FOOD WEB BIOMAGNIFICATION OF BROMINATED DIPHENYL ETHERS IN TWO GREAT LAKES FISH COMMUNITIES

D. Michael Whittle, D. Cameron MacEachen, David B. Sergeant and Michael .J. Keir

Department of Fisheries and Oceans, Great Lakes Laboratory for Fisheries & Aquatic Sciences, Burlington, ON. L7R 4A6

Introduction:

Polybrominated diphenyl ethers (PBDEs) have been previously reported in North American marine mammals [1], birds and bird eggs [2] and in Great Lakes fish [3]. In each of these studies the intent was to examine bioaccumulation of PBDEs in biota at the top of the food web surveyed. In this study, the objective was to compare the bioaccumulation and biomagnification of 40+ PBDE isomers through various trophic levels of two Great Lakes fish community food webs. The two Great Lakes systems monitored, Lake Michigan and Lake Ontario, traditionally have the highest level of persistent organic contaminants reported in fish communities of all the Great Lakes. Previous retrospective analyses of archived samples of lake trout from Lake Ontario documented an exponential increase in PBDE levels over the period 1978 to 1998 [4]. The accumulation pathways for several homologue groups differed among the various food web constituents both within each lake and between the two lake ecosystems studied. Biomagnification factors (BMFs) for prey species to lake trout ranged from > 27 to < 5 for food webs from both lake systems.

Materials & Methods:

Sample Collection:
At offshore stations in Lake Ontario and Lake Michigan, samples of lake trout (*Salvelinus namaycush*) , a top predator fish species and alewife (*Alosa pseudoharengus*), slimy sculpin (*Cottus cognatus*) and smelt (*Osmerus mordax*) representing major diet items of lake trout, were collected via bottom trawls and gill nets and immediately frozen whole on dry ice. In the laboratory, all lake trout were homogenized as individual whole fish. The forage fish species were composited in groups of 5 similar sized whole fish prior to homogenization.

Analyses:
Fish tissue homogenates, 10 g wet weight each, were ground with anhydrous sodium sulfate, poured into a chromatographic column spiked with 20 µl of 100-150 pg/µl ^{13}C labeled brominated diphenyl ether surrogate mixture and eluted with 300 ml of dichloromethane (DCM). Lipids were removed via automated gel permeation chromatography (GPC) using a 1:1 DCM:hexane elution solvent. The first 150 mL was discarded and the last 150 mL was collected. Fractionation was accomplished using 3% deactivated silica gel columns, eluted with 100 mL of DCM, as well as activated micro-alumina columns; eluted with 5 mL hexane and 10 mL toluene. Samples were evaporated to dryness at room temperature in autosampler vials and 20 µL of performance standard was added prior to analysis by high-resolution mass

spectrometry. Analyses of PBDEs was carried out on a VG AutoSpec-Q mass spectrometer connected to a Hewlett-Packard 5890 GC equipped with a CTC A200s autosampler. Gas chromatographic separation prior to MS was achieved using a 60 m X 0.25 mm X 0.25 µm Restek Rtx5 capillary column. Sample ionization was performed in electron ionization (EI) mode at an electron voltage ranging between 30 to 40 eV depending on the optimization parameters of the instrument. The mass spectrometer was operated in selected ion monitoring (SIM) mode using 8 descriptors to analyze the PBDE congeners. Samples were quantified by an internal standard using Mass Lynx® and VG OPUS 20/20® software programs, following EPA 8290 QA/QC protocols.

QA/QC:
The criteria for peak identification included acceptable retention times (+/- 0.05 min), peak shape, ion ratios (+/- 15%), method detection limits for each congener (defined as ±3 X the signal to noise ratio as established within each sample), and ^{13}C labelled brominated diphenyl ether surrogate spike recoveries. These recoveries ranged between 60-120% for PBDEs and the method detection limits for PBDEs ranged between 0.06-0.240 pg/g depending on the homologue group and individual congeners. Samples were not blank corrected.

