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BIOACCUMULATION OF LEGACY AND EMERGING FLAME RETARDANTS IN THE GREAT LAKES

J. Guo[1], M. Venier[1], A. Salamova[1], R. Hites[1]
[1]*Indiana University*

Introduction

Organobromine and organochlorine flame retardants can be environmentally persistent, and they may be toxic. The most well-known of the brominated flame retardants (BFRs) are the polybrominated diphenyl ethers (PBDEs), and they have been widely detected in sediment, water, fish, herring gull eggs, and air from and near the North American Great Lakes.[1-5] PBDEs have been replaced by several alternative FRs, including 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB), di-(2-ethylhexyl) tetrabromophthalate (BEHTBP), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and decabromodiphenylethane (DBDPE), all of which were found in air,[6] tree bark, and the food web from the Great Lakes.[7,8] Other widely used FRs are the Dechloranes – here called Decs - which are compounds produced from hexachloro cyclopentadiene. The most well-known among the Decs is Dechlorane, a chemical also used in the past as a pesticide under the name Mirex. The most recent category of FRs are the organophosphate esters (OPEs), which have been used in furniture foam, building materials, plastics, and electrical equipment and as plasticizers.[9]

In this study, we measured the concentrations of 83 flame retardants in fish, air, and water from the Great Lakes (see Table 1 for a complete list). The objectives of this study were to investigate the spatial trends of all these compounds in the Great Lakes fish and to examine their distributions between fish and air and between fish and water.

Materials and Methods

Lake trout (or walleye from Lake Erie) were collected in triplicate in 2010 from each of the five Great Lakes as part of the Great Lakes Fish Monitoring and Surveillance Program (GLFMSP). After sampling, the fish were kept frozen at -20 °C. Samples were spiked with surrogate standards and Soxhlet extracted with 1:1 n-hexane in acetone for 24 hrs. The extracts were cleaned up on a Florisil column followed by a gel permeation chromatography column packed with Bio-Beads SX-3. Each fraction was then concentrated, solvent exchanged to n-hexane, blown down to ~1 mL with N_2, and spiked with known amounts of the internal standards. The lipid content was determined gravimetrically using 10% of the extract. BFRs and Decs were analyzed on an Agilent 7890 series gas chromatograph (GC) coupled to an Agilent 5975C mass spectrometer (MS) operating in the electron capture negative ionization (ECNI) mode, and OPEs were quantified on an Agilent 6890 series GC coupled to an Agilent 5973 MS operating in the electron impact mode. Details on the air sample collection and analyses can be found elsewhere.**5** Water samples were collected in each of the Great Lakes, and the results have been previously published.[10]

Results and discussion

Concentrations: Among PBDEs, BDE-47 was the most dominant congener in these fish, air, and water samples, followed by BDE-100 and BDE-99. These relative abundances are similar to those from other studies on Great Lakes fish and herring gull eggs.[2,3] Concentrations of BDE-209 were relatively low in the fish (< 0.1 ng/g lipid) but relatively high in the air samples (mean: 1.8 pg/m3) and water (mean: 6.9 pg/L), presumably because BDE-209 is strongly adsorbed to particles and has a low water solubility. This observation is consistent with atmospheric deposition being the main source of BDE-209 to the Great Lakes.

Most of the alternative BFRs were rarely detected in the fish samples, despite being quite abundant in air and in water samples -see Figure 1. HBCDs were the most abundant alternative FRs in fish and in air (means: 32.5 ng/g lipid and 2.41 pg/m3, respectively). PBEB was the most concentrated non-PBDE FR in water, but its concentrations were generally low in air, and it was barely detected in fish. BEHTBP and EHTBB are found in air and water, but these compounds are not found in fish. We suspect that the levels of BEHTBP in fish are close to our instrument detection limit and that EHTBB was not detected in fish because it is metabolized to 2,3,4,5-tetrabromobenzoic acid, which was not extracted in our procedure.

