DETERMINATION OF LEVELS OF POLYBROMINATED DIPHENYL ETHERS (PBDE) IN FISH FROM EASTERN LAKE ERIE PROVIDING INSIGHTS ON FOOD WEB-MEDIATED TRANSPORT AND BIOACCUMULATION

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Introduction

Polybrominated diphenyl ethers (PBDEs) are used globally in many applications as flame retardants. In recent years increasing levels of these contaminants have been observed in wildlife.[1] The increase is due to the persistent and hydrophobic nature of PBDEs and thus their presence is a current concern for aquatic systems such as the Great Lakes. The occurrence of PBDEs in sediment from the Great Lakes is a well documented issue [2,3] although more recent studies show that levels in fish have been increasing in the last decades. [4,5] Therefore it is imperative to monitor various fish species for these compounds to better understand how food web structure can affect transport and bioaccumulation of PBDEs.

Lake Erie is the smallest of the Great Lakes in volume, but endures the largest impacts from urbanization, agriculture and industry.[6] It has been estimated that the total PBDE-loading in Lake Erie is around 3,400 kg/yr, coming from contaminated water inflows and atmospheric deposition.[2] Eastern Lake Erie has not been extensively studied for persistent organic pollutants related to biota, but this study provides valuable knowledge about currents levels.

PBDEs accumulate in fatty tissues and can be transported to fish allowing for movement to higher tropic levels. The amount of biomagnification in sport fish depends on the complexity of their food web thus it will be affected by the introduction of non-indigenous organisms. The presence of invasive species can create more links in the food web allowing for an increased potential for transport and biomagnification. PBDEs are of concern due to their ability to cause endocrine disruption and neurobehavioral deficits.[7]

The objective of this study is to measure PBDE concentrations at different food web levels in eastern Lake Erie including both native and exotic species. PBDE congener concentration is measured in sport fish (walleye, steelhead trout, and small mouth bass) as well as forage fish (yellow perch, and round gobies). The importance of this study is that it provides information on

the current levels of PBDEs in Lake Erie for a variety of fish species to give insights on the food web pathways for transport.

Materials and Methods

Biota samples were collected for each of the species in Lake Erie from August to October 2009. Five individual walleye *(Sander vitreus),* small mouth bass *(Micropterus dolomieu),* yellow perch *(Perca flavescens),* and ten individual (5 young of the year and 5 older) round gobies (*Neogobius melanostomus)* were collected in the Eastern Basin of Lake Erie. The five individual steelhead trout *(Oncorhynchus mykiss)* were collected in Lake Erie near Dunkirk. The fish were captured by trap net, or electrofishing techniques. Whole fish samples were homogenized individually using a meat grinder for the walleye, steelhead trout, small mouth bass, and yellow perch and in two group composites for the round gobies. Once processed the samples were stored in pre-cleaned glass jars at -20^{o}C until analysis.

Whole body samples were extracted for PBDE analysis using accelerated solvent extraction (ASE). Four grams of the whole fish composite was ground with eight grams of anhydrous sodium sulfate and spiked with a labeled surrogate mix containing ^{13}C-BDE congeners: 3, 15, 28, 47, 99, 153, 154, 183, 197, 207, and 209 (Welligton Laboratories). The fish mixture was then loaded into a 33-mL ASE cell containing Whatman circular (1.983-cm diameter) glass microfiber filter from Dionex Corporation (Sunnyvale, CA), 4 grams of anhydrous sodium sulfate and Hydromatrix™. The extraction was performed using a Dichloromethane:Hexane (50:50) mixture as the solvent with three cycles at a pressure of 70 bar and a temperature of 100^{o}C. The static time was 5 min, flush volume was 55%, and purge time was 90s. The final volume of the extract was approximately 40-50 mL and was reduced to dryness under nitrogen and reconstituted in 1 mL.

Extracts were then treated with a clean up step to remove co-extracted lipid using a gel permeation chromatography method. Finally the samples were fractionated using a silica gel: sulfuric acid 2:1 (v/v) column prior to analysis by gas chromatography-high resolution mass spectrometry in the electron ionization mode (GC-HRMS(EI)).

Analytes were determined using a Micromass Ultima HR-mass spectrometer coupled with an HP 6890 GC and a CTC A200 autosampler (WatersMicromass, Manchester, U.K.). Separation was achieved using a 15-m (250μm, 0.10μm) Restek capillary column. The temperature ramping program had an initial temperature of 100^{o}C (2 min), 25^{o}C/min to 250^{o}C, 1.5 ^{o}C/min to 260 ^{o}C and 25^{o}C/min to 325^{o}C which was held constant for 10 min. For all analyses the source temperature was 250^{o}C and the resolution of the magnetic sector mass analyzer was 10, 000. HRMS (EI) was operated under the selected ion monitoring (SIM) mode.