Results and Discussion:

The accumulation pathways for several homologue groups differed significantly among the various food web constituents within each lake and between the two lake ecosystems studied. Tetra BDE (#47) and penta BDEs (#99 & #100) were the most prominent congeners in all trophic levels (Table 1). These are the most common congeners found in a widely used brominated flame retardant. There was significant food chain accumulation with biomagnification factors (BMFs) for forage fish to the top predator species ranging from 3.7 to 21.9. There was a >5 fold difference in the concentration of the sum of BDE congeners accumulated in the 3 forage fish species from Lake Michigan (Figure 1). The concentration differential was less in the three Lake Ontario forage fish species. Age and feeding pattern were significant variables controlling accumulation in lake trout. Age of individual lake trout was significantly correlated ($r^2 > 0.9$) with PBDE accumulation over a range of fish from 4^+ to 11^+ years old.

		Lake Ontario	Lake Michigan
Lake trout	**BDE 99**	4.48	4.33
	BDE 100	4.44	4.29
Smelt	**BDE 99**	3.57	3.07
	BDE 100	3.38	3.04
Sculpin	**BDE 99**	3.50	2.29
	BDE 100	3.33	1.79
Alewife	**BDE 99**	3.56	3.61
	BDE 100	3.49	4.39

Table 1: Log Tetra BDE #99 and Penta BDE #100 Congener Concentration (pg/g wet weight) in Two Great Lakes Food Webs

