DISTRIBUTION OF POLYBROMINATED DIPHENYL ETHERS IN THE CANADIAN ENVIRONMENT

M. Alaee[1], J. Luross[2,3], D.B. Sergeant[2], D.C.G. Muir[1], D.M. Whittle[2], K. Solomon[3]

[1] Department of Environment, National Water Research Institute, 867 Lakeshore Road, P.O. Box 5050 Burlington, Ontario, Canada, L7R 4A6
[2] Department of Fisheries and Ocean, Great Lakes Laboratory for Fisheries and Aquatic Science, 867 Lakeshore Road, P.O. Box 5050 Burlington, Ontario, Canada, L7R 4A6
[3]University of Guelph, Guelph, Ontario.

Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardant chemicals that are added to manufactured products including paints, plastics, and textiles[1]. They can be released into environment when the products are discarded [2,3]. The annual production of PBDE in 1992 was 40,000 tons, and it continues to increase.[1] The extensive use of products containing BPDEs has resulted in the release of these compounds into the environment. PBDEs are lipophilic compounds and are shown to bio-accumulate through the food web.[4]

In 1979, the presence of BDE-209 (deca-BDE) in soil and sludge[5] were detected in the areas surrounding plants where PBDEs were manufactured in the United Stated.. Two years later, Anderson and Blommkvist[6] reported the presence of PBDEs in samples collected along Visken River in Sweden. Jansson et. al.[7] first indicated that PBDEs are global contaminants by demonstrating the presence of PBDEs in fish eating birds and marine mammals in samples collected from Baltic Sea, North Sea and Arctic Ocean. PBDE congeners were also observed in marine fish, shellfish, sediment[8], and in air particulate from Japan and Taiwan.[9] PBDEs were also reported in cod liver and herring from the North Sea, and in eels from fresh water systems in the Netherlands[10]. Stafford[11] reported the presence of PBDEs in eggs and tissues of fish-eating birds from 6 states in the U.S and from Ontario, Canada. Stanley et.al.[12] reported the presence of PBDEs in human adipose tissue. Norén and Meironyté[13] found PBDEs in human milk increasing over the past 25 years showing the concentrations PBDEs in breast milk doubling every 5 years.

The majority of the information on the levels of PBDEs are from European environments, while similar information from North America remains limited. Thus , there is a need for the determination of the levels of PBDEs in North American environments. The initial step was to develop an analytical method for the determination of PBDE in environmental samples which was presented last year at Dioxin 98.[14] This analytical procedure was then applied to various environmental samples, such as air, water, sediment and biota. In this report, data obtained from lake trout from the North American Great Lakes and marine mammals from arctic are presented.

Experimental:

Detailed experimental procedure were described preciously.[14] Thus a short description the procedure is given. Custom standard solutions were purchased from Cambridge Isotope Laboratories (Andover, Massachusetts). Anhydrous granular sodium sulfate reagent grade, dichloromethane distilled in glass and hexane 200 chromatography grade were acquired from Caledon Laboratories (Georgetown, Ontario). A 10 g aliquot of the homogenate was transferred

qualitatively to large mortars; and 130 g of anhydrous Na_2SO_4 was added. For marine mammal samples, 1g of adipose tissue was mixed with 10g of anhydrous Na_2SO_4. The mixture was spiked with the $^{13}C_{12}$-Tetra- through octa- chlorodiphenyl ether (CDPEs) surrogate mixture. The samples were eluted with DCM. Samples were concentrated by a combination of rotary evaporation and nitrogen evaporation and the lipids were removed using gel permeation chromatography (GPC).The sample was let evaporate to dryness at room temperature to minimize losses and 20 mL performance standard (100 pg/μL $^{13}C_{12}$ hexa-CDPE and tetra-PBDE) added for analysis. High resolution GC/MS 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.

Results and Discussion: Average concentrations of PBDEs in lipid from the Great Lakes lake trout were 545 ng/g for Lake Ontario, 237 ng/g for Lake Huron and 135 ng/g for Lake Superior. The homologue distribution of PBDEs in lake trout from the Great Lakes are presented in Figure 1. Similarities to other environmental contaminants such as PCBs was shown with lake trout from Lake Ontario having the highest concentrations followed by lake trout from Lake Huron. Lake trout from Lake Superior, a more pristine system, had the lowest concentrations. Tetra and penta PBDEs are the predominant homologue groups. The main congener in the tetra homologue group was 2, 2', 4, 4'-tetra-BDE, which was observed in all lake trout samples from each of the three Great Lakes, followed by 2,2',4,4',5-penta-BDE.[15] These same congeners were also found in Baltic herring, grey and ring seals, as well as osprey in Sweden[16]. Andersson and Blomkvist [6] also found high levels of 2, 2', 4, 4'-tetra-PBDE in pike from Swedish waters.