Results and Discussion

All walleye and steelhead trout samples collected and analyzed contained PBDE congeners, summarized in Table 1. BDE- 47 has been shown to be the predominate congener to bioaccumulate in biota. This held true in our study as BDE47 was the congener most frequently detected, with 100% detection in the samples. Along with BDE-47 the other dominate congeners detected were 99, 100, 153, and 154 all with 100% frequency. Both BDE 47 and 100 are known to have higher uptake efficiency which could be due to their smaller cross-sectional size allowing them to permeate cells more readily.[6] In this study BDE 47 and 100 were detected in both the walleye and steelhead trout with the highest concentrations.

In comparison with PBDE levels detected in organisms and other matrices collected from around the world the walleye and steelhead trout analyzed in this study have similar concentrations.[8] Batterman et al. reported concentrations for BDE 47, 99, 100, and 153 in walleye from Lake Erie collected in 2000 to be 28.28 ng/g, 5.29 ng/g, 5.20 ng/g, and 2.57 ng/g respectfully.[9] These values are lower than those reported in this study which is to be expected as BDE concentrations in Lake Erie have increased within the last decade. In 2006, Law et al. reported total PBDE (sum of 34 congengers) concentrations in walleye samples from Lake Winnipeg (Canada) to average 54.39 ng/g lipid weight.[10] Both walleye and steelhead are sport fish therefore it will provide an interesting comparison to look at the concentrations of PBDEs in forage fish (yellow perch and round gobies) and allow for conclusions about bioaccumulation and food web-mediated transport to be drawn. There are limited studies available about PBDE concentrations and transport in the Great Lakes of North America therefore this study provides key insights on the current impact of PBDEs on the fish community of Lake Erie.

Concentration of Individual PBDE Congeners in Whole Fish Samples (ng/g lipid)

Sample	3	15	17	28	47	49+71	66	85	99	100	119	126
Walleye												
1	n/d	0.02	n/d	n/d	22.8	3.36	n/d	0.02	5.51	8.78	0.32	0.05
2	n/d	n/d	n/d	n/d	27.4	3.43	0.28	0.02	3.88	6.66	0.20	0.02
3	0.05	n/d	n/d	n/d	54.9	11.4	n/d	0.03	13.3	22.56	0.29	0.14
Steelhead Trout												
1	n/d	n/d	n/d	n/d	61.2	9.10	n/d	0.06	12.2	15.5	0.23	0.03
2	n/d	n/d	n/d	1.78	62.2	6.34	1.75	0.07	7.88	13.5	0.21	0.04
3	n/d	0.13	0.31	2.13	69.1	10.7	n/d	0.10	10.6	11.2	0.50	0.05
4	n/d	0.15	0.25	1.81	60.8	7.95	n/d	0.06	9.99	13.7	0.16	0.03
5	0.06	n/d	n/d	1.38	64.8	7.06	n/d	0.07	7.13	13.9	0.15	0.03

Concentration of Individual PBDE Congeners in Whole Fish Samples (ng/g lipid)

Sample	138	153	154	156	183	184	191	196	197	206	207	209
Walleye												
1	0.01	3.06	5.72	n/d	0.06	0.01	n/d	0.01	0.01	0.02	0.02	0.71
2	n/d	1.69	3.36	n/d	0.04	0.01	n/d	n/d	n/d	n/d	0.01	0.24
3	0.03	8.69	15.8	n/d	0.06	0.01	n/d	0.01	0.01	0.02	0.02	0.56
Steelhead Trout												
1	0.02	3.79	7.31	n/d	0.30	0.06	0.02	0.07	0.07	0.08	0.09	2.43
2	0.03	3.97	7.84	0.02	0.12	0.04	0.01	0.03	0.04	0.15	0.10	2.72
3	0.02	3.54	7.08	n/d	0.18	0.05	0.01	0.05	0.05	0.08	0.08	1.74
4	0.02	3.42	6.45	n/d	0.15	0.04	n/d	0.03	0.06	0.06	0.06	1.24
5	0.02	3.40	7.01	n/d	0.08	0.03	n/d	0.02	0.03	0.06	0.05	1.06

Table 1. Concentrations of PBDE Congeners in Lake Erie Walleye and Steelhead Trout (Nanogram per gram of lipid)

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