MeO-BDE-28, 6′-MeO-BDE-49, and 6′-MeO-BDE-66) also did not increase significantly with TL ($P > 0.05$) (Table S5, Figure 1d). However, 2′-MeO-BDE-68 and 6-MeO-BDE-47 exhibited significant concentration increases ($P < 0.05$) over the food web, with TMFs equal to 2.3 and 2.6, respectively (Figure 1e,f).

The relationship between observed TMFs and octanol−water partition coefficient (K_{OW}) for PCBs, PBDEs, and MeO-PBDEs is shown in Figure 2. TMFs of PCBs are relatively high, increasing from 2 to 11 between K_{OW} of 10^5 and 10^7, dropping slightly after K_{OW} exceeds $10^{7.5}$. Conversely, TMFs of PBDEs range from 0.7 to 1.6 between K_{OW} of 10^7 and 10^8. Br_3−Br_7 PBDEs are shown to exhibit a substantially lower degree of trophic magnification in this Arctic marine food web compared to recalcitrant Cl_5−Cl_7 PCBs, with comparable K_{OW}s. Figure 2 also reveals that TMFs of 2′-MeO-BDE-68 and 6-MeO-BDE-47 (calculated log $K_{OW} = 7.3$) are above 1 and hence indicates biomagnification in this food web. However, TMFs of those MeO-PBDEs are relatively low compared to TMFs of recalcitrant PCBs with similar K_{OW}s.

Bioaccumulation Behavior and Potential Sources of OH- and MeO-PBDEs. Previous analyses of individual PBDE congeners in this food web (*30*) showed that the composition of PBDE concentrations in sediments and macroalgae were dominated by BDE-99, similar to PentaBDE mixture compositions, while BDE-47 is the dominant congener in higher trophic organisms (Figure S4). However, MeO-PBDEs, which were not detectable in ambient environmental media (i.e., sediments) or macroalgae, are dominant bromodiphenyl compounds in various organisms of the marine food web (Figure S5). For example, ΣMeO-PBDEs represent approximately 90% of the total bromodiphenyl ether burden in beluga whale tissues. OH-PBDE burdens in the food web are negligible compared to PBDEs and MeO-PBDEs.

ΣOH-PBDE to ΣPBDE and ΣMeO-PBDE to ΣPBDE concentration ratios, shown in Table 1, are comparable to those ratios reported in previous studies (*2, 4*). Mean ΣOH-PBDE/ΣPBDE values in beluga whale blubber was low (0.005, CI = 0.002−0.01), which indicates negligible formation/retention of OH-PBDEs in those animals. It is important to note that ΣOH-PBDE to ΣPBDE concentration ratios, which are sometimes used as transformation ratios to assess OH-PBDE formation/retention capacity, may be misleading due to the presence of OH-PBDEs of natural origin. Mean ΣMeO-PBDE/

