BIOACCUMULATION OF POLYBROMINATED DIPHENYL ETHERS IN THE LAKE ONTARIO PELAGIC FOOD WEB

Mehran Alaee[1], Jennifer M. Luross[2], D. Michael Whittle[2] and David B. Sergeant[2]

[1]Aquatic Ecosystem Conservation Branch, National Water Research Institute, Environment Canada, P.O. Box 5050, 867 Lakeshore Road, Burlington, Ontario, Canada, L7R 4A6

[2]Great Lakes Laboratory for Fisheries and Aquatic Sciences, Department of Fisheries and Oceans, 867 Lakeshore Road, Burlington, Ontario, Canada, L7R 4A6

Introduction

Polybrominated diphenyl ethers (PBDEs) are additive flame-retardants; added to textiles and polymers to reduce their flammability. As such they can be leached out of the polymers and then enter the food chain. Among many requirements for a flame retardant to be used in the polymers are stability and compatibility. Flame-retardants are expected to be stable during the lifetime of the component that they are applied to and as the result these compounds become persistent in the environment. Since most synthetic polymers used in electronic industry are based on petroleum products compatibility requirement results in the usage of hydrophobic compounds, which are susceptible to bioaccumulation and biomagnification. PBDEs, by most definitions, are persistent and are known to bioaccumulate in the environment. [1] Unlike most POPs whose usage is banned or restricted, there is no restriction in the usage of these compounds in North America. In fact, the global market demand for PBDEs rose from 40,000 tonnes in 1992[2] to 67,000 tonnes in 1999[3] and some industry experts estimated that the consumption of brominated flame-retardants will grow by 5 % annually.[4]

Occurrence of PBDEs in the environment was first reported by de Carlo in 1979 Subsequently there have been a number of reports on the occurrence on these compounds in the environment.[5,6] Recent data from Europe and Japan indicated that the levels of PBDEs are on decline, however, similar data from North America have indicated that the levels of these compounds have increased significantly during the past two decades[7,8,9]. One such area is the Great Lakes, where Luross *et al*.[8] reported that the levels of PBDEs increased by 300 fold over the between 1997 and 1997 in lake trout from Lake Ontario. Moisey et al[10] showed 60 fold increase in the level of PBDEs in herring gull eggs between 1981 and 1999 in the Great Lakes.

The dietary uptake of persistent organic pollutants (POPs) is the main route of exposure for animals at upper trophic levels. [11] Furthermore the bioaccumulation and biomagnification of POPs in top predators is influenced by the length and structure of the food web[12]. Therefore, in this study the trophodynamics of PBDEs in Lake Ontario pelagic food web was examined. The bioaccumulation and biomagnification factors are compared to other values for other food webs and are compared to other contaminants such as PCBs in Lake Ontario.

In this study concentration of PBDEs in archived plankton, *Mysis*, *Diporeia*, alewife, smelt, sculpin and lake trout samples collected in 1993 were determined; and trophodynamics of PBDEs in the Lake Ontario pelagic food web was investigated.

Experimental

As part of a Great Lakes binational contaminant survey program, biota samples were collected in eastern Lake Ontario near Main Duck Island by the Department of Fisheries and Oceans (DFO), Great

Lakes Laboratory for Fisheries and Aquatic Sciences (GLLFAS) in Burlington, Ontario, Canada. After capture, fish samples were frozen whole until processing, which involved determining the length, weight, age, and gender Whole fish samples were homogenized using a commercial meat grinder and stored at –25 °C before analysis.

Detailed extraction and cleanup procedures are described previously by Luross et al.[13], with the following modifications: more recent pre-mixed bromodiphenyl ether analytical standard solution consisted of 41 congeners (EO-4980), the bromodiphenyl ether surrogate standard solution (EO-4981), and the bromo/chlorodiphenyl ether performance standard solution (EO-4151), were acquired from Cambridge Isotope Laboratories in Andover, Massachusetts, USA. In brief, samples of whole biota homogenates were ground with anhydrous sodium sulphate. The mixture was spiked with 20 mL of ^{13}C labeled brominated diphenyl ether surrogate mixture, and eluted with 300 mL of dichloromethane (DCM). Gel permeation chromatography (GPC) was used for bulk lipid removal. Fractionation was accomplished using 3 % deactivated silica gel columns followed by activated micro-alumina columns. Samples were evaporated to dryness and reconstituted in 20 mL ^{13}C labeled bromo/chloro diphenyl ether performance standard.

