Hexabromocyclododecane (HBCD) isomers and brominated diphenyl ether (BDE) congeners in fish from Lake Winnipeg, Manitoba (Canada)

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INTRODUCTION

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 polybrominated diphenyl ethers (PBDEs). Part of the research appeal of these compounds is that they are similar in many ways to polychlorinated biphenyls (PCBs). 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.

MATERIALS AND METHODS

Extraction and clean-up of environmental samples. Extraction of HBCD and PBDEs from samples is done by accelerated solvent extraction (ASE). 100 mL ASE extraction cells are packed with ~20 g of dry-ice homogenized biota mixed with 10g of pre-cleaned pelleted diatomaceous earth (600°C, 6hrs). Cells are then packed with pre-cleaned Ottawa

Sand (600°C, 6hrs) to remove any dead volume. Recovery internal standards consisting of the three isomers of $^{13}C_{12}$-HBCD (10 µL of a 1 ng/µL solution) and three PCDE isomers (10 µL of a 1 ng/µL solution) are spiked into the ASE cell. Lipids are removed from biotic extracts using gel permeation chromatography (GPC). A GPC column packed with BioBeads (SX-3, 60 g) is eluted with 50:50 dichloromethane (DCM):hexane. Two fractions (F1, 2) are collected off the GPC: 150 mL fraction contained the lipids (F1), and F2, 200 mL contained PBDEs and HBCDs. Lipid free extracts and the sediment extract are then clean-up on a Florisil column (1.2% deactivated, 8 g, 300 mm × 10.5 mm i.d). Two fractions are collected: F1, 32 mL of hexane and 25 mL of DCM:hexane (15:85) contained PBDEs, and F2, 70 mL of DCM:hexane (15:85) contained HBCDs. F1 is exchanged into isooctane and concentrated to 150 µL, spiked with a known amount of aldrin (10 µL of a 1 ng/µL solution) and injected onto the GC/MSD. F2 extracts are exchanged into methanol and spiked with 5 ng (1 µL of a 5 ng/µL solution) of each d_{18}–HBCD to act as an instrument performance internal standard and then concentrated to a final volume of 200 µL and injected onto the LC/MS.

GC/MSD. All analyses were performed on an Agilent 5973 GC-MSD fitted with a 10m × 0.25mm id (0.25µm film thickness, J&W Scientific, CA). UHP helium was used as the carrier gas at a flow rate of 2 mL/min. Splitless injections of 2 µL were made by a 7683 Agilent autosampler with the injector set isothermally at 280°C. The initial oven temperature was set at 90°C with no hold time, ramped at 20°C/min to 310°C and held for 5 minutes. Quantitation was performed in the negative chemical ionization mode under selected ion monitoring conditions (SIM) using the $[Br]^-$ ions (*m/z* 79, 81) using an external standard for each reported congener. Source and quad temperatures were both set to 150°C. Confirmation was determined using the electron ionization mode under SIM conditions.

RESULTS AND DISCUSSION

PBDEs. Mean ΣPBDE (sum of 39 congeners) concentrations ranged from 11 ng/g (lw) in whitefish to 380 ng/g in goldeye. Mean concentrations in walleye (78 ng/g, lw) were approximately two times lower than that in sauger (150 ng/g, lw) and three times lower than in perch (212 ng/g, lw) and burbot (240 ng/g, lw). No correlation was found between ^{15}N–values and concentration.

On a congener basis, BDEs–28/33, –47, –66, –100, –99, –153, –154 and –209 were consistently detected in all the fish species. The concentration profiles of some of the major congeners are shown in Figure 1. BDE-209 accounted for the bulk of body burdens of PBDEs in walleye, perch, burbot and whitefish.

Interestingly, BDE–140 (2,2',3,4,4',6'), a known metabolite of BDE-209 in juvenile lake trout, was detected in all species of fish from this study [5]. Mean concentrations of BDE–140 in perch and goldeye were 0.13 and 0.9 ng/g (lw), respectively.

HBCD. All three HBCD isomers were detected in all the fish species from Lake Winnipeg. Mean ΣHBCD concentrations ranged from 3 ng/g (lw) in whitefish to 78 ng/g (lw) in burbot. Concentrations of HBCD in the other fish species were similar and ranged from 9 ng/g (lw) in sauger to 14 ng/g (lw) in walleye. Mean ΣHBCD concentrations in whitefish and walleye from Lake Ontario were 92 and 40 ng/g (lw), respectively, are significantly higher than that found for the same fish species from Lake Winnipeg.

