Project Title

Statewide Surveillance of Emerging Flame Retardant Contamination in Illinois Waters via Fish Monitoring

Principle Investigator

Dr. Da Chen
Cooperative Wildlife Research Laboratory and Department of Zoology
Southern Illinois University Carbondale
dachen@siu.edu
(618) 453-6946

Problem and Research Objectives

Human activities generate large amounts of a wide range of pollutants. These are subsequently released into water systems via point or non-point discharges. Some may impair water quality, aquatic ecosystem and human health. Current efforts of monitoring anthropogenic pollution in Illinois have mainly focused on legacy pollutants such as heavy metals, pesticides, and polychlorinated biphenyls (PCBs). There is a lack of information on the distribution of emerging contaminants, such as flame retardants (FRs), in Illinois aquatic environments. Flame retardants are of high concern as some of them are identified as High Production Volume (HPV) substances and have demonstrated environmental persistence, bioaccumulative and toxic potentials. They may impair aquatic ecosystems via bioaccumulation and biomagnification to reach high levels in aquatic species (e.g. fish and birds). The bioaccumulation in edible fish also represents potential risks to human health. However, to date nothing has been done to assess the contamination of FRs in Illinois waters and organisms on a state scale.

This project aimed to investigate the spatial distribution of BFRs in rivers and lakes across the State of Illinois via fish monitoring. The findings would reveal the status of FR contamination and associated risks to ecosystems in Illinois waters. Specific research objectives of this project were to: (1) determine priority FR contaminants and their levels in Illinois fish; (2) assess distribution patterns of FRs in Illinois waters; and, (3) identify impaired aquatic systems.

Methodology

Samples and study sites. Fish samples utilized by this project were retrieved from the Illinois Fish Contaminant Monitoring Program (FCMP). Common carp (*Cyprinus carpio*) and channel catfish (*Ictalurus punctatus*) were selected as the bio-monitoring species for this project. They were collected from a total of 35 selective aquatic systems across the state in 2011-2013 (Figure 1). These sites cover a number of ecologically or economically important aquatic systems and represent different water use types, including potential hotspots, unimpaired/impaired urban streams and lakes, and unimpaired /impaired rural/agricultural steams and lakes. At each site, 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. Fillet tissues were removed from individual fish and then combined to produce a composite fillet sample by species. A total of 42 carp composite and 31 catfish composite samples were analyzed for flame retardants.