Concentrations of PBDEs in ring seal and beluga blubber samples are presented in Figure

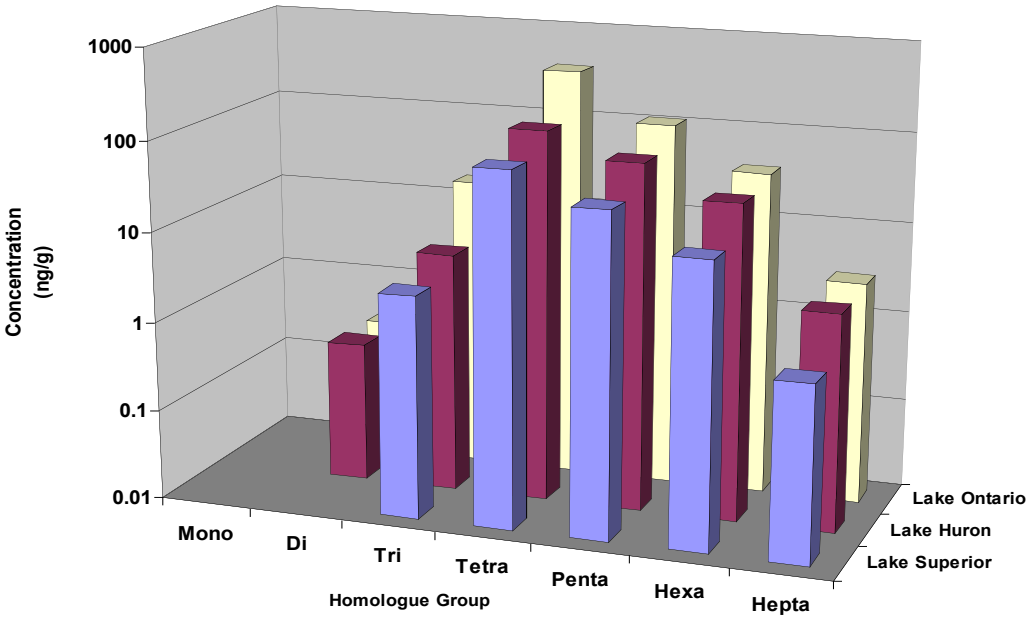

Figure 1. Concentrations of PBDEs (ng/g lipid) in Lake Trout from Lake Superior, Lake Huron, and Lake Ontario

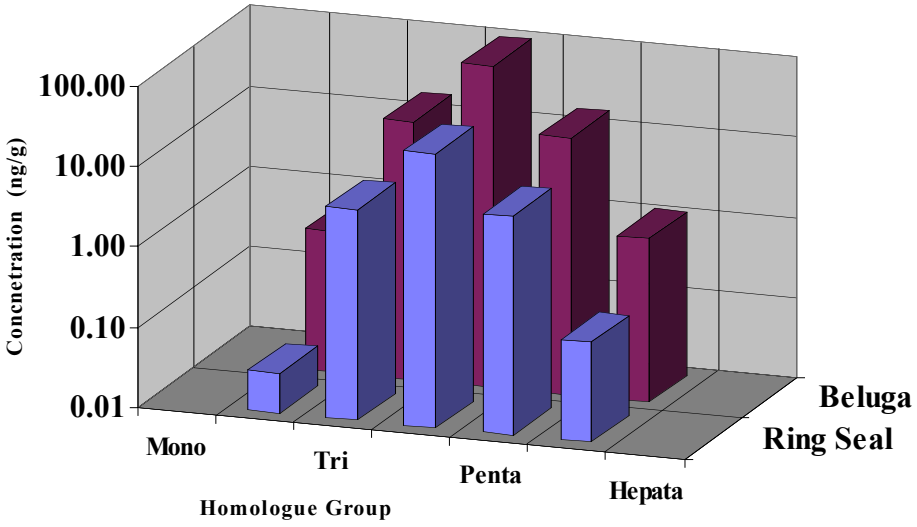

Figure 2. Concentration of PBDEs (ng/g lipid) in marine mammal blubber

2. This study identified PBDEs in marine mammals from the Canadian Arctic for the first time. Average concentrations for female ringed seals were 25.8 ng/g, male ring seals 50.0 ng/g; and average concentration for PBDEs were 81.2 ng/g and 160 ng/g for female and male belugas respectively. Similar to other lipophilic organochlorine compounds, lower concentrations of PBDEs in females marine mammals were found, which can be attributed to excretion of PBDEs via lactation. The congener pattern observed in marine mammals (2,2',4,4' tetra-BDE was the main congener found in the samples followed by 2,2',4,4',5-penta BDE) was consistent with the pattern observed in Great Lakes lake trout. The main homologue present in these samples was the tetra bromo group which was dominated by 2,2',4,4'-tetra-BDE. These results are consistent with those observed by Jansson et. al.[15].

Preliminary results from other studies showed detectable levels of PBDEs in dungeons crab and harbor seals from the strait of Georgia BC, and sturgeon from the Fraser River BC[17]. PBDEs were also detected in air samples from Alert, Northwest Territories[18]; and in wildlife tissue and eggs from Ontario and maritimes[19]. These results suggested that PBDEs are ubiquitous pollutants in the Canadian environment; and there is a need to further investigate the sources and fate of PBDEs in North America.

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