Among the Decs, DP was found at relatively low concentrations in fish (0.37 ng/g lipid) compared to air and water – see Figure 1. DP is such a large molecule that it may not be soluble in biological lipids, and thus, it may not be bioaccumulative. Although we did not detect Dec604-4 in our fish samples, other Dec604-related compounds such as Dec604-0, Dec604-1, Dec604-2, Dec604-3, and Dec604-Cl4, were all found in the fish with mean concentrations of 1.0, 28, 0.66, 0.34, and 3.5 ng/g lipid, respectively (see Figure 1). Three isomers of Dec604-1 were detected in our fish samples, and the most abundant isomer, presumably the para-substituted isomer, had concentrations higher than those reported by Shen et al. for this compound.[11] The concentrations of Dec604-2 and Dec604-3 reported here were lower than those reported by Shen et al. for Lake Ontario in 1998 or 1999, but our reported concentration of Dec604-0 was higher.[11] The concentrations of most of the Decs compounds in air were relatively low. Apart from DP, the Decs compounds were not measured in water. These results suggest that most Decs are bioaccumulative.

TPRP and TDCIPP were the most abundant OPEs in fish with mean concentrations of 314 and 242 ng/g lipid, respectively. TDCIPP was also the most abundant OPE in water with a mean concentration of 1340 pg/L. TNBP was detected in all fish samples with a mean concentration of 65 ng/g lipid; TNBP was the most concentrated OPE in air and the third most concentrated in water.

Bioaccumulation factors: We have investigated the concentrations we measured in the Great Lakes fish as a function of the concentrations we measured in Great Lakes air and water. We calculated a biota-air accumulation factor (BAAF) and a biota-water accumulation factor (BWAF) and we plotted them against log(KOA) and log(KOW), respectively. The log(BAAF) vs log(KOA) plot suggests three different partitioning mechanisms associated with three regions: log(KOA) < 9 includes protein binding compounds (i.e. OPEs); 9 < log(KOA) < 14 includes lipid binding compounds (i.e. PBDEs and Decs); and log(KOA) >14 includes high molecular weight compounds (i.e. BDE-209, DP, and DBDPE), which have low solubilities in biological lipids. A similar distribution trend was also observed for the fish vas. Water concentrations. This analysis allows us to explain why some compounds are detected in fish but not in air or in water or vice-versa.

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Table 1 Complete name and abbreviations of all the non PBDEs compounds measured in this study

Decs	Decs
Hexachlorophenyl norbornene (Dec604-0)	Dechlorane 601 (DEC601)
Dechlorane Plus mono-adducts (DPMAs)	Undecachloropentacyclooctadecadiene ($Cl_{11}DP$)
Chlordane (Mirex)	Monobromophenyl hexachloronorbornene (Dec604-1)
Dechlorane Plus (DP, syn- and anti)	3,5-Dibromophenyl hexachloronorbornene (Dec604-2)
Chlordecone (Kepone)	Tetrachlorophenyl hexachloronorbornene (Dec604-Cl_4)
Dechlorane 602 (DEC602)	2,4,6-Tribromophenyl hexachloronorbornene (Dec604-3)
2,3,4,5-Tetrabromophenyl-hexachloronorbornene (DEC 604)	4,6-Dibromo-2,3-dichlorophenyl hexachloronorbornene (Cl2Br2Dec604)
Dechlorane 604 component B (DEC604-3)	**Organophosphate Flame Retardants**
Dechlorane 603 (DEC603)	tris(2-Chloroethyl)phosphate (TCEP)
Chlordene Plus (CP)	tris(1-Chloro-2-propyl) phosphate (TCIPP)
Decachloropentacyclooctadecadiene ($Cl_{10}DP$)	tris(1,3-Dichloro-2-propyl) phosphate (TDCIPP)
Brominated Flame Retardants	tri-n-Butyl phosphate (TnBP)
Pentabromoethylbenzene (PBEB)	tris(2-Ethylhexyl) phosphate (TEHP)
Hexabromobenzene (HBB)	Triphenyl phosphate (TPP)
Decabromodiphenylethane (DBDPE)	tri-*o*-Tolyl phosphate (TOTP)
Hexabromocyclododecanes (HBCDs)	tri-*p*-Tolyl phosphate (TPTP)
1,2-bis (2,4,6-Tribromo-phenoxy)ethane (BTBDE)	tri-*m*-Tolyl phosphate (TMTP)
2-Ethylhexyl tetrabromobenzoate (EHTBB)	Tri-isopropyl phosphate (TIPRP)
bis(2-Ethylhexyl) tetrabromophthalate (BEHTBP)	tris-(2-Isopropylphenyl) (TIPPP)
Pentabromobenzene (PBBz)	Tripentyl phosphate (TPEP)
Pentabromotoluene (PBT)	2-Ethylhexyl diphenyl phosphate (EHDP)
Tetrabromo-*p*-xylene (pTBX)	tris(4-*tert*-Butylphenyl) phosphate (TBPP)

