Trophic transfer of some brominated flame retardants in a Lake Winnipeg food web

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Intoduction

Perhaps the most studied family of flame retardants are the ones based on bromine. Brominated flame retardants (BFRs) are a structurally diverse group of chemicals incorporated into a variety of consumer and industrial products to increase their flame-resistance. BFRs are either aromatic, aliphatic, or cycloaliphatic compounds containing between 50 to 85% bromine by weight [1]. To date, the bulk of the research done on BFRs has focused on polybrominateddiphenyl ethers (PBDEs). More recent research efforts have been given to hexabromocyclododecane (HBCD)[2-4] as reports suggest that HBCD may be replacing some PBDE formulations in Europe.

Lake Winnipeg is the tenth largest lake in the world with an estimated surface area of 25×10^3 km^2. Water enters the lake from as far away as the eastern slopes of the Rocky Mountains, NW Ontario near Lake Superior and the northern tips of South Dakota. The watershed is home to an estimated 5.6 million people. The south basin of Lake Winnipeg is home to many towns and cottage communities. Walleye (pickerel), whitefish and sauger are the main fish supporting the economic fishery of the lake.

The objectives of this study were to examine the extent of bioaccumulation and trophic transfer of brominated flame retardants (PBDEs and HBCDs) in the pelagic food web of Lake Winnipeg. We also report on the detection of bis (tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) in fish. To our knowledge, this is the first report of BTBPE in biota.

Materials and Methods

Standards and reagents. Native and mass labelled ($^{13}C_{12}$ and d_{18})α-, β-, γ-HBCD, chlorinated diphenyl ether (CDE) congeners (CDE-17, 99 and -170), BTBPE and DBDPE were obtained from Wellington laboratories (Guelph, ON, Canada). Distilled in glass methanol, dichloromethane (DCM), hexane, and acetone were obtained from Caledon. (Edmonton, AB, Canada). Optima grade water and methanol were obtained from Fisher Scientific (Nepean, ON, Canada).

Samples. Walleye, whitefish, emerald shiner, burbot, white sucker, goldeye, plankton and clam samples were collected in the south basin of Lake Winnipeg on the CCGS Namao between 2000-2002. 54 L (*n=6*) of water was sampled (in 2004) using a column packed with 50 g of XAD adsorbent. Water was first collected into eighteen 18 L pre-rinsed (with methanol) stainless cans, spiked with the recovery internal standard (18ng of a CDE-17, -99, -170 mixture (10uL of a 1.8 ng/uL solution), and 20ng of ^{13}C α-, β-, γ-HBCD mixture (2ul of a 10 ng/uL solution)) pumped through an inline pre-filter and then onto the head of a prior to XAD column at a flow rate of 400 mL/min.

Biotic analysis. Details of the sample extraction using accelerated solvent extraction has been described elsewhere[5]. Coextracted lipids were removed using an automated gel permeation chromatography column (J2 Scientific, Columbia, Missouri, USA) (29.5 mm i.d x 400 mm) packed with 60 g (dry weight) of 200-400 mesh S-X3 Envirobeads (ABC Instruments, MO). Extracts were further cleaned on a column (300 mm x 10.5 mm i.d.) of reagent-grade Florisil (1.2% deactivated (w/w), 8 g, 60-100 mesh size, Fisher Scientific). PBDEs were eluted using 40 mL of hexane followed by 30 mL of hexane:DCM (85:15, F1); HBCD and BTBPE were eluted using 7 mL of hexane:DCM

(85:15) followed by 50 mL of hexane:DCM (50:50, F2). F2 was reconstituted in isopropanol and both extract were then reduced in volume, F1 to 100 µL and F2 to 200 µL. F1 was then spiked with 10 mL of 2ng/uL aldrin, and F2 was spiked with 5 µL of 1 ng/µL d_{18} α- and γ-HBCD labelled instrument performance matrix internal standard. Plankton samples were frozen, sub-sampled then freeze dried and extracted in the same manner as biota samples except that F1 was copper treated before samples were put into GC-vials. HBCD was first analyzed by LC/MS/MS and then BTBPE and PBDE by GC-MS[5,6].

Water analysis. XAD columns were extracted using 200 mL of methanol followed by 300 mL of DCM. The extract was reduced in volume down to ~ 100 mL and spiked with 10 mL of water saturated with NaCl. The sample was extracted three times with 100 mL of hexane in a separatory funnel and the organic layer collected and reduced in volume to 1 mL and cleaned on a column of Florisil. PBDEs were detectable in 54 L of extracted water; 108 L of extracted water were required for analysis of the other BFRs.

Results and Discussion

BFR concentrations in biota. ΣPBDE concentrations in biota from Lake Winnipeg were consistently greater than the other BFRs examined in this study. Mean concentrations of ΣPBDEs ranged from 380 ng/g (lw) in burbot to 11 ng/g (lw) in whitefish. BTBPE, DBDPE and ΣHBCD concentrations were also greatest in burbot with respective concentrations of 1.3, 3.3 and 56.6 ng/g (lw)

Trophic magnification factors. The relative trophic status of Lake Winnipeg pelagic food web was elucidated using stable isotopes. The relative trophic status, as defined by $\delta^{15}N$ is: plankton, white fish→ goldeye, white sucker → burbot, walleye (top predators). Trophic magnification factors (TMFs) have been used to assess the food web magnification for entire food webs and are based on the relationship between $\delta^{15}N$ and contaminant concentration. A significant relationship (p=0.01) was found from the plot of natural log concentration of BDE-209 *vs* trophic level (TL, based on $\delta^{15}N$-values) for the Lake Winnipeg food web (Figure 1). TMFs for some other BFRs examined in this study are shown in Table 1.