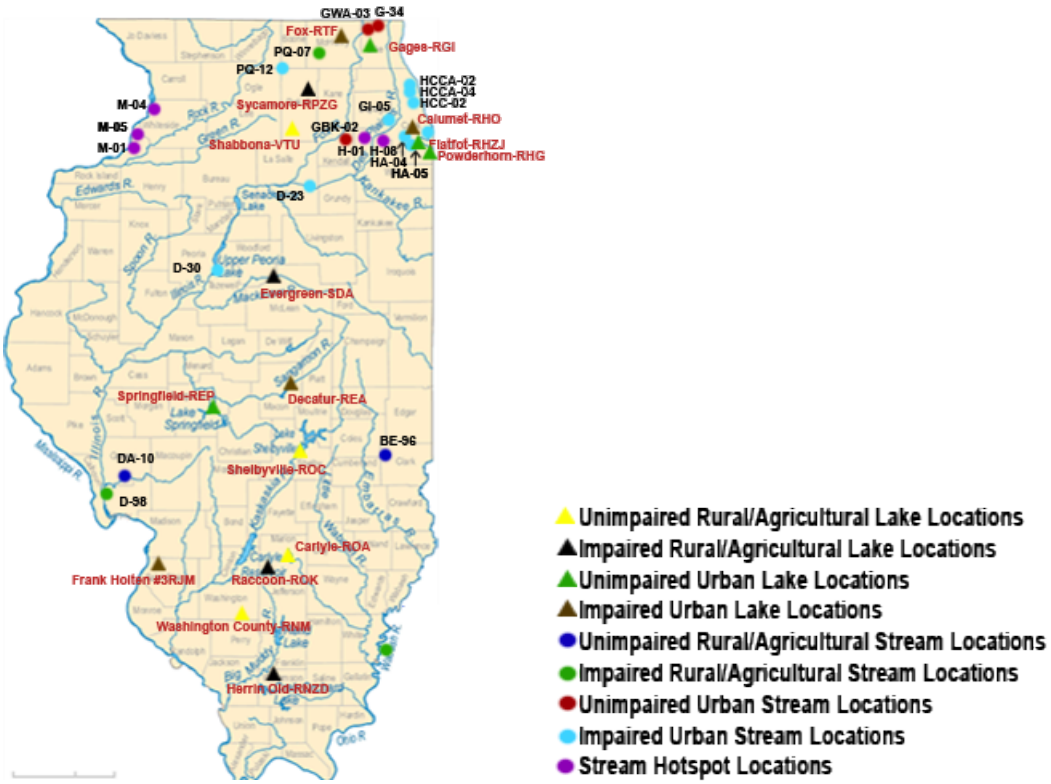

Figure 1. Station sites where fish samples were collected and analyzed in this project.

Residue analysis. Chemical residue analysis followed the protocols shown in Figure 2 (Chen et al., 2012). In brief, composite fish (2-3 gram) was ground with diatomaceous earth, spiked with internal standards, and then subject to accelerated solvent extraction. The extract was purified by gel permeation chromatography, followed by solid phase extraction cleanup. Final extract was analyzed on gas chromatography – mass spectrometry (GC-MS). A total of 20 polybrominated diphenyl ether (PBDE) congeners, 27 non-PBDE BFRs, and 19 DP-related compounds were determined in this project (Table 1).

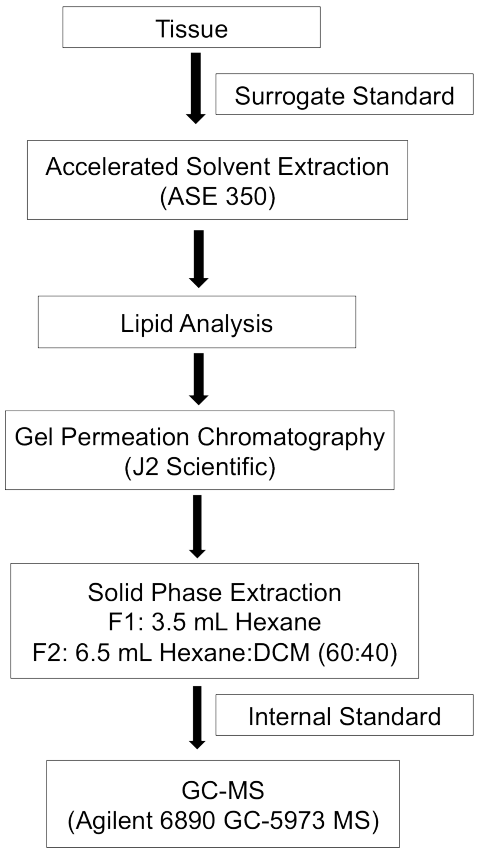

Figure 2. Flow chart of analytical methodology

Principle Findings and Significance

1. PBDEs are the main flame retardants in Illinois waters.

The data from this project revealed that PBDE compounds were the most abundant flame retardant pollutants in Illinois water. PBDE levels in fish were up to 8200 ng/g lipid weight (lw), comprising more than 98% of total FR concentrations in fish from all sites. Hexabromocyclododecane (HBCD) and dechlorane plus (DP) were also frequently detected, but at much lower concentrations (i.e. generally less than 100 ng/g lw). Other flame retardant analytes were generally below detection limits or detected at very low frequencies (i.e. < 4%). Although commercial PBDE products have been discontinued in 2004, the study revealed that PBDEs are still the main flame retardants present in Illinois aquatic environments. Their high concentrations in fish from some sites merit continuing monitoring.

2. Wide distribution of PBDEs in Illinois waters.

Although the levels differed between sites, PBDEs were detected in both species from all study sites, revealing a statewide contamination. PBDEs have been used for decades in a variety of consumer products. They can be released into the environment via multiple

pathways and persist in the environment for a long time. They are bioavailable to organisms, resulting in wide contamination in fishes. This is consistent with other studies in the US or the rest of the world, demonstrating a universal contamination of PBDEs in aquatic organisms (Law et al., 2014).

