Profile of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls among Licensed Anglers in the Great Lakes Basin of Western New York

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1 Introduction
Lake Erie and Lake Ontario and their surrounding rivers and tributaries provide both resources and recreation to over 4 million people of western New York state (NYS). Historic and current contamination of the waterways have led to communities at risk of exposure to legacy and emerging chemical contaminants including polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs)[1]. These chemicals have been associated with varied health effects from endocrine disruption to reproductive effects[2-4]. The Agency for Toxic Substances and Disease Registry (ATSDR) established the Biomonitoring of Great Lakes Populations program to assess human exposure to toxic chemicals among susceptible populations[5]. As part of the ATSDR program, the New York State Department of Health (NYSDOH) conducted the Healthy Fishing Communities Program which targeted two subpopulations who ate locally caught fish and had the potential for increased risk of exposure to persistent contaminants common to four Great Lakes Areas of Concern (AOCs) in western New York state from 2010-2015, licensed anglers and Burmese refugees[5-8]. This analysis focuses on the patterns and associations between congeners of PBDEs and PCBs among the licensed angler population.

2 Materials and Methods
Study sampling, recruitment, and enrollment activities were completed in 2013. The detailed study design and methods have been described previously[5,6,8]. The licensed angler population was randomly sampled from a fishing license database for zip codes that were within 10 miles of the four AOCs in western NYS: Buffalo River, Niagara River, Eighteen-mile Creek, and the Rochester Embayment[8]. Licensed anglers who were older than 18 years of age, ate at least one fish meal from any of the AOCs or surrounding water bodies within the past year and lived at the address listed on their fishing license for at least a year prior to screening were eligible to be enrolled in the study. A total of 409 licensed anglers were recruited to participate in the program.
All participants completed a questionnaire that focused on demographic characteristics, residential history, lifestyle behaviors, and behaviors around fish consumption. Participants also provided blood and urine samples for chemical analysis. Laboratory analysis of 5 PBDEs (PBDE 28, 47, 99, 100, and 153) and 35 PCBs[1] in serum samples was completed at NYSDOH Wadsworth Center using a published method[8]. Serum samples were extracted by solid-phase extraction and analyzed using gas chromatography-high resolution mass spectrometry. Concentrations were expressed as nanogram per gram of total lipid (ng/g lipid). Concentrations below the limit of detection (LOD) were assigned a value equal to $LOD/\sqrt{2}$.
Analyses were conducted using SAS version 9.4 (SAS Institute, Inc. Cary, NC). Descriptive analysis was performed for demographic characteristics such as age, gender, race/ethnicity, education, and smoking status. Sums of 5 PBDEs (ΣPBDE) and 35 PCBs (Σ35 PCB) were calculated for each participant. Geometric means and 95% confidence intervals (CIs) of ΣPBDE and Σ35 PCB were determined for the whole cohort and by selected sub-groups (Table 1). A heat map of Spearman correlations between individual PBDE and PCB congeners were created to visualize the relationships between congeners[9]. Serum concentrations of individual PCB congeners with >50% of results above LOD were included in Principal Component Analysis (PCA) to investigate what, if any, congener groupings drive much of the variance in the data. Using the PRINCOMP procedure in SAS, PCB concentrations were standardized so that all PCA scores would have a variance equal to one. PCA results were displayed in a component plot to illustrate clustering of congeners.

3 Results
Participants' demographic characteristics are presented in Table 1. Notably, participants were primarily male (86%), non-Hispanic white (84%), and had education beyond high school (62%). Mean age was 52 years old (range: 19-74 years), and 22% were current smokers. Geometric means for lipid-adjusted ΣPBDE and Σ35 PCB were 24.9 ug/g lipid (95% CI 22.3, 27.8) and 117 ug/g lipid (95% CI 104, 132) respectively and were generally similar to or lower than reported NHANES 2003-2004 levels (Σ35 PCBs: 134 (95% CI 129, 140); PBDE 28: 1.17 (95% CI 1.01, 1.37);