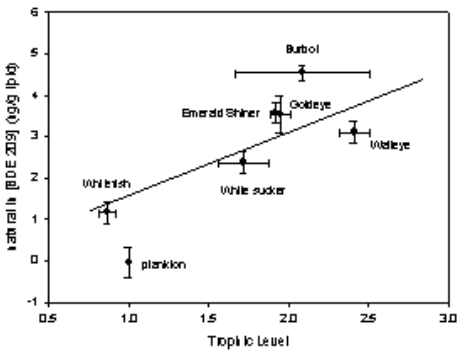

Figure 1. Mean (± standard error) ln BDE 209 concentration (ng/g, lipid and control corrected) - trophic level relationship (± standard error) for the Lake Winnipeg food web. Regression analysis: ln [BDE 209] = 2.2804 (TL) – 1.2225 (r^2= 0.7359, p = 0.01)

TMF values shown in Table 1 suggest that HBCD, certain PBDEs and DBDPE are biomagnifying within the food web. The calculated TMFs for total HBCD in Lake Winnipeg (3.1) was ~ 2 x smaller than that observed in the Lake Ontario (6.3) food web[2].

Table 1. TMF values for some BFRs in the Lake Winnipeg food web[a].

	a-HBCD	b-HBCD	g-HBCD	Total HBCD	DBDPE	BDE 47	BDE 99	BDE 100	BDE 154	BDE 209	Total PBDE
TMF	2.3	2.2	4.7	3.1	17.3	5.2	1.5	2.4	2.1	9.8	3.6
r^2	0.33	0.32	0.51	0.44	0.68	0.46	0.02	0.19	0.20	0.74	0.39
p-value	0.18	0.32	0.07	0.10		0.09	0.78	0.32	0.32	0.01	0.13

[a]TMFs were calculated using the model in natural ln concentration (lipid weight basis) = a + b(TL).

Predator/Prey Biomagnification Factors (BMFs). Table 2 presents lipid corrected BMFs of individual predator/prey feeding relationships. Calculated BMFs suggests that that HBCD, PBDEs and BTBPE all biomagnify

between certain feeding relationships. The individual BMF values are greatest for all three of these chemicals between the goldeye to whitefish predator-prey interaction. DBDPE was not included in this table as DBDPE was only detected in five species: walleye, goldeye, emerald shiner, burbot and whitesucker.

Table 2. BMFs for some BFRs in the Lake Winnipeg food web[a].

Predator/ prey	a-HBCD	b-HBCD	g-HBCD	BDE 47	BDE 99	BDE 100	BDE 153	BDE 209	Total PBDE	BTBPE
Walleye: whitefish	5.35	2.36	4.07	8.92	1.73	5.53	4.56	6.85	4.90	3.96
White suckers: Plankton	0.42	0.65	2.84	6.10	0.07	3.37	2.16	9.92	2.44	0.36
Burbot:white suckers	4.29	10.00	11.20	0.62	16.78	0.64	0.97	8.20	1.60	6.00
Goldeye: whitefish	7.03	2.05	4.81	46.14	78.31	56.62	74.45	11.55	34.37	2.24

[a]BMFs were calculated based on the ratio of the mean concentration in the predator to mean concentrations in the prey.

BFR concentrations in water. Mean water concentrations (± standard error, dissolved phase) of a-, b-, g-HBCD were 10 ± 4, 1.0 ± 0.5, and 2 ± 2 pg/L, respectively (*n=3*). DBDPE was below detection limits while BTBPE had a mean water concentration of 2 ± 1 pg/L (*n=3*) and BDE 209 had the highest concentration of the PBDEs (20 pg/L (*n=6*)); total PBDE concentration in the water was 67 ± 5 pg/L. ΣPBDE concentrations Lake Winnipeg water were 2 times smaller than concentrations in Lake Michigan water collected in 1999 (158 pg/L)[7]. BDE-209 concentrations in this study were in good agreement with those from the South Bay of the San Francisco estuary (range: 12 to 74 pg/L) [8].

An attempt was made to determine whether chemical concentrations of BDEs in the plankton were in equilibrium with those in water by plotting log bioaccumulation factors (BAFs, ratio of lipid corrected concentrations in the fish divided by concentration of chemical in the dissolved phase) versus the log K_{ow}. Log BAFs were well below the 1:1 equilibrium and would suggest that no biomagnification is occurring between plankton and the water.

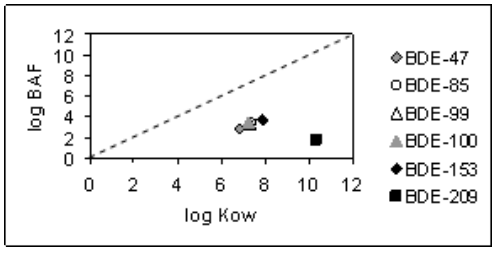

Figure 2. Relationship between log BAFs and measured plankton and water concentrations.

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