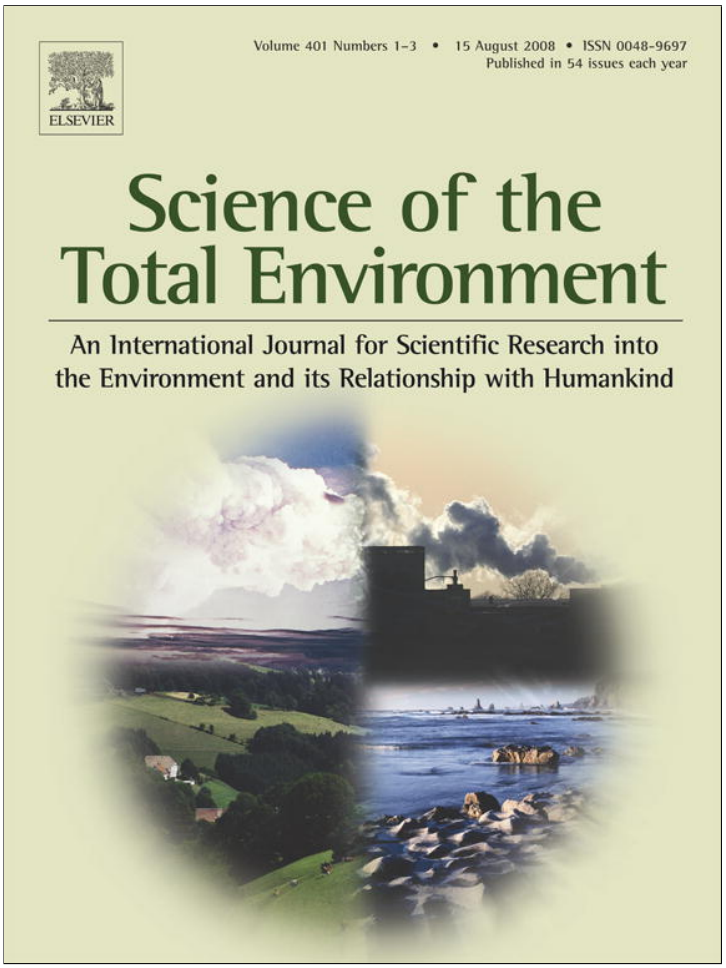

SCIENCE OF THE TOTAL ENVIRONMENT 401 (2008) 60–72

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Bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web

Barry C. Kelly[a], *Michael G. Ikonomou*[b], *Joel D. Blair*[a], *Frank A.P.C. Gobas*[a,*]

[a]*School of Resource and Environmental Management, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*
[b]*Contaminant Sciences, Institute of Ocean Sciences, Fisheries and Oceans Canada (DFO), 9860 West Saanich Road, Sidney, British Columbia, Canada V8L 4B2*

ARTICLE INFO

Article history:
Received 6 December 2007
Received in revised form
12 February 2008
Accepted 25 March 2008

Keywords:
PBDEs
POPs
Bioaccumulation
Arctic
Marine
Food web

ABSTRACT

A comparative analysis of the bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) was conducted involving simultaneous measurements of PBDE and PCB concentrations in organisms of a Canadian Arctic marine food web. Concentrations of individual PBDE congeners (BDE-28, -47, -99, -153, -154 and -183) in Arctic marine sediments (0.001–0.5 $ng \cdot g^{-1}$ dry wt) and biota (0.1–30 $ng \cdot g^{-1}$ wet wt) were low compared to those concentrations in biota from urbanized/industrial regions. While recalcitrant PCB congeners exhibited a high degree of biomagnification in this food web, PBDE congeners exhibited negligible biomagnification. Trophic magnification factors (TMFs) of PCBs ranged between 2.9 and 11, while TMFs of PBDEs ranged between 0.7 and 1.6. TMFs of several PBDE congeners (BDE-28, -66, -99, -100, -118, -153 and -154) were not statistically greater than 1, indicating a lack of food web magnification. BDE-47 was the only PBDE with a TMF (i.e. 1.6) statistically greater than 1, hence showing evidence of biomagnification in the food web. However, the TMF of BDE-47 (1.6) was substantially lower than TMFs of recalcitrant Cl_5–Cl_7 PCBs (TMFs ~ 9–11). Species-specific bioaccumulation factors (BAFs) of PBDEs in homeotherms were much smaller than those for PCBs. This further indicates the low degree or absence of biomagnification of PBDEs compared to PCBs in this food web. The field observations suggest PBDEs exhibit a relatively rapid rate of depuration though biotransformation in Arctic marine organisms, which is consistent with laboratory studies in fish and rats.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are an important class of brominated flame retardants (BFRs), used as additives in consumer products such as polyurethane foams, textiles, furniture, appliances and computers. Similar to polychlorinated biphenyls (PCBs), there are 209 possible bromodiphenyl ether (BDE) congeners, based on the halogenation of the phenyl rings. PBDEs are often classified as lower brominated (Br_1–Br_6) or higher brominated (Br_7–Br_{10}) congeners and vary widely in physical–chemical properties such as molecular weight (MW), octanol–water partition coefficients (K_{OW}s) and octanol–air partition coefficients (K_{OA}s), (Harner and Shoeib, 2002; Wania et al., 2002; Braekevelt et al., 2003; Kuramochi et al., 2007). Commercial PBDE mixtures, which include PentaBDE, OctaBDE and DecaBDE formulations, generally contain a small number of dominant congeners (La Guardia et al., 2006). For example, 2,2′,4,4′ tetrabromodiphenyl ether (BDE-47) and 2,2′,4,4′,5 pentabromodiphenyl ether (BDE-99) comprise >80% (w/w) of PentaBDE mixtures. OctaBDE mixtures contain mainly 2,2′, 3,3′, 4,4′,6,6′ octabromodiphenyl ether (BDE-197), 2,2′, 3,4,4′,5′,6 heptabromodiphenyl ether

* *Corresponding author*. Tel.: +1 778 782 5928; fax: +1 778 782 4968.
E-mail address: gobas@sfu.ca (F.A.P.C. Gobas)

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doi:10.1016/j.scitotenv.2008.03.045

(BDE-183) and 2,2′, 3,3′, 4,4′,5,5′, 6,6′ decabromodiphenyl ether (BDE-209), while the DecaBDE formulation is comprised almost entirely of BDE-209 (>90%, w/w).

Since the onset of commercial PBDE production in the early 1970s, increasing global demand has led to extensive manufacturing of these three technical mixtures. PBDEs are relatively persistent with potential for long-range transport (LRT) and bioaccumulation in wildlife and humans. PBDEs are commonly detected in environmental and biological samples, including samples from remote regions such as the Arctic (Ikonomou et al., 2002a; Wolkers et al., 2004). PBDE levels in wildlife and humans have risen exponentially since the 1980s (Noren and Meironyte, 2000; Ikonomou et al., 2002a). In terms of toxicity, various PBDE congeners/mixtures can elicit a range of toxic effects in laboratory test animals, including developmental neurotoxicity and thyroid hormone disruption (Darnerud et al., 2001; Hallgren et al., 2001; Branchi et al., 2002; Eriksson et al., 2002; Zhou et al., 2002; Darnerud, 2003).

Historical emissions of persistent organic pollutants (POPs) such as PCBs and DDTs resulted in global distribution and biomagnification in food chains. Currently, the United States, Canada, member states of the European Union (EU) and several other countries are evaluating the environmental behaviour of current-use chemicals as part of their obligation as signatories of the Stockholm Convention and under mandate of domestic regulations. These global initiatives generally seek the virtual elimination of chemicals that are persistent (P), bioaccumulative (B), toxic (T) and pose a significant risk to the environment and/or human health. PBDEs are not currently included in the Stockholm Convention. However, some jurisdictions have taken regulatory action on certain PBDE mixtures. For example, in 2004 the EU banned Penta- and OctaBDE formulations. Similarly, the major North American producer has voluntarily ceased production of Penta- and OctaBDEs. Consequently, chemical manufacturers are now only producing the DecaBDE flame retardant mixtures (de Wit, 2002).