Analyses of PBDEs were carried out separately on a Micromass AutoSpec Ultima mass spectrometer connected to a Hewlett-Packard 6890 GC equipped with a CTC A200s autosampler. The GC injection port was configured for a 1 mL splitless injection, held constant 275 °C. Gas chromatographic separation prior to MS was achieved using a 60 m X 0.25 mm X 0.25 mm Restek Rt_x5 capillary column. The GC column was maintained at 110 °C for 1 min, then ramped at 15°C/min to 180 °C, and further ramped at 2 °C/min to 280 °C and held there for 60 min. Sample ionization was performed in the electron ionization (EI) mode, the source temperature was 270 °C and the resolving power of the analyzer was 10 000.

Results and Discussion

The dietary uptake of hydrophobic contaminants is the major route of exposure in piscivorous fishes and birds[14,15]. Furthermore, the food web length and structure can influence the accumulation of these contaminants in the top predators[11]. It is well known that persistent organic pollutants in the abiotic compartments (air, water, soil and sediment) can enter the food web.[16]

The observed rise in the concentration of PBDEs in lake trout and herring gull eggs in Lake Ontario could be caused by several factors, including increases in the usage of these compounds, changes in the food web composition, and local and long-range atmospheric sources.

Lake Ontario pelagic food web consists of three trophic levels. Lake trout (*Salvelinus namaycush*) are a top predator fish species in Lake Ontario, which feed on forage fish including alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*) and slimy sculpin (*Cottus cognatus*); in turn these fish feed on *Mysis* and *Diporeia* ; which feed on phytoplankton, and zooplankton sampled as netplankton. Previous studies on biota from Lake Ontario showed an increase in the concentration of organochlorine contaminants with each successive level of the food web[13].

The concentrations of PBDEs in the Lake Ontario food web are presented in Figure 1; the concentrations of PBDEs in lake trout from Lake Ontario in 1993 were presented in previous study[8]. Similar to organochlorine contaminants, concentrations of BDE –47, -100, and -153 are increasing at each step up the food chain with biomagnification factors ranging between 7.1 for BDE-99 for biomagnification between netplankton and benthic organisms and 1.7 for BDE-100 for biomagnification between lake trout and forage fish. The exception to this trend was the biomagnification of BDE-99 from benthic organisms to forage fish, which had a biomagnification facto of 0.8. This is an indication of the breakdown of BDE-99, in fact the PBDE profile in plankton, *Mysis* and *Diporeia* resembled to the penta-BDE formulation, which indicates that BDE-99 bioaccumulate in the invertebrates and starts to be metabolized by forage fish.