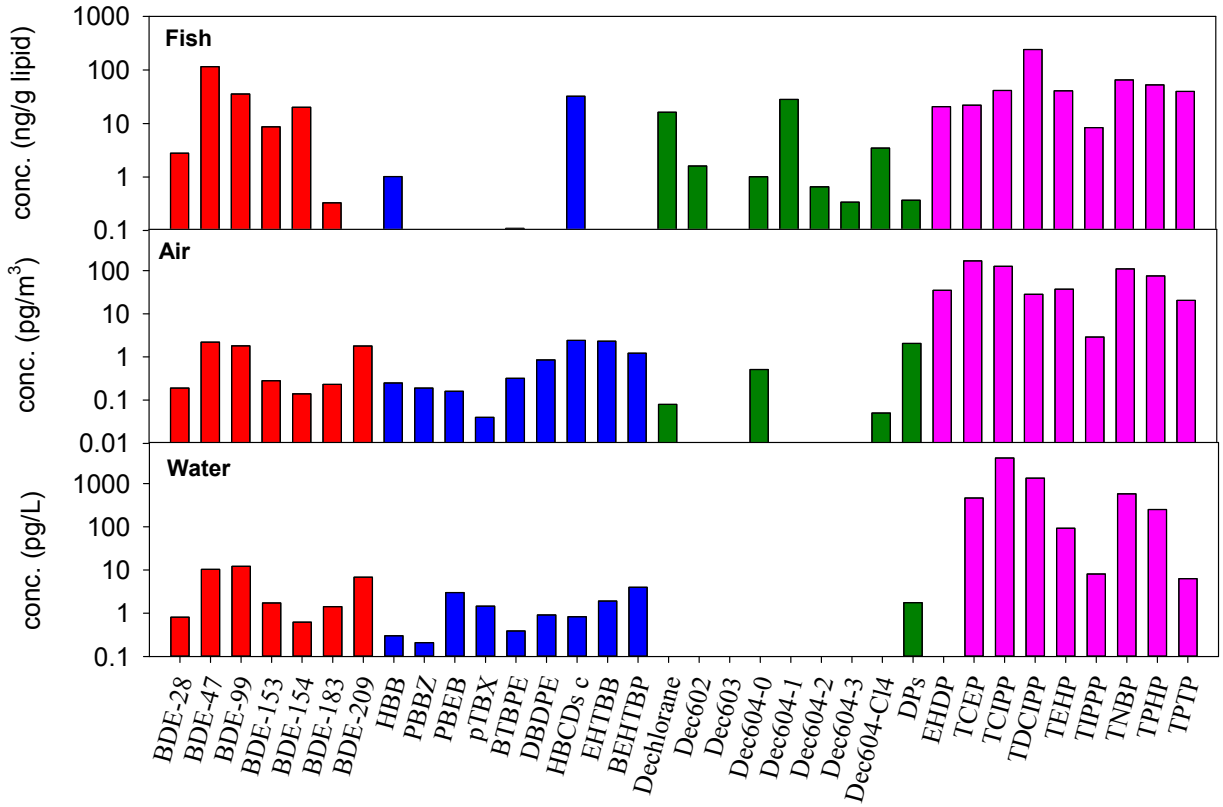

Figure 1. Geometric mean concentrations of the major target compounds in Great Lakes fish, air and water.