Regulatory agencies worldwide generally identify bioaccumulative substances as fat-soluble chemicals with high K_{OW}s (i.e., ≥100,000). Because PBDEs exhibit similar physical–chemical properties as well-known bioaccumulative substances such as PCBs (i.e., K_{OW}s of PBDEs range between 10^6 and 10^{11}) it is anticipated that their bioaccumulation potential is comparable to that of PCBs. However, only a limited number of field studies investigating the bioaccumulation behaviour of PBDEs have been reported and with variable conclusions. For example, analyses of PBDEs in biota from the North Sea (Boon et al., 2002) and Baltic food webs (Sellström et al., 1993; Haglund et al., 1997), indicated BMFs of BDE-47 in grey seals (seal/herring lipid) and guillemot eggs (egg/sea salmon lipid) of 7 and 17, respectively. BMFs of BDE-47 in polar bears (bear/seal) from the Norwegian Arctic were relatively low, between 1 and 7 (Wolkers et al., 2004; Muir et al., 2006). However, relatively high BMFs of BDE-153 were observed in polar bears from the Canadian Arctic and Alaska (Muir et al., 2006). For example, mean BMFs of BDE-153 in those polar bears ranged between 91 and 130. Also, relatively high BMFs of BDE-47, -99 and -100 (between 20 and 60) were reported in beluga whales from Svalbard (Wolkers et al., 2004). Combining all observations, lipid corrected biomagnification factors (i.e., ratio of lipid normalized chemical concentrations in predator and prey) of individual PBDE congeners reported in marine wildlife (seabirds, seals, whales and polar bears) range between 1 and 130. One of the difficulties associated with the calculation of BMFs, is the uncertainty in organism and prey concentrations related to temporal and spatial variations in prey composition. To gain further insights into the bioaccumulation behaviour of PBDEs it is advantageous to investigate changes in PBDE concentration over the entire length of food webs.

The objective of this study was to determine the bioaccumulation behaviour of PBDEs in a marine food web containing fish, mammals and bird species. To minimize the effect of local point source contamination, we selected a food web in a remote Northern Canadian location. To minimize confounding errors in the measurement of food web bioaccumulation associated with the characterization of predator–prey relationships and trophic status, we used combined analyses of PCBs and PBDEs to study the bioaccumulation behaviour of PBDEs in relation to the well characterized bioaccumulation behaviour of PCBs. The study provides PBDE concentrations as a function of trophic level and contains information on PBDE contamination in wildlife species utilized for subsistence by the indigenous Inuit people of northern Canada.

2. Materials and methods

2.1. *Samples*

During the months of May to September between 1999 and 2003 sediment and biota samples were collected along the eastern Hudson Bay coastline in close proximity to the Inuit village Umiujaq (64° 15′N 113° 07′ W), (Fig. 1). Marine bottom sediments were collected using a petit ponar grab at between 25 and 80 m depths. Biota samples included lichens (*Cladina rangiferina*), macroalgae (Fucus gardneri), bivalves (*Mytilis edulis*), fish: Arctic cod (*Boreogadus saida*), capelin (*Mallotus villosus*) and sculpin (*Myoxocephalus scorpioides*), and tissues and organs of common eider ducks (*Somateria mollissima sedentaria*) and marine mammals including beluga whales (*Delphinapterus lecuas*) and ringed seals (*Pusa hispida*). Tissue samples of sea ducks and marine mammals, including stomach contents, liver, muscle, blubber and/or milk, were collected as part of northern Quebec Inuit hunts. Beluga whale samples were collected from the E. Hudson Bay beluga stock summering habitat, near the Nastapoka River estuary and the Inuit village of Umiujaq during the summer hunts. Ringed seal and sea duck samples were obtained from Hudson Strait (Quaqtaq, Salluit). Samples were collected in individual 50 mL solvent-rinsed glass jars with aluminum foil lined caps and stored at −30 °C prior to chemical analysis. Tissue samples from fish and beluga whale tissues were excised using solvent-rinsed disposable surgical blades. Ringed seal blubber and sea duck liver and adipose tissue samples were provided by D.C.G. Muir (Environment Canada's, National Water Research Institute, NWRI, Burlington, ON) and M. Kwan (Nunavik Research Centre, NvRC, Kuujuaq, Quebec), respectively. Sample sizes are given in Table 2. The PCB concentration data for these Arctic marine sediment and biota samples are reported in our recent study investigating the bioaccumulation behaviour of POPs in this food web (Kelly et al., 2007). To develop a more comprehensive account of the

Fig. 1 – Map of the Eastern Hudson Bay region of the Canadian Arctic where field sampling was conducted.

distribution of PBDEs in the food web, we also compiled previously reported concentrations of PBDEs and PCBs from biomonitoring programs, including levels in samples of Arctic air (Stern et al., 1997; Su et al., 2007), invertebrates (Hargrave et al., 1992), walrus (Muir et al., 1995), polar bears (Norstrom et al., 1998; Muir et al., 2006) and breast milk from Inuit women (Muckle et al., 2001; Ryan et al., 2002; Pereg et al., 2003).

2.2. *Chemical analysis*

Extraction, cleanup and analysis of PBDEs using gas chromatography/high resolution mass spectrometry (GC-HRMS) were conducted at the Institute of Ocean Sciences (IOS), Canadian Department of Fisheries and Oceans (DFO) in Sidney, BC. Details of our methods for PBDE determinations in environmental and biological samples and QA/QC procedures have been previously described elsewhere (Ikonomou et al., 2001; Ikonomou and Rayne, 2002; Ikonomou et al., 2002a,b; Rayne et al., 2003, 2004). Briefly, tissue samples (approximately 20–50 g wet wt for lichens, macroalgae and sediment, 5–15 g for fish, 2 g for beluga whale liver and 0.5 g for blubber were homogenized with Na_2SO_4 with mortar and pestle. Sub-samples of tissues used for analysis were excised from the interior of frozen samples to reduce potential contact contamination during collection and/or storage. The homogenate powder was transferred to a glass extraction jar, spiked with ^{13}C-labeled procedural internal standards (Cambridge Isotope Laboratories, Andover, MA), approx. 2000–5000 pg of each ^{13}C PBDEs (^{13}C BDE-3, -15, -28, -47, -77, -118, -99, -100, -153, -183). The spiked samples were then extracted with 30 mL of 1:1 (v/v) DCM/Hexane in a Branson 5210 ultrasonic water-bath (Branson Ultrasonics Co., CT) for 20 min. Once the suspended particles settled, the supernatant was removed and then extraction was repeated two more times with fresh solvent. The combined extracts were concentrated to ca. 2 mL with a gentle stream of high-purity nitrogen. Relatively low lipid samples (<5% lipid) such as cod and sculpin tissue were quantitatively transferred onto a 350 mm × 10 mm i.d. glass column packed with 8 g 100% activated Florisil (60–100 μm mesh, activated at 400 C overnight). High lipid samples (>5% lipid) such as salmon and beluga blubber were first passed through a Gel Permeation Column (GPC) filled with 70 g of BioBeads, S-X33 (BioRad) in 50% DCM/hexane solution (v/v). The lipid fraction from the GPC (180 mL) was collected and discarded, while the remaining 300 mL of eluent from the GPC was collected, evaporated to near dryness and solvent exchanged into hexane for further cleanup by Florisil. The Florisil column was eluted with 200 mL of 50% DCM/Hexane, which was then evaporated to a final volume of 100 μL.

Quantification of PBDEs was determined by GC-HRMS using a Micromass Ultima HR-mass spectrometer coupled with an HP 5890 Series II GC and a CTC A200S autosampler (CTC

Analytics, Zurich, Switzerland). The GC column used was a 15 m high temperature DB-5-HT (0.225 mm i.d. × 0.1 μm film thickness). The GC was operated in splitless mode, with the purge valve activated 2 min following sample injection. Ultra high-purity helium at 80 kPa was used as the carrier gas using the following temperature program: hold at 100 °C for 1 min, 2 °C min^{-1} to 140 °C, 4 °C min^{-1} to 220 °C, 8 °C min^{-1} to 330 °C and hold for 1.2 min. For all analyses, the MS was operated at 10,000 resolution in the positive ion mode at 39 eV energy and data were acquired in the single ion resolving mode (SIR). Analytes were identified by retention time (RT) comparison relative to authentic calibration standards. For Br_1 and Br_2 homologues and Br_4–BDE-77, the two most abundant isotopes representing the parent ion $[M^+]$ were monitored. For all other homologues (Br_3–Br_7 congeners) the two dominant isotopes representing the $[M–2Br]^+$ fragment were monitored. Quantification ions were *m/z* 323.8785 for Br_4–PBDEs, 403.7870 for Br_5–PBDEs, 481.6975 for Br_6–PBDEs and 561.6060 for Br_7–PBDEs. Concentrations were calculated by the internal standard isotope dilution method using mean relative response factors (RRFs) determined from a calibration standard, run prior to and following sample analyses. A total of 31 individual Br_1–Br_7–BDE congener peaks and three co-eluting bands (each composed of two congeners) were identified and quantified, constituting a data set of 37 congeners overall: BDE-1, -2, -3, -7, -8/11, -10, -12, -13, -15, -17, -25, -28/33, -30, -32, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -119, -138/166, -140, -153, -154, -155, -181, -190.