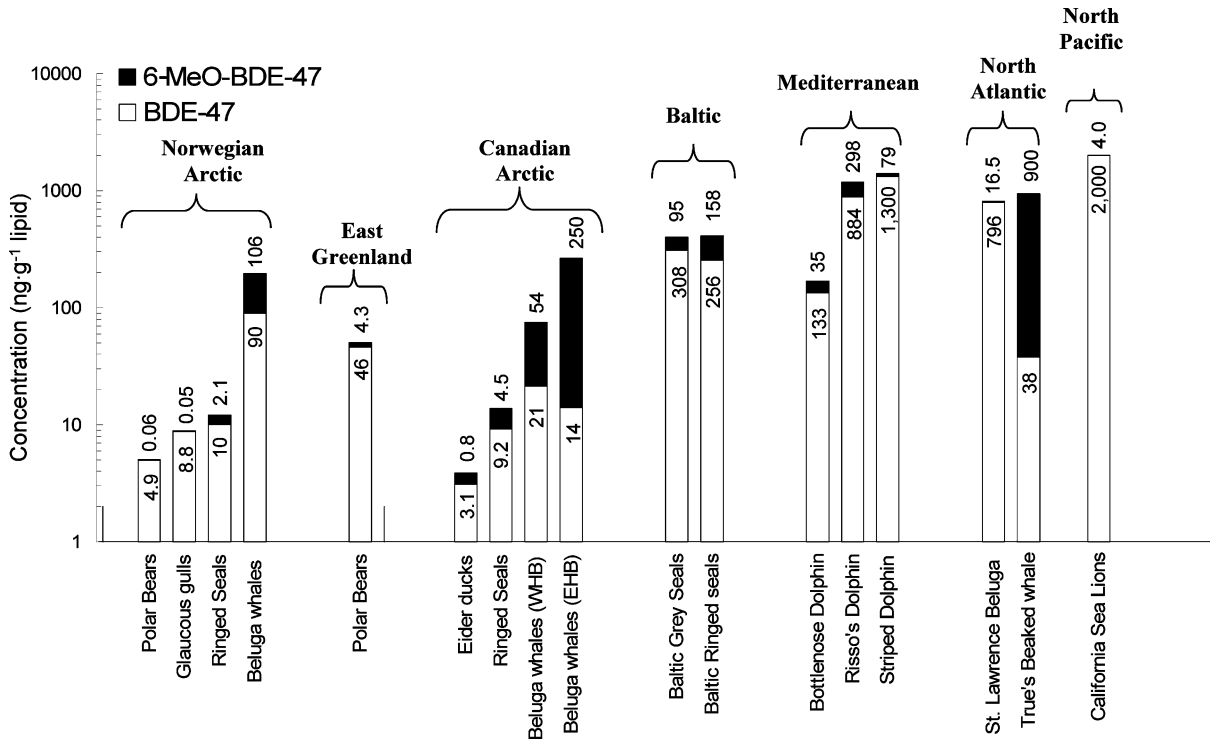

FIGURE 4. Measured concentrations (ng·g^{-1} lipid) of BDE-47 and 6-MeO-BDE-47 in marine wildlife from the Canadian Arctic (this study) compared to reported levels in marine wildlife. Compiled concentration data include data for glaucous gulls (*L. hyperboreus*), ringed seals (*P. hispida*), beluga whales (*D. leucas*), and polar bears (*U. maritimus*) from the Norwegian Arctic ((*2*), (*36*)); Baltic gray seals (*Halichoerus grypus*) and ringed seals (*P. hispida*) (*7*), bottlenose dolphin (*Tursiops truncatus*), striped dolphin (*Stenella coeruleoalba*), Risso's dolphin (*Grampus griseus*), and fin whales (*Balaenoptera physalus*) from the Mediterranean (*42*); St. Lawrence beluga whales (*38*) and a True's Beaked whale (*Mesoplodon mirus*) from the North Atlantic (*28*); and California sea lions (*Zalophus californianus*) from the North Pacific (*37*). Data for Western Hudson Bay (WHB) beluga whales in the Canadian Arctic are from ref *38*.

ΣPBDE values in cod, sculpin, and seaducks were low (mean range: 0.02−0.6) compared to those values in bivalves, salmon, and beluga whales (mean range: 1.3−7.1) (Table 1).

Figure 3 shows a positive relationship between 6-MeO-BDE-47 and BDE-47 concentrations in tissue samples of beluga whales, ringed seals, and seaducks. A strong correlation was observed between 6-MeO-BDE-47 and BDE-47 in beluga whale samples ($r^2 = 0.7$, $p < 0.001$). Similar positive relationships were observed for other MeO-PBDEs such as 6-MeO-BDE-99 versus BDE-99 ($r^2 = 0.7$) and 6′-MeO-BDE-66 and 6-MeO-BDE-49 and 4-MeO-BDE-42 versus BDE-47 ($r^2 = 0.6$−0.8). Verreault et al. also observed strong correlations of 6-MeO-BDE-47 versus BDE-47 as well as 6-OH-BDE-47 versus BDE-47 in glaucous gull (*Larus hyperboreus*) plasma (*2*). Conversely, Kierkegaard et al. did not observe a relationship between 6-MeO-BDE47 and BDE-47 concentrations in pike from Swedish lakes (*27*).

No relationships were observed between OH-PBDEs and corresponding PBDE precursors in beluga whale blubber or milk samples. Correlation of a given OH- or MeO-PBDE with a corresponding PBDE precursor could be indicative of metabolic transformation of the parent PBDE congener (*2*). However, it is also possible that correlation between PBDEs and their OH- and MeO- analogues may be the result of comparable bioaccumulation of ambient concentrations of OH-PBDE and MeO-PBDE residues present in the environment.