Table 1. Summary of target analytes

PBDEs	Non-PBDE BFRs	DP-related compounds
BDE-28	2,4,6-tribromophenyl allyl ether	Di-dechlorinated DP
BDE-47	2,2',4,5,5'-pentabromobipheny	Mono-dechlorinated DP
BDE-49	2,2',4,4'5,5'-hexabromobiphenyl	Chlordene Plus
BDE-66	Bis(2-ethyl-1-hexyl)tetrabromophthalate	Dibromoaldrin
BDE-85	1,2-bis-(2,4,6-tribromophenoxy)ethane	Dechlorane Plus Mono Adduct
BDE-99	decabromodiphenyl ethane	DEC-601
BDE-100	2,3,-dibromopropyl tribromophenyl ether	DEC-602
BDE-138	ethylenebistetrabromophthalimide	DEC-603
BDE-153	2-ethylhexyl-2,3,4,5-tetrabromobenzoate	DEC-604
BDE-154	hexabromobenzene	DEC-604CB
BDE-183	hexabromocyclododecane	Br-DEC604
BDE-196	Hexachlorocyclo-pentadiene	Br_2-DEC604
BDE-197	Hexachlorocyclopentadienyl-dibromocyclooctane	Cl_4-DEC604
BDE-201	Pentabromobenzyl acrylate	Br_2Cl_2-DEC604
BDE-202	pentabromobenzyl bromide	Hexachloro(phenyl)norbornene
BDE-203	Pentabromobenzene	VCH-dechlorane plus
BDE-206	pentabromoethylbenzene	syn-dechlorane plus
BDE-207	Pentabromochlorocyclohexane	anti-dechlorane plus
BDE-208	Pentabromophenyl allyl ether	
BDE-209	2,3-dibromopropyl pentabromophenyl ether	
	Pentabromotoluene	
	TetraBromo-p-Xylene	
	1,3,5-Tribromobenzene	
	1,2,5,6-tetrabromocyclooctane (alpha-TBCO)	
	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	
	tetrabromo-o-chlorotoluene	
	2,3,5,6-tetrabromo-p-xylene	

3. PBDE levels differed between water use types.

In this project, our study sites include multiple water use types, i.e. potential hotspots, unimpaired/impaired urban streams and lakes, and unimpaired /impaired rural/agricultural steams and lakes. The data indicated statistically significant differences in PBDE levels in fish from different water use types (Analysis of Variance or ANOVA, $p < 0.001$) (Figure 3). Fish from stream hotspot sites (N = 5) and impaired urban lakes/streams (N = 12) contained much greater PBDE concentrations than those from unimpaired rural/agricultural/urban lakes (N = 14) and from impaired rural/agricultural lakes (N = 4). For example, common carp and channel catfish from stream hotspots

contained median ΣPBDE concentrations of 3,210 and 2,950 ng/g lw, respectively. These two species contained median ΣPBDE concentrations of 2,174 and 2,910 ng/g lw, respectively, at impaired urban lakes and streams. Fish from impaired rural/agricultural lakes or unimpaired waters contained median concentrations of generally lower than 70 ng/g lw.