Moisture content was determined by comparing wet and dry weights after oven-drying 1 g of sample at 125 °C for 24 h. Lipid contents were determined gravimetrically using an extracted 5 g sub-sample. Lipid contents (% lipid) were expressed as a percentage of the original wet wt. Organic carbon content of sediments (% OC of dry weight) was determined on a 1 g sub-sample by combustion/non-dispersive infrared gas analysis using a Shimadzu 5050A Total Organic Carbon (TOC) analyzer. TOC was calculated as the difference between the measured total carbon and total inorganic carbon.

2.3. Quality assurance

Each batch of twelve samples consisted of one procedural blank and one duplicate sample. Analytes were identified only when the GC-HRMS data satisfied all of the following criteria: (i) two isotopes of the analyte were detected by their exact masses with the HRMS operating at 10,000 resolution during the entire chromatographic run; (ii) the retention time of the analyte peak was within 3 s of the predicted time obtained from analysis of authentic compounds in the calibration standards (where available); (iii) the maxima for both characteristic isotopic peaks of an analyte coincided within 2 s; (iv) the observed isotope ratio of the two ions monitored per analyte were within 15% of the theoretical isotopic ratio; and (v) the signal-to-noise ratio (S/N) resulting from the peak response of the two corresponding ions was ≥3 for proper quantification of the analyte. Recoveries of individual internal standards were between 40 and 120% for all analyses. Method detection limits (MDLs) for sediments and biota samples were determined as 3 × SD of procedural blanks (n = 12). The instrument detection limit (IDL = 3 × S/N) was used when analyte concentration in procedural blanks was below IDL. MDLs were calculated using the average sample mass extracted (g) and lipid equivalent content (% lipid equivalent) for a given matrix. MDLs in sediments ranged between 0.001 and 0.02 ng·g^{-1}dry wt. MDLs in biota (ng·g^{-1}lipid equivalent) were as follows: lichens (0.003–0.5), macroalgae (0.002–0.4), bivalves (0.01–0.9), fish (0.01–1.9), sea duck liver (0.01–0.8), blubber (0.01–0.9). PBDE contamination observed in procedural blanks (i.e., mainly BDE-47, BDE-99, BDE-100 and BDE-153) was negligible compared to analyte contributions originating from the sample (i.e., 0–10% of the analyte concentration in the sample was due to background levels). Hence, reported concentrations were not blank subtracted.

2.4. Food web characterization

2.4.1. Stable isotope analysis

Stable nitrogen isotope analysis is a well established technique for assessing predator–prey interactions and organism trophic levels (TL) of complex food webs (Peterson and Fry, 1987; Hobson and Welch, 1992; Hanson et al., 1997; Hobson et al., 2002). Specifically, $\delta^{15}N$, the concentration ratio of $^{15}N/^{14}N$, expressed relative to a standard (i.e., atmospheric N_2), has been shown to increase with increasing trophic level due to the preferential excretion of the lighter nitrogen isotope (DeNiro and Epstein, 1981). Previous studies of nitrogen isotopes in Arctic marine food webs have reported mean $\delta^{15}N$ values (parts per thousand, ‰) in various organisms, including primary producers (6–9‰), invertebrates (9–15‰), fish (10–16‰), seabirds (12–17‰) and marine mammals (13–21‰), (Hobson and Welch, 1992; Fisk et al., 2001; Hobson et al., 2002).

In the present study we determined $\delta^{15}N$ values for several marine organisms from E. Hudson Bay. To analyze stable nitrogen isotopes, approximately 1–30 mg of sample was freeze dried and ground to a homogenous powder using a wig-l-bug grinder (Crescent Dental Company, Chicago, Illinois). Samples were analyzed for natural abundance of stable nitrogen isotopes at the University of Victoria, British Columbia using a Costech CHNS Elemental Analyser coupled with a Thermo Scientific Delta V Isotope Ratio Mass Spectrometer. $\delta^{15}N$ (‰) was determined using the following equation:

$$\delta^{15}N = \left[\left(^{15}N/^{14}N_{SAMPLE}/^{15}N/^{14}N_{STANDARD}\right) - 1\right] \times 1000 \quad (1)$$

where $^{15}N/^{14}N_{STANDARD}$ represents atmospheric N_2 (Air). Internal laboratory standards (Dogfish Muscle, DORM-2; National Research Council Canada) were analyzed every 10 samples and indicate measurement errors of ±0.1‰.

2.4.2. Trophic level calculations

Following previous studies (Hobson and Welch, 1992; Fisk et al., 2001; Hobson et al., 2002), trophic levels of a given Arctic marine organism ($TL_{CONSUMER}$) was determined relative to herbivorous zooplankton (assumed to occupy trophic level 2), using the following equation:

$$TL_{CONSUMER} = 2 + \left(\delta^{15}N_{CONSUMER} - \delta^{15}N_{ZOOPLANKTON}\right)/3.8 \quad (2)$$

where $\delta^{15}N_{ZOOPLANKTON}$ was 7.9‰, representing the $\delta^{15}N$ value for the copepod *Calanus hyperboreus* from northeastern Canadian Arctic waters (Hobson et al., 2002) and 3.8 is the isotopic

enrichment factor. Following Fisk et al. (2001), TL of birds was calculated using the equation:

$$TL_{BIRD} = 3 + \left(\delta^{15}N_{BIRD} - \left(\delta^{15}N_{ZOOPLANKTON} + 2.4\right)/3.8\right) \quad (3)$$

where 2.4 represents a diet-tissue isotopic fractionation factor of +2.4‰, previously observed for liver tissue during captive-rearing studies on birds (Hobson and Clark, 1992). Table 1 summarizes the $\delta^{15}N$ values and trophic level determinations for the various organisms of this Arctic marine food web. Observed $\delta^{15}N$ values and TL estimates in organisms from Hudson Bay (shown in Table 1) are comparable to previous reports of Canadian Arctic marine biota (Hobson and Welch, 1992; Fisk et al., 2001; Hobson et al., 2002).

2.5. Data analysis

2.5.1. Data treatment

Measured PBDE and PCB concentrations in sediments and biota (ng·g^{-1} lipid equivalent) are reported as geometric means (GM). Asymmetric errors were calculated as 1 standard deviation (SD) and 95% confidence intervals (CI). Contaminant concentrations in sediments were expressed on a dry wt basis (ng·g^{-1} dry wt) and organic carbon corrected (ng·g^{-1} OC wt). Concentrations in biota were normalized to a common unit, i.e. ng·g^{-1} lipid equivalent, to compare chemical concentrations between various organisms. Wet weight concentrations of a given sample matrix i (Ci,, wet wt) were expressed on a lipid equivalent basis (LEq) as $Ci_{,LEq}$ according to $Ci_{,LEq} = Ci$ wet wt $\div \phi_{LEq}$, where ϕ_{LEq} is the lipid equivalent fraction of the sample. For biota, ϕ_{LEq} was determined as the sum of lipid (ϕ_L), proteins (ϕ_P) and carbohydrates (ϕ_C) fractions, i.e. $\phi_{LEq} = \phi_L + 0.05\phi_P + 0.1\phi_C$, where the constants 0.05 and 0.1 are proportionality constants representing the sorptive capacity of proteins and carbohydrates relative to lipid (deBruyn and Gobas, 2007). Chemical concentrations were determined on a lipid equivalent rather than lipid basis to recognize that biological matrices with very low lipid fractions ($\phi_L < 1\%$), such as plants and algae tend to store a significant fraction of their contaminant body burden in non-lipid organic matter (Skoglund et al., 1996; Axelman et al., 1997; Seth et al., 1999; Mackintosh et al., 2004). It is important to note that lipid equivalent concentrations in very low lipid content samples (lichens, macroalgae and bivalves) are lower than concentrations based on extractable lipids. However, lipid equivalent concentrations in relatively high lipid samples (fish, seaducks, marine mammal tissue) are generally comparable to lipid corrected values.