[1] 35 PCBs: 31/28, 44, 49/43, 52/73, 66/80, 74/61, 87/117/125/116/111/115, 99, 90/101/89, 105/127, 110, 118/106, 128, 138/164/163, 146/161, 149/139, 151, 153, 156, 157, 167, 170/190, 172/192, 177, 178, 180, 183, 187/182, 189, 194, 195, 196/203, 199, 206, 209

PBDE 47: 19.5 (95% CI 16.5, 23.1); PBDE 153: 5.41 (95% CI 4.83, 6.05))[8]. Of note, as levels of these persistent chemicals have been steadily decreasing over time as they are no longer manufactured, this population's levels of PCBs and PBDEs may be higher if compared to later NHANES cycles, for which individual participant data is not available (these analytes have been measured in pooled samples after 2004). When stratified on demographic characteristics, there was a significant difference in the geometric mean of Σ35 PCBs among participants less than or equal to 50 years of age compared to older participants (Table 1). All other stratified geometric means did not show statistical differences between categories.

Table 1: Demographic characteristics and geometric means (95% CI) of serum Σ35 PCBs and ΣPBDEs in the licensed angler participants (n=409).

Characteristics	N (%)*	Geo Mean Σ35 PCB (95% CI), ng/g lipid	Geo Mean ΣPBDE (95% CI), ng/g lipid
Age (years)			
≤50	152 (37.2%)	70.0 (58.1, 84.4)	24.4 (20.7, 28.8)
51-64	176 (43.0%)	136 (114, 162)	23.8 (20.0, 28.2)
65+	81 (19.8%)	221 (172, 284)	28.7 (21.6, 38.2)
BMI (kg/m^2)			
≤25	68 (16.6%)	145 (116, 181)	29.6 (22.2, 39.5)
25-<30	152 (37.2%)	103 (82.5, 128)	22.4 (18.8, 26.8)
≥30	189 (46.2%)	120 (101, 143)	25.5 (21.7, 30.0)
Race/Ethnicity			
Hispanic	14 (3.5%)	101 (43.2, 235)	21.4 (12.1, 37.6)
Non-Hispanic White	344 (84.9%)	113 (98.9, 128)	23.6 (20.9, 26.7)
Non-Hispanic, other	47 (11.6%)	168 (115, 246)	38.4 (29.3, 50.5)
Sex			
Male	353 (86.3%)	116 (102, 133)	24.8 (22.0, 28.0)
Female	56 (13.7%)	122 (91.9, 161)	25.5 (18.8, 34.6)
Education			
≤High school diploma	154 (37.7%)	118 (97.3, 143)	23.4 (19.6, 28.0)
Some college or college degree	255 (62.3%)	116 (99.5, 136)	25.9 (22.5, 29.8)
Smoking Status			
Current	88 (21.7%)	91.0 (71.5, 116)	25.8 (20.6, 32.3)
Ever	176 (43.3%)	129 (107, 156)	24.9 (20.8, 29.8)
Never	142 (35.0%)	121 (97.8, 149)	24.5 (20.4, 29.4)

* Total sample sizes by characteristic may not equal to 409 due to missing values.

The Spearman correlations of these congeners with each other is illustrated as a heat map in Figure 1. PBDEs were all significantly positively correlated with one another (correlation coefficients ranged from 0.28 to 0.80), and PCBs had a wide range of significant correlations with one another (ranged from -0.03 to 0.93). Between the two chemical groups, there was no strong correlation (ranged from -0.10 to 0.30). PCBs 52, 66, 74, and 99 showed a slight correlation with PBDE 28 (ranged from 0.19 to 0.30). Also of note, PCB 149 and 195 were not found to be strongly associated with any other PCB congener.

The component plot in Figure 2 presents the patterns in the congener profiles seen in the licensed angler participants. Component 1 (C1) explained 44.5% of the total variance in the data and Component 2 (C2) explained 14.1%. All congeners were positively associated with C1. A grouping of congeners with eigenvector values greater than one for both C1 and C2 is seen at the top of the figure, containing primarily congeners with 2,5 substitution (PCBs 52, 101, 151) and 2,3,6 substitution (PCBs 110, 149) (Group A). Additionally, Group A features PCB 28 and PCB 66, which are more chlorinated and persistent. Group B is also positively associated with both components (C1>1, C2>1), and mostly consists of penta- to heptachlorinated congeners (PCBs 99, 105, 118, 128), apart from PCB 74. Lower on the graph, Group C (C1>1, C2<1) consists of tightly clustered hexa- to heptachlorinated congeners (PCBs 138, 146, 153, 156, 157, 167, 170, 172, 177, 180, 187), and Group D contains some of the most highly chlorinated congeners (PCBs 194, 195, 196/203, 199, 206, 209).