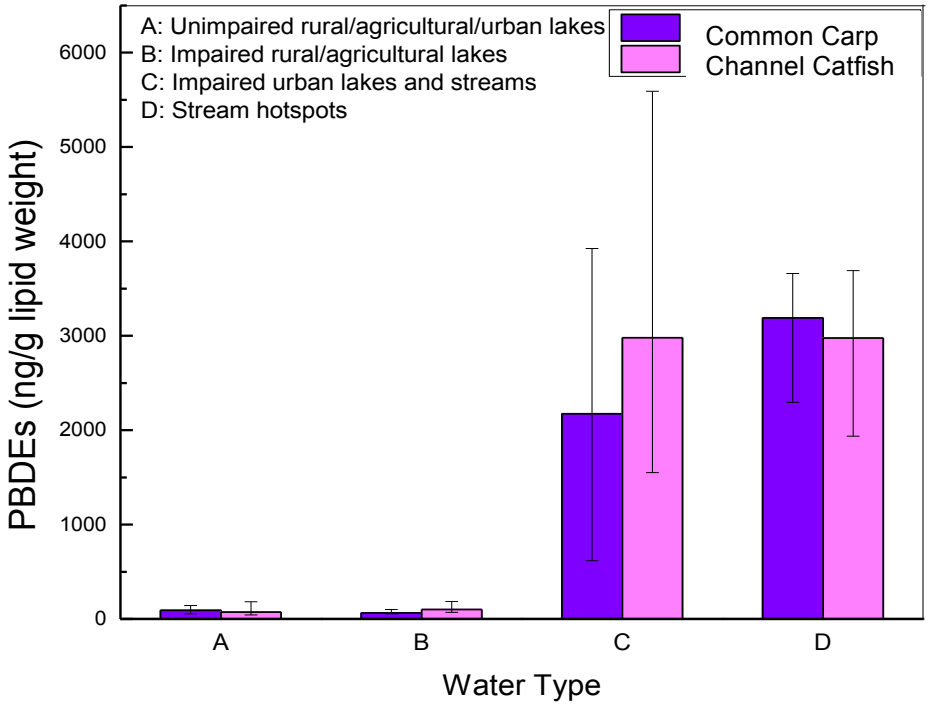

Figure 3. Median PBDE concentrations (ng/g lw) in fish from different water use types. Error bars represent 75 and 25 percentiles, respectively.

The elevated PBDE contamination in urban waters was likely due to greater human population densities in urban versus agricultural/rural areas. A greater human population density may be associated with a more abundance of consumer products (e.g. thermoplastics, textiles, and electronics) that contain PBDEs, which consequently resulted in an elevated release of PBDEs to the environment. Typical sources of PBDEs in urban waters may include wastewater effluents, surface runoff, or industrial releases.

High contamination in fish from some impaired urban rivers, such as the sites at the Cal-Sag Channel at Rt. 83 and the Little Calumet River, may indicate potential sources nearby. The future work is needed to identify sources and transport pathways in order to prevent or reduce the contamination. High levels in fish may also represent potential human health risks via the consumption of edible fishes collected from these rivers. Currently there is a lack of fish consumption advisory for PBDEs in Illinois.

4. Comparison with international studies

A comparison with international studies revealed that PBDE contamination in fish from impaired Illinois urban waters (including hotspots and impaired urban lakes/streams) was at the higher end of the range of concentrations (Table 2).

Table 2. Reported PBDE concentrations (ng/g lw) in carp from this study and studies from other regions.

Watershed	Country	PBDE Concentration Range and Median (in parentheses)	Reference
Impaired IL urban waters	US	642-8200 (2350)	This study
Hyco River, NC	US	1500-12900 (9140)	Chen et al. 2011
Dan River, NC	US	310-1900 (1120)	Chen et al. 2011
Roanoke River, NC	US	160-1300 (440)	Chen et a. 2011
Hardley Lake	US	760-2500 (1600)	Dodder et al. 2002
Detroit River	US	29-50.2 (40.7)	Rice et al. 2002
Gila River, AZ	US	0.2-108 (24.9)	Echols et al. 2013
Lake Erie	US	1.5-101.8 (11)	Perez-Fuentetaja et al. 2010
Canal Lake	Belgium	Non-detection-420 (140)	Covaci et al. 2005
Anoia and Cardener River	Spain	29-744 (43)	Labanderia et al. 2007
Tai Lake	China	1.1-97.6 (23.1)	Su et al. 2014
Dongjiang River	China	42-263 (115)	He et al. 2012
Yangtze River	China	17-1100 (140)	Xian et al. 2008

5. PBDE congener profiles were consistent across sites.

Although PBDE concentrations differed between water use types, the BDE congener compositions (i.e. percentage of each congener to the total PBDEs in concentration) were consistent across sites. The congener compositions were dominated by BDE-47, followed by BDE-100, -99, -154, and -153 (Figure 4). This represents a typical pattern resulting from the PentaBDE contamination (Law et al., 2014). The U.S. has consumed the majority of the world's PentaBDE production. Major congeners in the commercial PentaBDE products, such as BDE-47 and -99, are highly bioaccumulable compared to other congeners. Therefore, BDE-47 dominates the PBDE contamination patterns in most aquatic organisms.