Table 1 – Stable nitrogen isotope values (mean ± standard deviation) and derived trophic level (TL) of Canadian Arctic marine biota

Organism	n	$\delta^{15}N$ (‰)	Trophic level (TL)
		–	
Macroalgae	6	6.1±0.2	1.0
Zooplankton[a]	–	7.9±0.1	2.0
Bivalves[b]	–	9.1±0.7	2.3
Salmon	3	11.9±1.2	3.1
Capelin	5	12.8±0.13	3.3
Arctic cod	5	13.7±0.5	3.5
Sculpin	5	14.1±0.9	3.6
Eider duck	5	12.1±0.5	3.5
White-winged scoters	5	13.8±0.8	3.9
Beluga whale	18	15.3±0.7	4.0
Ringed seal[c]	–	17.5±0.2	4.5
Polar bear[d]	–	21.1±0.3	5.5

[a] $\delta^{15}N$ data are for copepod *Calanus hyperboreus* from northeastern Canadian Arctic waters (Hobson et al., 2002). This value was used to represent trophic level 2 (primary herbivores) of the E. Hudson Bay marine food web.
[b] $\delta^{15}N$ data are for bivalve *Astarte* sp. from northeastern Canadian Arctic waters (Hobson et al., 2002). This value was used to determine TL of E. Hudson Bay bivalves.
[c] $\delta^{15}N$ data are for ringed seals from northeaster Canadian Arctic waters (Hobson et al., 2002). This value was used to determine TL of Hudson Bay/Hudson Strait ringed seals.
[d] $\delta^{15}N$ data are for polar bears from northeaster Canadian Arctic waters (Hobson et al., 2002). This value was used to determine TL of E. Hudson Bay polar bears.

2.5.2. Physical–chemical properties

K_{OW}s and K_{OA}s for PCBs and PBDEs were compiled from various sources (Hawker and Connell, 1988; Mackay et al., 1992; Harner and Mackay, 1995; Harner and Bidleman, 1996; Lei et al., 2000; Harner and Shoeib, 2002; Wania et al., 2002; Braekevelt et al., 2003) and are listed in Tables 3 and 4. To compare BAFs in warm-blooded animals (homeotherms) to K_{OA}, we calculated the K_{OA} at 37 °C from previously determined temperature dependent relationships (Harner and Bidleman, 1996; Harner and Shoeib, 2002).

2.5.3. Bioaccumulation parameters

Trophic magnification factors (TMFs), which are markers of cumulative bioaccumulation across the food web, were determined from the log-linear regression between the base-10 logarithm ($\log_{10}$) of the lipid equivalent concentration in biota (C_B) and trophic level (TL):

$$\text{Log } C_B = (m \times TL) + b \quad (4)$$

where m and b are the empirical slope and y-intercept, respectively. TMFs were calculated as the antilog of the slope (m), (i.e., TMF = 10 ^{m}). It is important to note that TMFs reported in the present study are calculated using lipid equivalent concentrations and hence may differ somewhat from comparable analyses using only lipid corrected concentrations. These differences can be important when analyses include concentrations of low lipid samples such as algae or invertebrates. To avoid the possibility of the method of normalization seriously biasing TMF values, we did not include concentration data for algae and lichens in the calculation of the TMF.

Bioaccumulation factors (BAFs) in marine wildlife (sea ducks, ringed seals, beluga whales, polar bears) and humans were determined as the ratio of the chemical concentrations in the organism (C_B, mol·m^{-3} lipid equivalent) and freely dissolved (gas-phase) air concentrations (C_{AG}), (i.e., $BAFs = C_B/C_{AG}$ mol·m^{-3}). BAFs were determined using Arctic air concentrations rather than seawater concentrations because respiratory elimination kinetics in these air-breathing homeotherms is controlled by lipid–air exchange not lipid–water exchange (as is the case for fish). We therefore compared observed BAFs to predicted equilibrium concentrations, based on chemical K_{OA} at 37 °C (core

Table 2 – Polybrominated diphenyl ether (PBDE) concentrations in samples of marine sediments (ng·g^{-1} dry wt) and biota (ng·g^{-1} lipid equivalent wt.) collected from E. Hudson Bay and Hudson Strait between 1999-2003

	Sediments (ponar grabs)	Lichens (*C. rangiferina*) (tissue)	Macroalgae (*F. gardneri*) (tissue)	Bivalves (*M. edulis*) (muscle)	Capelin (*M. villosus*) (whole body)	Cod (*B. saida*) (muscle)	Sculpin (*M. scorpioides*) (muscle)	Salmon (*Salmo* sp.) (muscle)	Eider ducks (*S. mollissima*) (liver)	White-winged scoters (*M. fusca*) (liver)	Female beluga (Age 5–35) (*D. leucas*) (blubber)	Male beluga (Age 16–35) (*D. leucas*) (blubber)	Female ringed seals (*P. hispida*) (blubber)	Male ringed seals (*P. hispida*) (blubber)
	(*n*=12)	(*n*=11)	(*n*=11)	(*n*=11)	(*n*=8)	(*n*=12)	(*n*=12)	(*n*=7)	(*n*=6)	(*n*=5)	(*n*=14)	(*n*=21)	(*n*=6)	(*n*=5)
Percent OC±SD	0.18±0.1	–	–	–	–	–	–	–	–	–	–	–	–	–
Percent lipid equivalent (L_{Eq})±SD	–	2.30±0.01	1.63±0.20	1.8±0.12	2.81±0.15	1.12±0.05	1.24±0.16	5.41±0.27	3.47±0.81	5.65±1.25	89.7±0.17	89.4±0.53	71.2±2.81	73.4±4.63
BDE-17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05 (0.02–0.2)	0.06 (0.02–0.2)	ND	0.02 (0.01–0.04)
BDE-28	ND	ND	2.3 (0.80–6.7)	ND	ND	0.30 (0.07–1.2)	1.1 (0.2–4.9)	0.19 (0.07–0.54)	0.11 (0.03–0.47)	0.08 (0.02–0.32)	0.24 (0.08–0.76)	0.48 (0.17–1.4)	0.24 (0.05–1.2	0.28 (0.1–0.71)
BDE-47	0.06 (0.008–0.39)	3.6 (1.1–11)	68 (8.8–530)	2.9 (0.74–11)	7.3 (3.1–17.4)	5.3 (1.5–18)	25.9 (3.0–220)	3.6 (1.2–11)	3.70 (0.9–15)	15 (4.5–47)	6.6 (1.7–26)	15 (5.5–42)	6.4 (0.9–44)	9.2 (3.4–25)
BDE-49	0.01 (0.003–0.07)	ND	7.9 (2.4–25.8)	0.34 (0.1–0.9)	0.71 (0.3–1.5)	0.61 (0.1–2.6)	3.1 (0.7–15)	0.43 (0.2–1.2)	ND	1.2 (0.47–3.0)	1.1 (0.2–6.2)	1.5 (0.34–6.9)	0.15 (0.02–1.32)	0.12 (0.03–0.44)
BDE-66	0.01 (0.001–0.06)	ND	6.1 (1.9–19.1)	0.29 (0.073–1.1)	ND	1.0 (0.43–2.5)	2.4 (0.44–13)	0.25 (0.10–0.65)	ND	ND	0.21 (0.07–0.62)	0.34 (0.12–0.95)	0.12 (0.02–0.59)	0.13 (0.04–0.4)
BDE-100	0.03 (0.005–0.2)	0.84 (0.26–2.7)	30 (3.2–280)	0.94 (0.3–3.9)	1.7 (0.7–3.9)	1.3 (0.35–4.76)	8.7 (0.9–76)	1.1 (0.32–3.2)	3.5 (0.9–13)	18 (5.6–59)	1.6 (0.44–5.8)	3.1 (1.0–9.1)	0.88 (0.13–6.1)	1.0 (0.35–2.9)
BDE-101	ND	ND	3.3 (1.2–9.6)	ND	ND	ND	0.69 (0.2–3)	0.17 (0.058–0.48)	ND	ND	0.28 (0.060–1.3)	0.39 (0.096–1.6)	0.023 (0.002–0.23)	0.02 (0.008–0.05)
BDE-99	0.1 (0.02–0.9)	4.1 (1.3–13)	160 (16–1,600)	2.6 (0.40–17)	5.2 (2.20–12)	2.1 (0.55–8.0)	28 (2–390)	2.1 (0.69–6.3)	3.6 (0.98–13)	5.9 (2.0–17)	1.5 (0.4–6.4)	2.3 (0.79–6.9)	1.6 (0.24–12)	2.0 (0.75–5.3)
BDE-118	ND	ND	2.4	ND	ND	ND	0.61 (0.3–1.4)	ND	ND	ND	0.04 (0.010–0.204)	0.09 (0.027–0.28)	0.031 (0.002–0.46)	0.044 (0.02–0.13)
BDE-85	0.02 (0.003–0.2)	ND	14 (4.3–48)	0.53 (0.15–1.9)	ND	0.27 (0.07–1.1)	3.9 (1.1–14)	ND	ND	ND	0.02 (0.003–0.09)	ND	0.025 (0.005–0.13)	0.031 (0.01–0.09)
BDE-126	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.11 (0.02–0.55)	0.25 (0.08–0.79)	ND	ND
BDE-155	ND.	ND	ND	ND	ND	ND	ND	ND	0.15 (0.05–0.48)	0.40 (0.09–1.9)	0.06 (0.003–1.2)	0.15 (0.02–1.2)	0.08 (0.02–0.37)	0.04 (0.008–0.19)
BDE-154	0.02 (0.003–0.1)	0.41 (0.13–1.4)	33 (11–102)	0.22 (0.06–0.83)	2.4 (0.9–6.9)	0.39 (0.1–1.6)	6.5 (1.6–27)	0.71 (0.16–3.1)	3.3 (0.79–14)	14 (4.3–46)	0.98 (0.25–3.9)	1.6 (0.48–53)	0.14 (0.02–1.18)	0.12 (0.04–0.43)
BDE-153	0.01 (0.04–0.06)	0.49 (0.14–1.6)	22 (2.3–210)	0.46 (0.16–1.28)	ND	0.24 (0.060–0.94)	8.1 (2.2–30)	0.36 (0.1–1.1)	3.7 (0.83–16)	13 (4.9–34)	0.50 (0.13–1.9)	0.79 (0.2–2.9)	0.41 (0.03–5.5)	0.32 (0.13–0.83)
BDE-183	ND	ND	ND	ND	ND	ND	ND	ND	1.5 (0.33–6.8)	2.9 (0.76–11)	0.07 (0.02–0.23)	0.08 (0.02–0.27)	0.05 (0.01–0.19)	0.04 (0.02–0.1)
∑PBDEs	0.1 (0.01–1.6)	9.3 (2.9–30)	324 (34–3,100)	5.4 (0.86–33)	18 (7.7–42)	9.8 (2.6–36)	73 (6.4–820)	9.3 (3.0–28)	20 (4.9–78)	71 (29–177)	16 (4.4–59)	34 (13–96)	11 (1.5–73)	14 (5.0–37)