Similar to PBDEs, no correlation was found between HBCD concentrations and ^{15}N–values. This is in contrast to the Lake Ontario food web study by Tomy *et al*. (2004) in which a significant relationship was found between trophic level (a numerical value determined from ^{15}N) and HBCD concentration.

The isomer distribution of α– and γ–HBCD in fish analyzed in this study are shown in Figure 1. The β–isomer was consistently detected at much lower levels than the α– and γ–isomers. The distribution of α– and γ–isomers varies among species, whereas in Lake Ontario food web, the α–isomer was consistently higher than the γ–isomer.

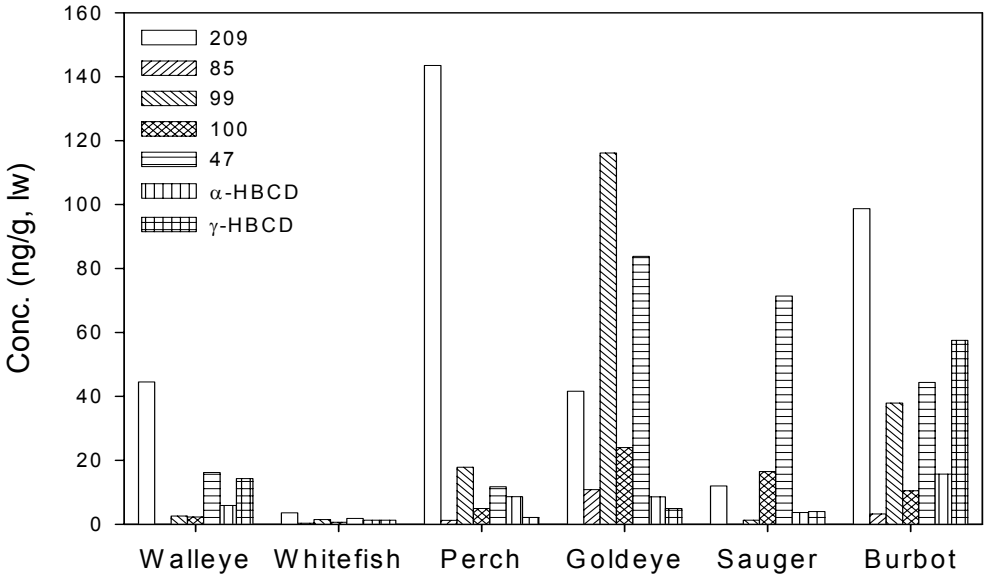

Figure 1. Concentrations profiles of the major BDE congeners and HBCD isomers in fish from Lake Winnipeg.

PBDEs and HBCD levels compared to chlorinated organic compounds. Table 1 presents the mean concentrations of PBDEs and HBCDs determined in this and the concentrations of PCBs, DDT and total chlordane (CHL) reported by Stewart *et al*. [6].

Mean ΣPBDEs and ΣHBCD levels are consistently lower than that of ΣPCBs and ΣDDT in all the fish species. In fact, in some instances, the differences are orders of magnitude.

Compared to ΣCHL, ΣPBDEs levels are only lower walleye; in perch and sauger, however, ΣPBDE levels are three and two times higher than ΣCHL, respectively.

Table 1. Levels of PBDEs, HBCDs (this study) and other chlorinated organic compounds expressed in ng/g lw[a].

	ΣPBDEs	ΣHBCD	ΣPCBs	ΣDDT	ΣCHL
Walleye	78	14	2077	646	147
Whitefish	11	3	--	--	--
Perch	212	12	1083	461	68
Goldeye	381	15	--	--	--
Sauger	150	9	476	243	62
Burbot	240	78	--	--	--

[a]Concentrations of PCBs, DDT and CHL (chlordane) taken from Stewart *et al*. [6]

CONCLUSIONS

This is the first report of brominated flame retardants in the pelagic food web of Lake Winnipeg. PBDE levels were higher than HBCD but much lower than PCBs. The dominant congener in many of the fish species analysed was BDE-209. BDE-140, a bioformed product of BDE-209 [5], was also detected at low ng/g levels in all the species of fish examined. Of the three HBCD isomers, the β–isomer was consistently lower than α– and γ–isomers.

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