



Statewide surveillance of halogenated flame retardants in fish in Illinois, USA[☆]



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ABSTRACT

In order to better understand the exposure of aquatic systems to halogenated flame retardant contaminants, the present study investigated a variety of legacy and emerging flame retardants in common carp and largemouth bass collected from 58 stations across Illinois (United States). The data revealed that polybrominated diphenyl ethers (PBDEs) generally dominated the flame retardant residues in Illinois fish. Concentrations of Σ PBDEs (including all detectable PBDE congeners) ranged from 24.7 to 8270 ng/g lipid weight (median: 135 ng/g lw) in common carp and 15–3870 ng/g lw (median: 360 ng/g lw) in largemouth bass. In addition to PBDEs, Dechlorane analogues (i.e. Dec-603, Dec-604, and Chlordane Plus) were also frequently detected. Median concentrations of Σ Dechloranes (including all detected Dechlorane analogues) were 34.4 and 23.3 ng/g lw in common carp and largemouth bass, respectively. Other emerging flame retardants, including tetrabromo-*o*-chlorotoluene (TBCT), hexabromobenzene (HBBZ), 2-ethylhexyltetrabromobenzoate (EH-TBB), and bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP), were also detected in 40–78% of the fish at the monitored stations. Spatial analysis revealed significantly greater PBDE concentrations in fish living in impaired urban streams and lakes compared to those from the impaired agricultural and unimpaired agricultural/urban waters, demonstrating a significant urban influence on PBDE contamination. Future studies and environmental monitoring are recommended to focus on temporal trends of PBDEs and alternative flame retardants, as well as human exposure risks via edible fishes, in the identified Areas of Concern within Illinois.

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1. Introduction

Flame retardants are chemicals added to textiles, polyurethane foams, thermoplastics, electronic products, and building materials to increase their fire resistance (Alaee et al., 2003; de Wit et al., 2010; Covaci et al., 2011). To date, more than 75 different flame-retardant substances have been commercially manufactured (Birnbaum and Staskal, 2007; Covaci et al., 2011). Flame retardant substances can be divided into two classes, additive or reactive, depending on how they are added to the polymer (Alaee et al., 2003). Additive halogenated flame retardants, which include polybrominated diphenyl ethers (PBDEs) as the most often used additives, are not chemically blended in the polymer, and are more likely to leach out of consumer products than reactive types (Alaee

et al., 2003; Watanabe and Sakai, 2003). As a consequence of substantial, long-term use, PBDEs are ubiquitous in the environment, and have been measured in air, water, fish, birds, marine mammals, and humans, even in remote areas (Hites, 2004; Law et al., 2014; Letcher et al., 2010; de Wit et al., 2010). Although all three commercial mixtures of PBDEs (i.e. PentaBDE, OctaBDE, and DecaBDE) were phased out in North America by 2013, they are still present in many currently in-use or discarded consumer products (Law et al., 2014). Leaching from the in-use and discarded products may continue for decades (Chen et al., 2013). In addition, some PBDE congeners are persistent, bioaccumulative, and toxic (Hites, 2004; Darnerud, 2003). Toxicological studies suggest that PBDEs may impact thyroid hormone levels; thyroid, liver, and kidney morphology; liver ethoxyresorufin-*O*-deethylase activity; neurodevelopment; reproductive success; and, fetal toxicity/teratogenicity (Darnerud, 2003).

Flame retardants may enter aquatic systems through releases in municipal or industrial wastewater treatment plant effluents and surface runoff (Song et al., 2006; Pérez-Fuentetaja et al., 2010; Chen

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et al., 2011). In addition to aquatic wildlife exposure, humans may be at risk via intake of contaminated fishes (Hites, 2004; Cruz et al., 2015). Water quality in Illinois has been monitored by projects, such as the Illinois Fish Contaminant Monitoring Program (FCMP). To date, these projects have largely focused on heavy metals, pesticides, and polychlorinated biphenyls (PCBs). Information on the spatial and temporal distributions of halogenated flame retardants in Illinois waters remained extremely limited. Additionally, restrictions on PBDE applications have resulted in increased use of alternative flame-retardant chemicals to meet flammability standards. For example, decabromodiphenylethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) were considered as potential DecaBDE or OctaBDE replacements, whereas 2-ethylhexyltetrabromobenzoate (EH-TBB) and bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) were suggested as PentaBDE replacements (Covaci et al., 2011; United States Environmental Protection Agency, 2014). However, nothing is known about the levels and distributions of the alternative flame retardants in Illinois water.

The present study aimed to investigate the contamination status of a suite of halogenated flame retardants in rivers and lakes across the state of Illinois via the analysis of fish fillet tissues. Specific objectives were to: (1) determine the levels and composition of halogenated flame retardant substances in Illinois fish; and, (2) elucidate the differences in flame retardant exposure among different water use types across the State of Illinois and identify the Areas of Concern.