Organic carbon contents (% OC) and lipid equivalent contents (% L_{Eq}) are arithmetic mean±standard deviation. PBDE concentration data are geometric means, along with 95% confidence intervals (CI) in brackets. ND = non-detectable concentration.

body temperature). Thus, biomagnification occurs when those BAFs exceed predicted lipid–air equilibrium concentrations. It is important to correct the chemical K_{OA} to 37 °C due to the fact that the fugacity capacity of octanol (Z_O) and hence lipids (Z_L) at this core body temperature (i.e., 310 K) of homeotherms is substantially lower than Z_O and Z_L at ambient temperatures (e.g., 263–293 K). For example, based on temperature dependent observations of PBDEs (Harner and Shoeib, 2002), we estimate Z_L of BDE-47 at 37 °C is approximately 200 times lower than Z_L of BDE-47 at 0 C. Since the BAFs report concentration ratios at different temperatures (i.e. 37 °C in the animal versus a mean annual temperature of approximately −10 °C in sampled air), it is appropriate to correct the chemical's K_{OA} to reflect a similar temperature difference between octanol and air. However, this correction factor (i.e. the ratio of the chemical fugacity capacity in air (Z_A) at 263 K and 310 K or $Z_{A,263K}/Z_{A,310K}$, i.e. 263/310 or 0.85) is small enough to be ignored.

3. Results and discussion

3.1. PBDE concentrations

Observed PBDE concentrations in Arctic marine sediments (ng·g^{-1} dry wt) and biota (ng·g^{-1} lipid equivalent) from E. Hudson Bay are summarized in Table 2. Fifteen congeners were routinely detected in sediments and biota, with BDE-47, -99, -100 and -154 being the most dominant compounds. E. Hudson Bay sediments exhibited very low organic carbon contents (kg OC/kg dry sediment) with a mean of 0.16% (CI = 0.08–0.27). ∑PBDE concentration in the sediments ranged between 0.009 and 2.7 ng·g^{-1} dry wt with a geometric mean concentration of 0.1 ng·g^{-1} dry wt (CI = 0.01–1.6). This is equivalent to a mean organic carbon corrected concentration in sediments of 62.5 ng·g^{-1} OC wt. (CI = 6.3–1000). The observed ∑PBDE concentrations in E. Hudson Bay sediments is comparable to previously reported ∑PBDE concentrations in sediments from the high Canadian Arctic (range: 0.11 to 0.29 ng·g^{-1} dry wt), (DIAND, 2003).

∑PBDE concentrations in terrestrial lichens ranged between 6.8 and 23.6 ng·g^{-1} lipid equivalent. These concentrations were much lower than those found in macroalgae, which ranged between 314 and 979 ng·g^{-1} lipid equivalent. Mean ∑PBDE concentrations in fish and wildlife (ng·g^{-1} lipid equivalent) were 5.4 ng·g^{-1} in bivalves, 9.8 ng·g^{-1} in cod, 13.6 ng·g^{-1} in male ringed seals, 19.7 ng·g^{-1} in eider ducks, 34 ng·g^{-1} in male beluga whales, 71.3 ng·g^{-1} in white-winged scoters and 72.8 ng·g^{-1} in sculpin. Observed PBDE concentrations in E. Hudson Bay biota were generally comparable to previously reported concentrations in Arctic marine biota (Christensen et al., 2002; Law et al., 2003; McKinney et al., 2006; Riget et al., 2006; de Wit et al., 2006; Muir et al., 2006). For example, mean BDE-47 concentrations of 15 ng·g^{-1} lipid (CI = 5.4–42) in E. Hudson Bay male belugas (this study) was comparable to BDE-47 concentrations reported in male beluga whales from nearby S.E. Baffin Island (9.7 ± 4.2 ng·g^{-1} lipid) and Western Hudson Bay (21.2 ± 6.4 ng·g^{-1} lipid), (Law et al., 2003; McKinney et al., 2006). Conversely, BDE-47 in E. Hudson Bay male beluga blubber (mean = 15 ng·g^{-1} lipid, CI = 5.5–41.5) was much lower (6 times) than BDE-47concentrations reported in blubber of juvenile beluga whales from Svalbard in the Norwegian Arctic (mean = 90 ng·g^{-1} lipid, CI = 60.8–133), (Wolkers et al., 2004). The significance of the apparent differences in PBDE concentrations in belugas from these regions is difficult to assess because of the limited number of samples for Svalbard belugas (n = 4).