Figure 4 illustrates concentrations of BDE-47 and 6-MeO-BDE-47 in marine wildlife from E. Hudson Bay (this study), compared to marine wildlife from the Norwegian Arctic, East Greenland, Baltic, Mediterranean, North Atlantic, and North Pacific (*2, 7, 28, 36*−*38*). 6-MeO-BDE-47 concentrations in E. Hudson Bay beluga whales (130 ng·g^{-1} lipid, CI = 25−690) were comparable to 6-MeO-BDE-47 concentrations reported in blubber of gray seals (95 ng·g^{-1} lipid) and ringed seals (160 ng.g^{-1} lipid) from the Baltic (*7*). Conversely, concentrations of 6-MeO-BDE-47 in beluga whales were substantially higher than levels observed in plasma of male glaucous gull (0.05 ± 0.01 ng·g^{-1} lipid) and female polar bears (<0.02−0.1 ng·g^{-1} lipid) from the Norwegian Arctic and substantially lower than 6-MeO-BDE-47 concentration reported in blubber of a True's Beaked whale (900 ng.g^{-1} lipid wt) from the North Atlantic (*28*). Figure 4 reveals no positive relationship between 6-MeO-BDE-47 and BDE-47 concentrations in the various organisms. For example, organisms with the highest BDE-47 concentrations (California Sea Lions, 2000 ng·g^{-1} lipid in blubber) exhibit very low concentrations of 6-MeO-BDE-47. This indicates residues of 6-MeO-BDE-47 in those marine wildlife are not associated with BDE-47 exposure and are more likely the result of direct bioaccumulation of this naturally occurring compound, which is consistent with radiocarbon measurements reported by Teuten et al. (*28*).

Based on previous field and laboratory investigations (Table S1), residues of 5-OH-BDE-47 observed in beluga whales may be a metabolite of BDE-47. Also, 4-MeO-BDE-42, 5-MeO-BDE-47, 6-MeO-BDE-47, and 6′-MeO-BDE-66 may in part be formed by methylation of corresponding alcohols, which are known metabolites of BDE-47. Conversely, observed residues of ortho substituted OH- and MeO-PBDEs such as 6′-OH-BDE-49, 2′-OH-BDE-68, 6-OH-BDE-90, 6-MeO-BDE-17, 2′ -MeO-BDE-28, 6-MeO-BDE-47, 6′-MeO-BDE-49, 6′-MeO-BDE-66, 2′-MeO-BDE-68, 2′-OH-BDE-75, 6-MeO-BDE-90, and 6-MeO-BDE-99 may be of natural origin. The presence of a local natural source of OH- or MeO-PBDEs in this Arctic marine food web is not apparent, as no measurable quantities were observed in ambient environmental media (i.e., sediments) or macroalgae. The absence of MeO-PBDEs in sediments and macroalgae was somewhat

surprising due to the fact that concentrations of those compounds in the food web were comparable or greater than concentrations of PBDEs, which were detected in those samples (Table 1). Future measurement of OH- and/or MeO-PBDEs in Arctic air, precipitation, and water would undoubtedly provide more insight into sources, long-range transport potential, and environmental fate of these compounds. Currently, the data indicate that OH- and MeO-PBDE residues in Arctic marine food webs are the result of either (i) bioformation in organisms via cytochrome P450 mediated metabolism of PBDEs, (ii) bioaccumulation of local or atmospherically derived PBDE degradation products, or (iii) bioaccumulation of local or atmospherically derived marine natural products.

In summary, Br_3-Br_7 PBDEs exhibit negligible biomagnification in this Arctic marine food web, indicating a high degree of biotransformation. The reduced biomagnification potential of PBDE congeners observed in this Arctic marine food web is likely due to relatively high rates of debromination (*39*) and/or CYP mediated metabolism of PBDEs in these animals. However, the lack of primary metabolite residues (i.e., OH-PBDEs) observed in blood/tissues of fish and marine mammals indicates limited formation of those compounds and/or limited retention (due to further biotransformation/elimination processes such as conjugation and oxidation). Consequently, impacts of OH-PBDEs on thyroid hormone function, due to competitive binding to TTR, are seemingly low for the studied Arctic wildlife species. MeO-PBDE residues in this food web are likely the result of bioaccumulation rather than biotransformation processes. This is particularly true for ortho MeO-substituted compounds, which have been previously identified as marine natural products. Further field monitoring and laboratory investigations of PBDEs and their hydroxylated and methoxylated analogues would be useful to better understand key mechanisms governing biotransformation and bioaccumulation behavior of these compounds.

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Supporting Information Available

Tables S1−S5 and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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