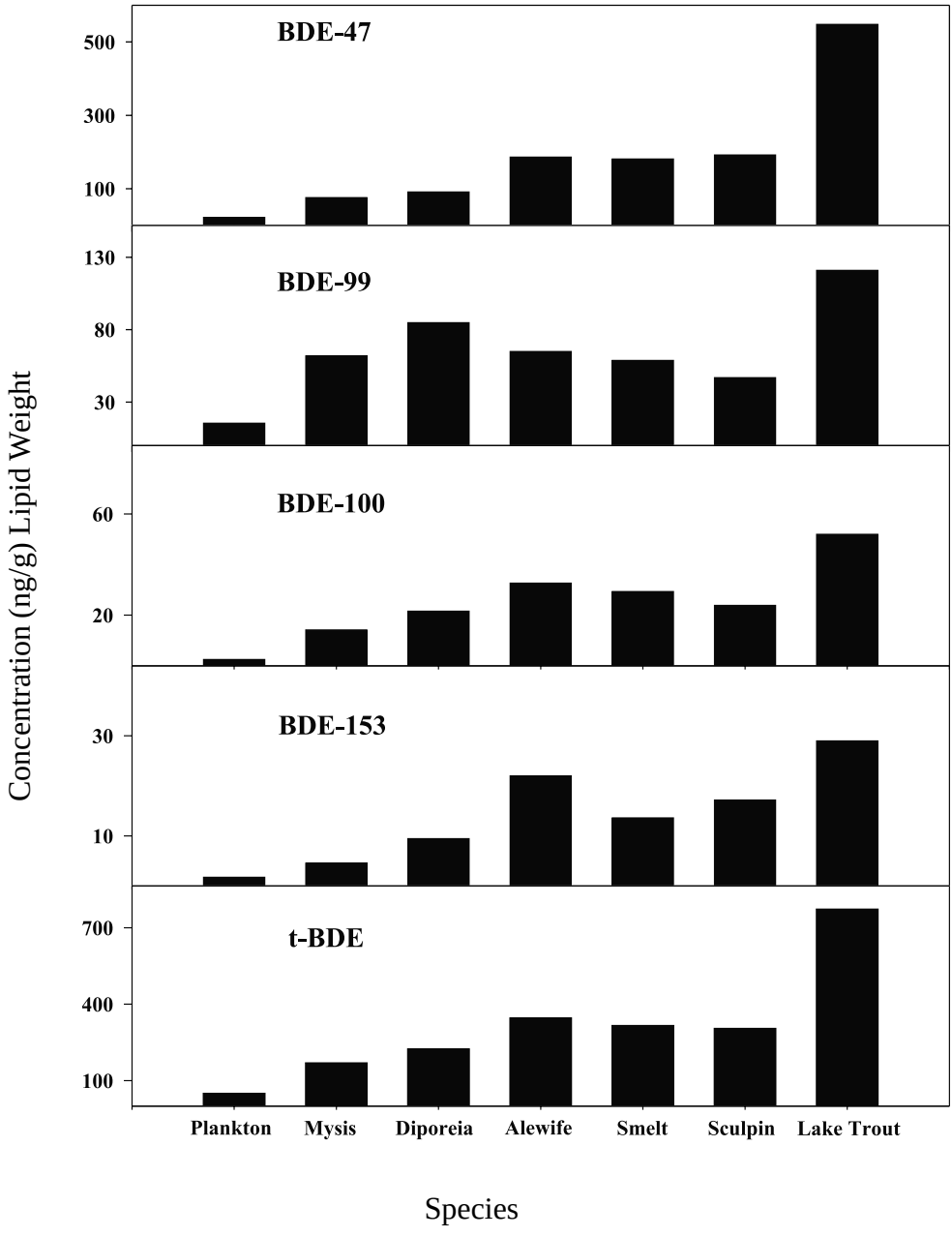

Figure 1. Concentration of PBDEs in Lake Ontario pelagic food web.

Acknowledgement

Funding for this study was provided by the Toxic Substances Research Initiative, a research program of Health and Environment Canada.

References

1. U. Sellström Ph.D. Thesis, Stockholm University, Stockholm, Sweden 1999.
2. G.J. van Esch, 1994. Environmental Health Criteria 162: Brominated Diphenyl ethers. World Health Organisation. Geneva (ISBN 92 4 157162 4).
3. BSEF 2000. http://205.232.112.21/bsef/docs/Major_Brominated.doc, Brussels, Belgium
4. A.H. Tullo, CN&E Dec 4, 2000, pp21-31.
5. C. de Wit, Chemosphere, 46, 583, 2002.
6. J. de Boer, K. de Boer, J.P. Boon, in The Handbook of Environmental Chemistry: New Type of Persistent Halogenated Compounds, J. Passivirta (ed.) Springer-Verlag Berlin Heidelberg, 2000, 61-95.
7. J. She, M. Petreas , J. Winkler P. Visita, M. McKinney, D. Kopec *Chemosphere*, 46, 697-708, 2002.
8. J.M. Luross, M. Alaee, D.B. Sergeant, D.M. Whittle, K.R. Solomon, *Organhalogen Compounds*, 47,73-76, 2000.
9. G.A. Stern, M.G. Ikonomou, *Organhalogen Compounds*, 47, 81-84, 2000.
10. J. Moisey, M. Simon, B. Wakeford, D.Weseloh and R. Norstrom, in The Second International Workshop on Brominated Flame Retardants. L. Asplund et al. editors, pp 153-162, 2001.
11. R.M. Kiriluk.M. R, Servos, D. M. Whittle, G. Cabana, J.B. Rasmussen *Can. J. Fish. Aquati. Sci. 52:2660-2674* ,1995..
12. J.B.Rasmussen, , Rowan D.J., Lean D.R.S. and Carey J.H. *Can. J. Fish. Aquat. Sci.* 47:2030-2038, 1990.
13. J.M Luross, M.Sc Thesis, University of Guelph, Guelph, Ontario, Canada, 2001.
14. B.G. Oliver and A.J Niimi., *Environ. Sci. Technol.*22: 388-397 1988.
15. U. Borgmann and D.M Whittle, *J Great Lakes Res.* 17: 368-381, 1991.
16. S. Sharp and D. Mackay *Environ. Sci. Technol* 34, 2373-2379, 2000.