PBDE levels in E. Hudson Bay biota are substantially lower than PBDE concentrations reported in biota from more urbanized/industrialized marine systems (She et al., 2002; Rayne et al., 2003; Lebeuf et al., 2004; Rayne et al., 2004; Elliott et al., 2005). For example, the mean BDE-47 concentration in E. Hudson Bay Arctic cod (23 ng·g^{-1} lipid) was 8 times lower than the BDE-47 concentration in Columbia River whitefish from western Canada (190 ng·g^{-1} lipid), (Rayne et al., 2003). Mean BDE-47 concentrations observed in E. Hudson Bay male beluga blubber (15 ng·g^{-1} lipid) were 15 to 140 times lower than mean BDE-47 in St. Lawrence male beluga blubber (210 ng·g^{-1} lipid) (Lebeuf et al., 2004), southern resident male killer whales from British Columbia (450 ng·g^{-1} lipid), (Rayne et al., 2004) and male harbour seals from San Francisco Bay (2040 ng·g^{-1} lipid), (She et al., 2002). Mean BDE-47 concentrations measured in liver of eider ducks

Table 3 – Regression results and trophic magnification factors (TMFs) of PBDEs and PCBs in the Arctic marine food web

	Log K_{OW} 25 °C	log[C_B] = $mx+b$	R^2	P value	TMF	95% CI
PBDEs						
BDE-28	6.9	−0.02·(TL) + 0.44	0.0003	0.88	0.96	0.57–1.6
BDE-47	7.3	0.20·(TL) + 0.17	0.095	0.0006	1.6*	1.2–2.0
BDE-49	7.3	0.07·(TL) − 0.35	0.006	0.51	1.2	0.73–1.9
BDE-66	7.4	−0.36·(TL) + 0.90	0.12	0.005	0.44*	0.25–0.77
BDE-100	7.4	−0.02·(TL) + 0.37	0.0004	0.80	0.96	0.72–1.3
BDE-99	7.6	−0.12·(TL) + 0.90	0.02	0.07	0.76	0.57–1.0
BDE-154	7.8	−0.08·(TL) + 0.37	0.005	0.46	0.81	0.47–1.4
BDE-153	7.9	−0.55·(TL) + 0.13	0.003	0.59	0.88	0.54–1.4
PCBs						
PCB-28	5.0	0.45·(TL) − 1.4	0.54	6.1×10^{-18}	2.9*	2.4–3.4
PCB-52	5.9	0.92·(TL) − 2.4	0.57	1.6×10^{-17}	8.3*	6.1–11
PCB-101	6.4	0.99·(TL) − 2.3	0.58	2.9×10^{-12}	9.8*	6.8–14
PCB-138	6.8	1.0·(TL) − 2.1	0.70	3.0×10^{-17}	10*	7.6–13
PCB-153	6.9	1.0·(TL) − 2.2	0.76	6.0×10^{-18}	11*	8.6–14
PCB-180	7.5	1.0·(TL) − 2.7	0.60	4.1×10^{-17}	10*	7.2–14
PCB-195	7.8	0.65·(TL) − 2.7	0.25	2.6×10^{-4}	4.3*	2.0–9.2
PCB-206	8.1	0.71·(TL) − 2.8	0.26	4.3×10^{-5}	5.1*	2.4–11
PCB-209	8.4	0.59·(TL) − 2.6	0.20	2.7×10^{-5}	4.0*	2.1–7.4

* TMF is significantly different than 1 ($P < 0.05$).

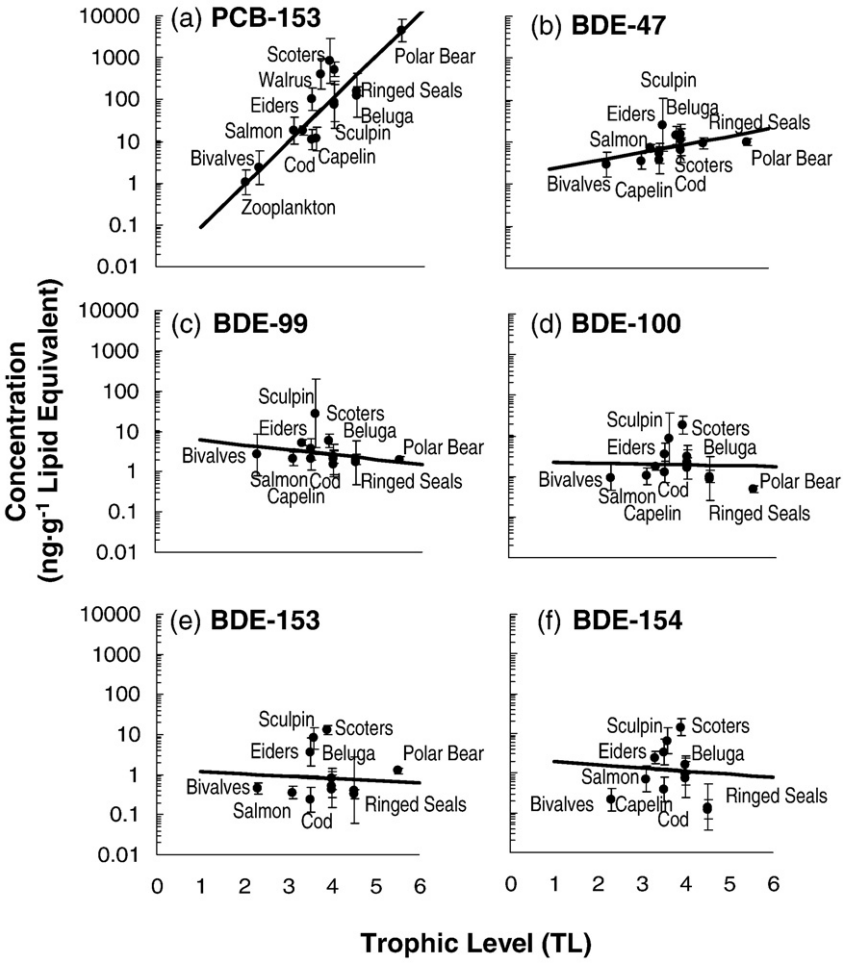

Fig. 2 – Chemical concentrations in organisms of the Arctic marine food web (ng·g^{-1} lipid equivalent) versus trophic level (TL) for (a) PCB-153, (b) BDE-47, (c) BDE-99, (d) BDE-100, (e) BDE-153 and (f) BDE-154. Solid line represents log-linear regression of C_B-TL relationship over the entire food web. PCB-153 concentration shown for polar bears is for E. Hudson Bay animals (Belcher Islands), (Norstrom et al., 1998). PBDE concentrations shown for polar bears are for Western Hudson Bay animals (Muir et al., 2006).

(4 ng·g^{-1} lipid) and white-winged scoters (15 ng·g^{-1} lipid) from E. Hudson Bay were 15 to 300 times lower than BDE-47 concentrations reported in eggs of double crested cormorant (*Phalacrocorax auritus*), great blue herons (*Ardea herodias*) from the Georgia Basin-Puget Sound near Vancouver, Canada, measured at 250 and 1365 ng·g^{-1} lipid, respectively (Elliott et al., 2005).

3.2. *Trophic magnification factors (TMFs)*

Table 3 and Fig. 2 illustrate that strong positive relationships between chemical concentration (log C_B) and trophic level (TL) were observed for recalcitrant PCB congeners. For example, concentrations of PCB-153 in biota increased significantly ($P<0.05$, $R^2=0.76$) with increasing TL (Fig. 2a). A TMF of 11 was observed for PCB-153. TMFs for PCB congeners ranged between 2.9 and 11 (Table 3). This indicates that all recalcitrant PCBs showed clear evidence of chemical biomagnification in the food web. The biomagnification of PCBs in food webs has been reported in many studies. The observed biomagnification of PCBs in this food web implies that the food web sampling conducted as part of this study is sufficient to detect the occurrence of biomagnification in the food web. However, in the same food web and in identical samples used for the PCB analyses, concentrations of the majority of PBDEs did not show

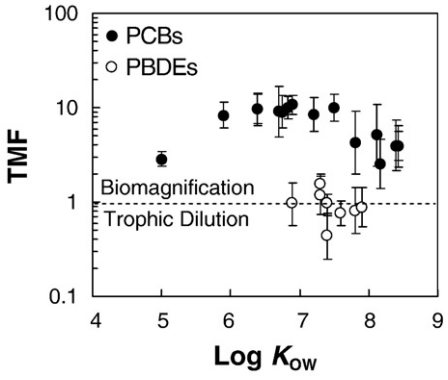

Fig. 3 – Observed TMFs for individual PBDE and PCB congeners in the Arctic marine food web versus log K_{OW}.

significant increases ($P>0.05$) with TL (Table 3), (Fig. 2c–f). An exception was BDE-47 (Fig. 2b), which exhibited slight concentration increases with increasing trophic level ($P<0.05$), with a TMF of 1.6 (CI=1.2–2.0). TMFs of other PBDEs (BDE-28, -49, -66, -99, -100, -153 and -154 ranged between 0.96 and 1.2 and were not statistically different from 1. As the occurrence of biomagnification is defined by a TMF statistically greater than 1, the data indicate that these PBDE congeners do not biomagnify in the food web. Fig. 3 illustrates that TMFs of PCBs increase from 2 to 11 between K_{OW} of 10^5 and 10^7 and drop with increasing K_{OW} when 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. The data demonstrate that Br_3–Br_7 PBDEs exhibit a substantially lower degree of trophic magnification in this marine food web compared to recalcitrant Cl_5–Cl_7 PCBs with comparable K_{OW}s.