2. Materials and methods

2.1. Chemical and reagents

Reference standards for the 20 PBDE congeners (Table S1) were purchased from AccuStandard (New Haven, CT, USA). Reference standards of *syn*- and *anti*-Decchlorane Plus (DP) and other Decchlorane analogues were purchased from Wellington Laboratories (Guelph, ON, Canada), including *syn*- and *anti*-DP, mono-dechlorinated DP (C11-DP), didechlorinated DP (C10-DP), Decchlorane 601 (Dec-601), Dec-602, Dec-603, Dec-604, Dec-604 Component B (Dec-604CB), and Chlordane Plus (CPlus). Additional flame retardant chemicals, including pentabromobenzene (PBBZ), pentabromobenzyl bromide (PBBB), pentabromoethyl benzene (PBEB), hexabromobenzene (HBBZ), tetrabromo-*o*-chlorotoluene (TBCT), BTBPE, DBDPE, BEH-TEBP and EH-TBB, were purchased from AccuStandard or Wellington Laboratories. Surrogate standards, including 2,4,6-tribromodiphenyl ether (BDE-30), 2,3,3',4,4',5-hexabromodiphenyl ether (BDE-156) and 2,2',3,3',4,5,5',6,6'-nonabromo-4'-chlorodiphenyl ether (4PC-BDE-208), as well as an internal standard, decachlorodiphenyl ether (DCDE), were purchased from AccuStandard. Diatomaceous earth and sodium sulfate (10–60 mesh) were purchased from Fisher Scientific (Hanover Park, IL, USA) and treated in a muffle furnace at 600 °C overnight (>12 h) prior to use. Copper (50 mesh, granular, reagent grade) and high-performance liquid chromatography grade solvents were purchased from Fisher Scientific. Isolute[®] silica sorbent (average pore size: 60) was purchased from Biotage Inc. (Charlotte, NC, USA) and baked at 130 °C prior to use.

2.2. Samples

Fishes (common carp, *Cyprinus carpio*; largemouth bass, *Micropterus salmoides*) were collected at 58 stations located in a number of streams and lakes across the state of Illinois in 2013–2014 (Fig. 1). Fish collection was conducted by the Illinois FCMP. Depending on water use type, stations were classified by the Illinois

FCMP into three categories, including unimpaired rural, agricultural, or urban streams and lakes (N = 25; Type 1), impaired agricultural streams and lakes (N = 12; Type 2), and impaired urban streams and lakes (N = 21; Type 3) (Rousey, 2013). Type 1 stations represent aquatic systems not known to have received pollution from any agricultural or urban sources. Type 2 stations represent the aquatic systems receiving known influences from agricultural activities. Type 3 stations represent aquatic systems near or within metropolitan regions and receiving known influences from urban sources (e.g. wastewater treatment discharges or urban runoff). At each station, a minimum of three (and preferably five) fish, with the smallest fish being at least 75% of the length of the largest fish, were collected and comprised for each composite fillet sample (Rousey, 2013). The average (\pm standard deviation) lengths were 57.9 \pm 7.2 cm and 35.2 \pm 5.5 cm for common carp and largemouth bass, respectively. The composite fillet samples were prepared by removing scales and leaving skin on the fish. The fish were then filleted to remove bones and ground into a composite. Fish composite samples were stored at –20 °C prior to chemical analysis.

2.3. Analysis

The extraction and cleanup procedures were based on Chen et al. (2011) and Chen et al. (2013) with modification. In brief, one to three grams of fish composite were ground with diatomaceous earth. After spiking with surrogate standards (BDE-30, BDE-156, and 4-PC-BDE208), the sample was subject to accelerated solvent extraction (ASE350; Thermo Scientific, Sunnyvale, CA, USA) with dichloromethane (DCM) at 100 °C and 1500 psi. The extract was subject to gravimetric determination of lipid content by using 10% of the extract (Chen et al., 2011). The remaining extract was purified by gel permeation chromatography (GPC) (CO100 GPC Column, J2 Scientific, Inc.; Columbia, Missouri, USA) to remove bulk lipids; then further purified on a 2-g silica gel solid phase extraction (SPE) cartridge. The first fraction collected from the SPE cartridge was eluted with 3 mL of hexane and discarded. The second fraction was eluted with 6.5 mL of a 60:40 hexane/DCM mixture (v/v) followed by 7 mL of DCM. The second fraction contained all contaminants of interest and was concentrated for instrumental analysis. The internal standard DCDE (100 ng) was added prior to instrumental analysis.

All flame retardants of interest were analyzed on an Agilent 6890N gas chromatography coupled to a 5973 mass spectrometry (GC-MS, Agilent Technologies, Palo Alto, CA, USA) in electron capture negative ionization (ECNI) mode. The column was a 15-m DB-5HT column (0.25 mm i.d., 0.1 μ m film thickness, J&W Scientific, Folsom, CA, USA). The injector was operated in pulsed-splitless mode, held at 240 °C. Injection volume was 1 μ L. The initial column temperature was held at 50 °C for 3 min; increased to 300 at 10 °C/min and held for 15 min. The GC and MS interface temperature was set at 280 °C. Identification and quantification of FR substances on GC-MS was achieved via selected ion monitoring (SIM) of characteristic ions (Table S1; Supplemental material).

2.4. Quality assurance and control

Several measures were employed to ensure QA/QC for the present study, including matrix spiked experiments, analysis of Standard Reference Materials (SRMs), process of procedural blanks, and examination of surrogate standard recoveries. Known amounts (20–100 ng) of flame retardant analytes of interest were spiked into a composite of fish (*Tilapia*, *Oreochromis niloticus*) filets purchased from local supermarket and analyzed using the methodology described above to determine the analyte recoveries throughout the analysis. These fish filets were tested prior to the

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