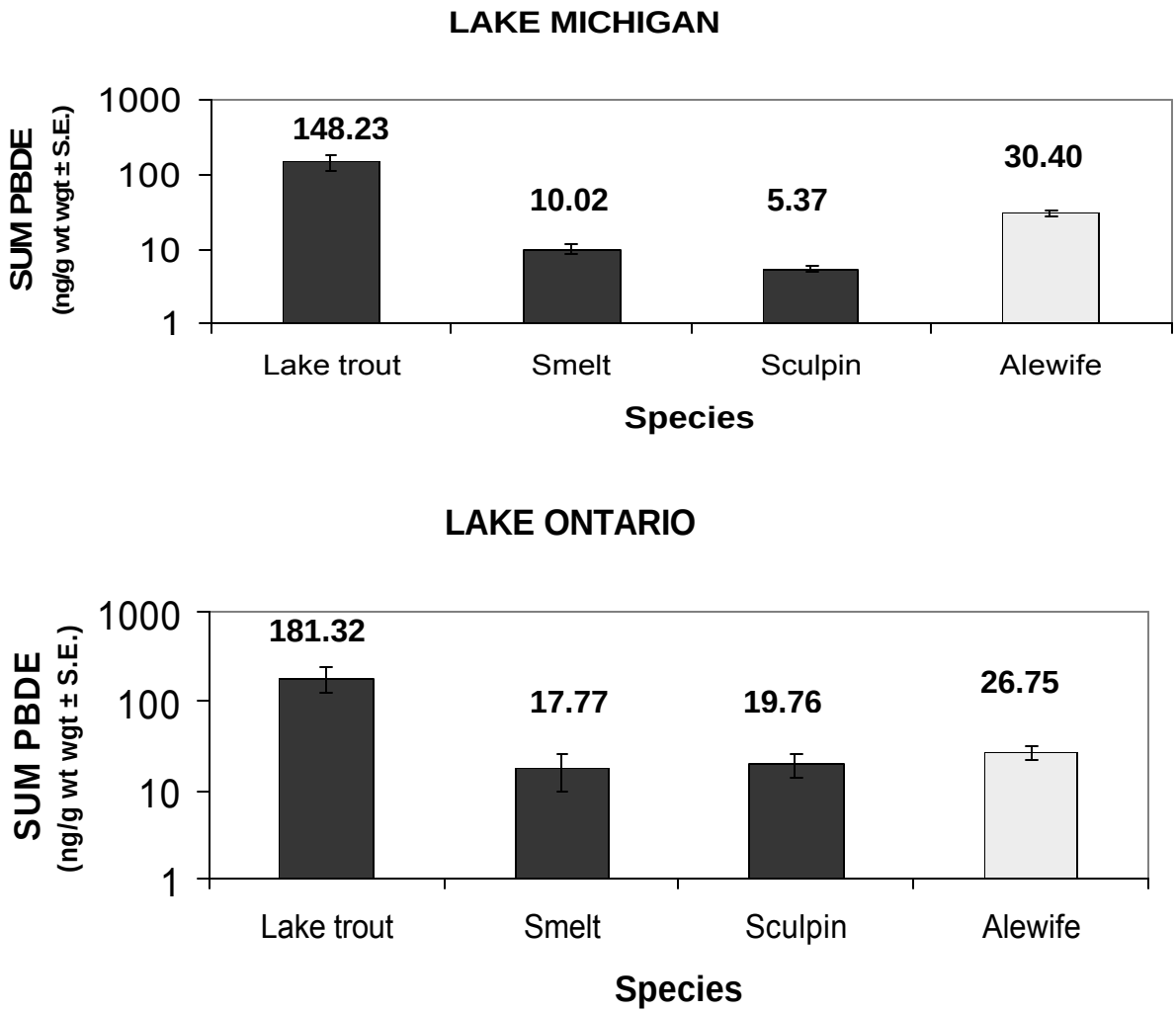

Figure 1: PBDE Concentrations (ng/g, wet weight ± S.E.) in Two Fish Communities from the Great Lakes

In the fish communities of both lakes surveyed, alewife samples consistently had the highest total PBDE concentrations of the three major forage species analysed. Alewife, in comparison to smelt and sculpin, often represent > 95% of the diet of lake trout > 500 mm in length. The proportion of alewife in the diet of adult lake trout from Lake Ontario has increased substantially over the past 5 years. For lake trout between 500 and 600 mm total length, alewife represented 27% of the diet by weight in 1997 increasing to > 90% in 2000 [5]. In lake trout greater than 750 mm total length, alewife accounted for >99% of the diet in samples collected in 1999. Thus, the trend of increasing total PBDE concentrations in Lake Ontario lake trout may be partially accounted for by a diet shift with a proportionally increased consumption of a more contaminated prey species.

Among the major lake trout diet items, alewife represent a planktivous species while sculpin are primarily a benthic feeding fish. Smelt consume a variety of invertebrates and are classified as omnivorous. Additional analyses of major invertebrate dietary components of the three prey species of lake trout with their unique diets would provide data on the predominant pathways of BDE congeners in Great Lakes food webs. These invertebrates would include *Diporeia*, a benthic amphipod and *Mysis*, a macro zooplankton which exhibits a diurnal migration pattern while feeding throughout the water column. Analyses of BDE congener levels in plankton and other invertebrate samples potentially would provide data to explain the elevated concentrations observed in alewife samples.

Acknowledgements:

M. Malecki, M. Moles and S. Blunt provided valued technical assistance in the laboratory for this study. R. Gay and A. Read, Captain and Seaman on the CCGC Shark provided vessel support and technical assistance.

References:

1. Ikonomou, M.G., S. Rayne, M. Fischer, M.P. Fernandez & W.J. Cretney. 2002. Occurrence and congener profiles of polybrominated diphenyl ethers (PBDEs) in environmental samples from coastal British Columbia, Canada. Chemosphere 46 (5), 649-664

2. Simon M., & B. Wakeford. 2001. Analysis of polybrominated diphenyl ethers (BDEs) in Herring Gull eggs collected from Snake Island (Lake Ontario); Retrospective Study 1981-99. In: Alaee, M., C.M.Cannon, J.M. Luross & D.B. Sergeant (Eds.). Proceedings of a Workshop on Brominated Flame Retardants in the Environment. Burlington, ON. June 5-6, 2000. NWRI Contribution No. 01-004. pp 240-258.

3. Luross, J.M., M. Alaee, D.B. Sergeant, C.M. Cannon, D.M. Whittle, K.R. Solomon & D.C. G. Muir. 2002. Spatial distribution of polybrominated diphenyl ethers in lake trout from the Laurentian Great Lakes. Chemosphere 46 (5), 665-672.

4. Whittle, D.M., M.J. Keir & A.A. Carswell. 2002. Trends in Contaminant Burdens of Great Lakes Fish (1977-2001). State of the Lakes Environment Conference (SOLEC) Report. pp 76-89.

5. O'Gorman, R. 2003. U.S. Geological Survey, Great Lakes Science Center, Lake Ontario Biological Station, Oswego, New York, (pers. comm.).