3.3. *Bioaccumulation factors (BAFs)*

Calculated BAFs of PBDE and PCB congeners in eider ducks, beluga whales, ringed seals, polar bears and humans (Inuit breast milk) are summarized in Table 4. Fig. 4a shows that lipid equivalent normalized BAFs of PCBs with a K_{OA} less than 10^{10} in all homeotherms increased sharply with increasing K_{OA} and that BAFs were much greater (up to 4 orders of magnitude) than corresponding K_{OA}s. This indicates that these PCBs biomagnify, achieving concentrations in these air-breathing

Table 4 – Calculated bioaccumulation factors (log BAFs) of PBDEs and PCBs in Arctic marine wildlife and humans from the Canadian Arctic

	Log K_{OA} 37 °C [a]	Observed [b] air concentration	Eider duck [c]	Beluga whale [d]	Ringed seal [e]	Polar bear [f]	INUIT women [g]
		(C_{AG}, pg·m^{-3})	Log BAF (C_B/C_{AG})	Log BAF (C_B/C_{AG})	Log BAF (C_B/C_{AG})	Log BAF (C_B/C_{AG})	Log BAF (C_B/C_{AG})
PBDEs							
BDE-17	8.8	0.06	–	9.0	8.5	–	–
BDE-28	9.0	0.2	8.9	9.5	9.3	–	–
BDE-47	9.9	0.29	10.1	10.7	10.5	8.8	9.0
BDE-49	9.8	0.02	–	10.9	9.8	–	–
BDE-66	10.1	0.004	–	10.8	10.5	–	–
BDE-100	10.4	0.01	11.5	11.5	10.9	8.0	–
BDE-99	10.7	0.06	10.8	10.6	10.5	7.9	8.1
BDE-153	11.2	0.001	12.6	11.9	11.5	8.8	8.8
BDE-154	11.3	0.001	12.5	12.2	11.1	–	8.0
BDE-183	11.4	0.001	12.2	10.9	10.7	–	–
PCBs							
PCB-28	7.5	0.57	9.8	9.7	10.1	–	
PCB-52	7.9	1.1	8.8	11.1	10.0	10.7	10.1
PCB-101	8.6	0.49	9.6	11.7	10.9	–	–
PCB-118	8.5	0.53	–	11.4	10.9	11.3	–
PCB-153	9.1	0.18	11.8	12.5	11.4	13.4	12.3
PCB-138	9.2	0.23	11.4	12.2	11.6	12.6	12.0
PCB-180	9.9	0.05	11.7	12.3	11.7	13.6	12.4
PCB-194	10.0	0.07	10.8	11.2	10.5	13.1	–
PCB-206	10.3	0.05	11.0	10.7	10.1	–	–
PCB-209	10.6	0.06	11.0	10.3	9.6	–	–

Also shown are previously reported Canadian Arctic air concentrations (C_{AG}, pg·m^{-3}) and log K_{OA}s (calculated at 37 °C) of PBDEs and PCBs.

[a] Temperature corrected octanol–air partition coefficients (log K_{OA}s) were determined from Harner and Shoeib, 2002, Harner and Bidleman, 1996.

[b] PCB concentrations (pg·m^{-3}) are seasonal means observed gas-phase concentrations (C_{AG}) using high volume samplers at Alert, Nunavut in 1994 under the Northern Contaminants Program (NCP), (Stern et al., 1997). Air concentrations of PBDEs are means from high volume samplers at Alert between 2001 and 2004 (Su et al., 2007). Gas-phase concentrations of PBDEs were determined from total PBDE (gas+particulate) using experimental observations of particle bound fractions at 0 °C (Harner and Shoeib, 2002).

[c] BAFs were calculated as mean lipid equivalent concentration in eider ducks (C_B, mol·m^{-3}) divided by mean gas-phase air concentration (C_{AG}, mol·m^{-3}).

[d] BAFs were calculated as mean lipid equivalent concentration in male beluga whales (C_B, mol·m^{-3}) divided by mean gas-phase air concentration (C_{AG}, mol·m^{-3}).

[e] BAFs were calculated as mean lipid equivalent concentration in male ringed seals from Hudson Strait (C_B, mol·m^{-3}) divided by mean gas-phase air concentration (C_{AG}, mol·m^{-3}).

[f] BAFs of PCBs were calculated as mean lipid equivalent concentration in E. Hudson Bay (Belcher Islands) polar bears (C_B, mol·m^{-3}), (Norstrom et al., 1998) divided by mean gas-phase air concentration (C_{AG}, mol·m^{-3}). BAFs of PBDEs were calculated as mean lipid equivalent concentration in Western Hudson Bay polar bears (C_B, mol·m^{-3}), (Muir et al., 2006) divided by mean gas-phase air concentration (C_{AG}, mol·m^{-3}).

[g] BAFs were calculated as mean lipid equivalent concentration in Inuit breast milk from northern Quebec (C_B, mol·m^{-3}), (DIAND, 2003; Muckle et al., 2001) divided by mean gas-phase air concentration (C_{AG}, mol·m^{-3}).

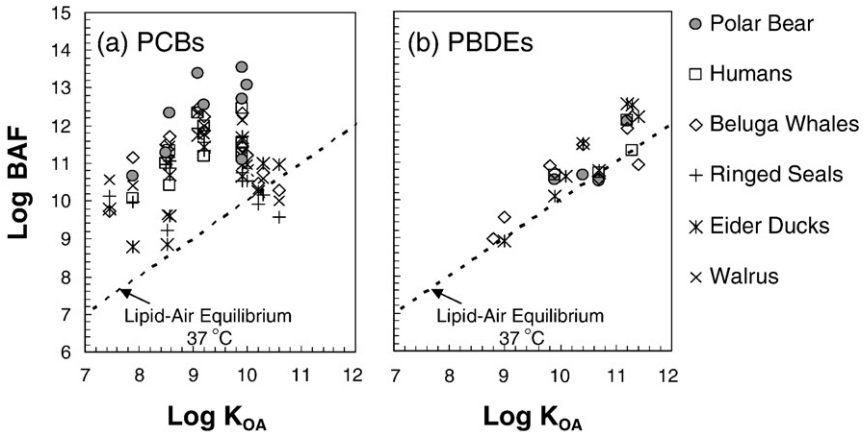

Fig. 4 – Logarithms of the bioaccumulation factor (log BAFs) in Arctic marine wildlife and humans for (a) PCBs and (b) PBDEs versus log K_{OA} (calculated at 37 °C). Dashed line represents the lipid–air equilibrium predicted by chemical K_{OA} at an assumed core body temperature of 37 °C.

animals that greatly exceed lipid–air equilibrium concentrations at 37 °C. PCBs with $K_{OA}>10^{10}$ (Fig. 4a) do not show this relationship and BAFs fall sharply with increasing K_{OA}, which may reflect the reduced dietary uptake rates of these congeners. Fig. 4b shows that BAFs of PBDEs also increase with increasing K_{OA} but are generally equal to corresponding K_{OA}s (at 37 °C) over the entire range of K_{OA}. This indicates that PBDE concentrations in these air-breathing animals are close to expected lipid–air equilibrium concentrations and are not subject to a magnification process, which can elevate the concentration above the equilibrium value. The lack of a drop in the BAFs for PBDEs with a $K_{OA}>10^{10}$ indicates that there is no apparent maximum K_{OA} which prevents the bioaccumulation of the PBDE congeners studied here.