5. Further studies are needed to elucidate non-PBDE flame retardant contamination in Illinois waters.

Our data revealed that PBDEs were still the major flame retardants in Illinois fishes and that non-PBDE flame retardants were not detectable or detected at very low frequencies. However, given that commercial PBDE mixtures have been phased out from the North American market, many alternative flame retardant chemicals are used to replace PBDEs in a variety of consumer products (Covaci et al., 2010). Some of them have already demonstrated environmental persistence and bioaccumulation (Covaci et al., 2010).

Future studies are needed to monitor the contamination and distribution of these alternative flame retardants in Illinois aquatic ecosystems.

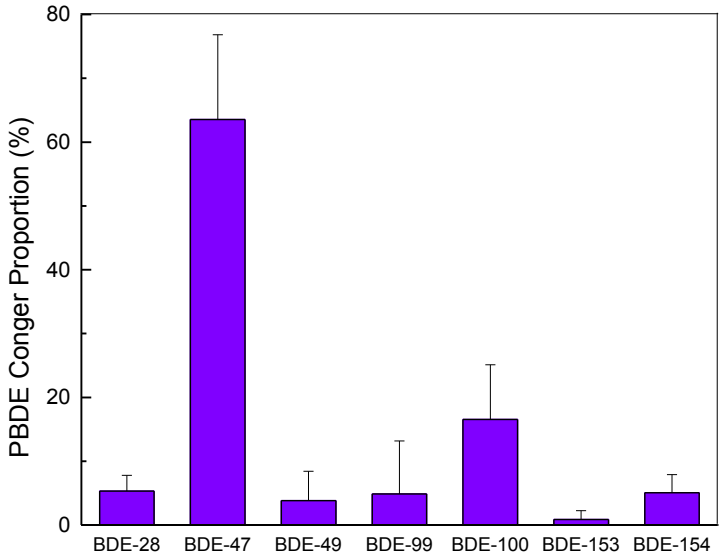

Figure 4. PBDE conger compositions in Illinois fish. Error bars represent standard deviations.

Notable Achievements

(1) The project revealed PBDEs are the most abundant flame retardant pollutants in Illinois waters. Although commercial PBDE products have been discontinued in 2004, their high environmental concentrations merit continuing monitoring. The project also raised the need of monitoring HBCD and DP, as well as many other non-PBDE flame retardants in Illinois fishes. These emerging flame retardants are subject to increased usage in order to replace PBDEs in many applications, which may result in increasing concentrations over time.

(2) The project mapped the spatial contamination pattern of flame retardants in Illinois waters. It developed a baseline for understanding flame retardant contamination in Illinois aquatic systems and identified contamination hotspots. The levels in fish collected from impaired urban waters are in the higher end of the range of concentrations reported in international studies. Potential human exposure and heath risks via edible fishes from impaired urban waters merit further investigations. The findings would essentially contribute to the database of water pollution developed by the Illinois EPA Fish Contaminant Monitoring Program and other agencies.

Students Supported With Funding

Malgorzata Widelka, Department of Zoology, Southern Illinois University, Bachelor of Science (awarded in May 2014).

Hillary Marler, Department of Zoology, Southern Illinois University, doctoral student (expected to be awarded in December 2017).

Publications and Presentations

Widelka, M., H. Marler, M. Lydy, T. Hornshaw, D. Chen. 2014. Statewide Surveillance of emerging flame retardant contamination in Illinois waters via fish monitoring. Illinois Water Conference, Urbana, Illinois, October 14-15.

Widelka, M., H. Marler, M. Lydy, T. Hornshaw, D. Chen, 2014, Statewide Surveillance of emerging flame retardant contamination in Illinois waters via fish monitoring, Southern Illinois University Carbondale Annual Undergraduate Research and Creative Activities Forum, Carbondale, IL, April 7.

Widelka, M., H. Marler, M. Lydy, T. Hornshaw, D. Chen, 2013, Statewide Surveillance of emerging flame retardant contamination in Illinois waters via fish monitoring, The 34th Society of Environmental Toxicology and Chemistry (SETAC) North American Annual Meeting, Nashville, TN, November 17-21.

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