3.4. *Bioaccumulation behaviour of PBDEs*

The high degree of biomagnification for Cl_5–Cl_7-PCBs (K_{OW} range 10^5–10^7) is generally explained by the efficient dietary assimilation and slow elimination rates of those compounds. For example, dietary absorption efficiencies (E_D) of Cl_5- to Cl_7-PCBs are typically between 50–80% in fish and 90–100% in birds and mammals (Kelly et al., 2004) and chemical half-lives ($T_{1/2}$) of recalcitrant PCBs such as PCB-153 in organisms can exceed 1000 days (Mackay et al., 1992). The comparative analyses of TMFs and BAFs of PBDEs and PCBs (Figs. 3 and 4) indicate that PBDEs are absorbed by homeotherms and accumulated but do not biomagnify in the food web. The lack of PBDE biomagnification in the E. Hudson Bay marine food web suggests that PBDEs exhibit lower dietary absorption efficiencies and/or greater biotransformation rates than PCBs. Previous studies in fish have indeed shown very low E_Ds for BDE-153 (4%) in juvenile carp (Stapleton et al., 2004a) compared to PCBs. Biotransformation has also been observed by Stapleton et al. (2004b) who reported *in vivo* debromination of BDE-99→BDE-47 and BDE-183→BDE-154 within the intestinal tract of common carp, and by Kierkegaard et al. (2001) and Stapleton et al. (2004c), who showed debromination of BDE-209 to BDE-154 and several unidentified Br_5–Br_8-PBDEs in pike (*Esox lucius*) and carp (*Cyprinus carpio*). It has further been shown that hydroxylated metabolites of PBDEs (OH-PBDEs) can be formed in biota. For example, formation of OH-PBDEs following BDE-47 exposure has been demonstrated in laboratory studies with fish and rats (Kierkegaard et al., 2001; Malmberg et al., 2005). OH-PBDEs have also been reported in tissues of wildlife, including Arctic glaucous gulls (*Larus hyperboreus*) and polar bears (*Ursus maritimus*), (Verreault et al., 2005).

While debromination acts to enhance PBDE depuration of higher brominated congeners, it also acts to slow the depuration of the lower brominated congeners such as BDE-47 due to the formation of these lower molecular weight reaction products. This may explain why the TMF of BDE-47 was among the highest observed for PBDEs. The relative enrichment of BDE-47 compared to BDE-99 in higher trophic animals has previously been observed in other food webs (Sellström et al., 1993; Boon et al., 2002; Wolkers et al., 2004). Elevated BDE-47 tissue burdens in organisms are of toxicological importance due to the higher toxicity of BDE-47 compared to higher brominated congeners (e.g., BDE-209), (Darnerud, 2003). The accumulation 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 (Hallgren and Darnerud, 2002). While our study did not observe biomagnification of PBDEs, it is unclear whether OH-PBDEs can biomagnify in food webs.

Congener-specific biotransformation of PBDEs undoubtedly plays an important role in the bioaccumulation behaviour of PBDEs. Species-specific differences in PBDE biotransformation rates may be a key factor causing the wide ranging estimates of PBDE biomagnification observed in various species of fish and wildlife (Sellström et al., 1993; Haglund et al., 1997; Boon et al., 2002; Wolkers et al., 2004; Muir et al., 2006). Thus, in addition to uptake and elimination kinetics of PBDEs, the extent of biotransformation and bioformation of a given congener in organisms will greatly influence the observed levels and congener patterns along the food web.

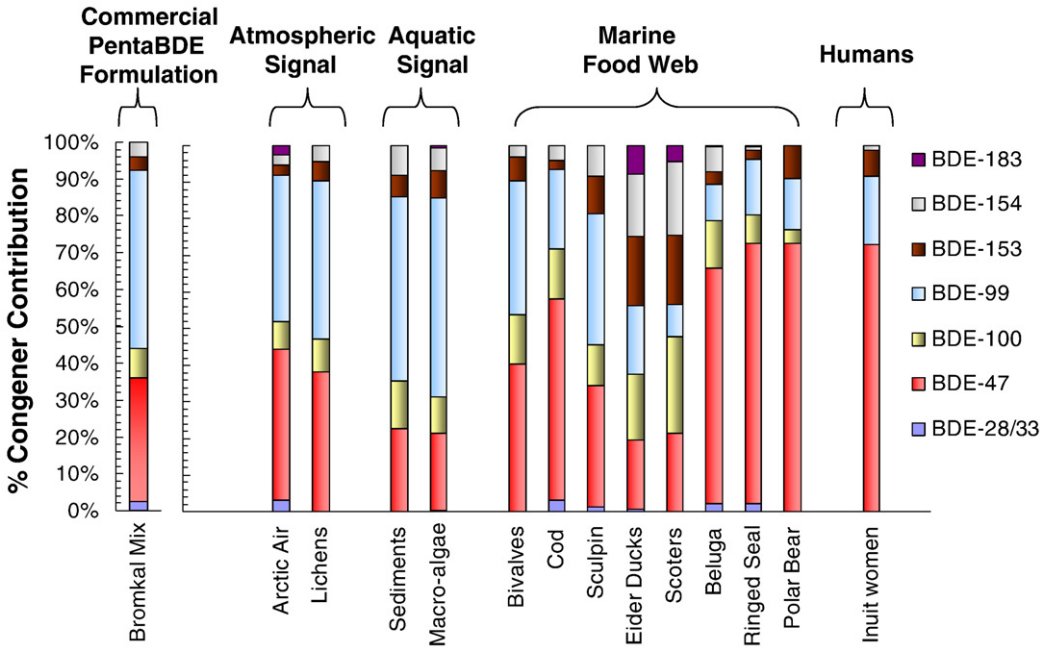

Fig. 5 – Composition of seven major PBDE congeners (% congener contribution) in a commercial PentaBDE technical mixture (Bromkal 70-5DE) compared to the observed congener composition in Arctic air, lichens, sediments, macroalgae, fish, wildlife and humans (breast milk).

3.5. *Considerations for risk assessment*

Fig. 5 illustrates that PBDE congener composition profiles vary substantially among organisms of this Arctic marine food web. The commercial Bromkal® PentaBDE mixture (Bromkal 70-5DE) consists mainly of Br_5-PBDEs (50–62% w/w) and Br_4-PBDEs (24–38%), with the two dominant congeners being BDE-99 (50% w/w) and BDE-47 (35% w/w), (La Guardia et al., 2006). The observed congener composition in lichens (representing the ambient atmospheric signal) and sediments and macroalgae (representing the ambient aquatic signal) are also dominated by BDE-99 (40–50%) and BDE-47 (20–30%), hence comparable to the Bromkal mixture. However, the PBDE congener composition in bivalves, fish, sea ducks, marine mammals and humans is different from the Bromkal mixture in that BDE-47 is the dominant congener rather than BDE-99. For example, BDE-47 is 60–70% of the total PBDE burden in marine mammals and humans (Fig. 5). Common eiders and white-winged scoters exhibit a different PBDE congener pattern than other organisms in that a substantial contribution (35–40%) of the PBDEs is from Br_6-PBDEs (i.e., BDE-153 and BDE-154). These substantial differences in PBDE composition among different food web components should be an important consideration in risk assessments of PBDEs.

4. Summary

PBDE and PCB concentrations were measured in sediments and biota from a Canadian Arctic marine food web. PBDE congeners were detected at low parts per billion concentrations (0.001–30 $ng \cdot g^{-1}$ wet wt). While recalcitrant PCB congeners exhibited a high degree of biomagnification in this food web, PBDE congeners exhibited negligible biomagnification in this food web. Trophic magnification factors (TMFs) for recalcitrant PCBs ranged between 2.9 and 11, while TMFs of PBDEs ranged between 0.7 and 1.6. TMFs of several PBDE congeners (BDE-28, -66, -99, -100, -118, -153 and -154) were not statistically different than 1. BDE-47 exhibited a small degree of biomagnification, increasing slightly with increasing trophic level. However, the TMF of BDE-47 (1.6) was substantially lower than TMFs of recalcitrant Cl_5–Cl_7 PCBs (TMFs ~ 9–11). BAFs of PBDEs were found to be much lower than those of PCBs, which further indicates the lack of biomagnification of PBDEs compared to PCBs. The findings suggest that PBDEs are biotransformed in these marine organisms, likely through debromination and/or cytochrome P450 enzyme mediated oxidative metabolism.

Acknowledgement

We thank M. Kwan, S. Sang, B. Doidge, D. Muir, A. Morin, M. Fischer, T. Fraser, N. Crewe and M. Gibbs and acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) and Environment Canada's Northern Ecosystems Initiative (NEI) for financial support, Fisheries and Oceans Canada for chemical analysis support and the Northern Quebec Inuit communities of Umiujaq and Inukjuaq for assistance with the collection of field samples.

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