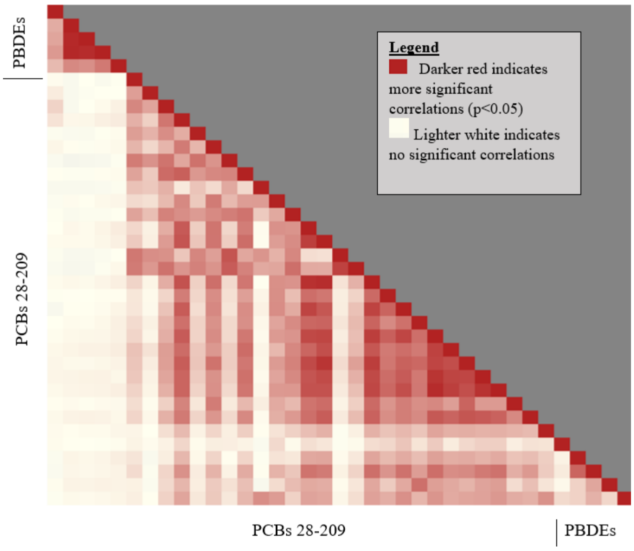

Figure 1. Heat Map of Spearman Correlations among PCB and PBDE congeners in licensed angler participants.

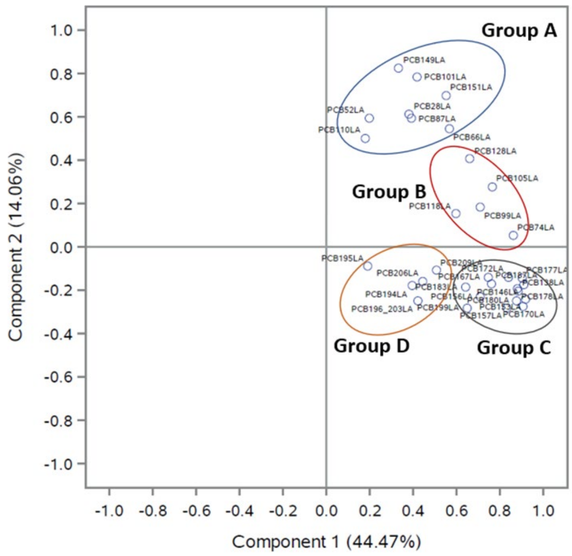

Figure 2. Component pattern plot of individual PCB congeners in licensed angler participants.

4 Discussion

The Great Lakes Basin has a long history of contamination, and while mitigation efforts have resulted in lower levels of contamination overall, there is still concern over human exposure to persistent chemicals[10-12]. The profile of persistent chemicals in humans and body burdens are influenced by a myriad of factors, from exposure routes and time of exposure, half-lives, behavioral patterns, dietary patterns, and demographic characteristics [9,13,14].To help people make healthier choices about the fish they eat, NYSDOH has issued guidance on fish to eat and fish to avoid in NYS waters since the 1980s, which is available in multiple languages, both online and in-print with over 40 separate titles. Outreach and education resources related to fish advisories and guidance include color coded maps, children's coloring books, magnets, and other promotional items that highlight the benefits of making healthy eating choices when eating fish caught locally. This analysis highlights the specific profile pattern seen in this population of Great Lakes fish consumers and contributes to a greater understanding of how these chemicals correlate with each other in humans. Principal Component Analysis was used to illustrate patterns in the congener profiles of the licensed angler participants. Of note, the clustering patterns seen in this licensed angler subpopulation are similar to patterns shown previously in NHANES and highly PCB-exposed residential populations[15,16]. Examination of congener grouping patterns can be applied in further analyses such as multivariate modeling. Grouping of PCB congeners by chlorination has been a routine practice, and these results support such groupings in this population.

5 Conclusions

The results generated from the NYS Healthy Fishing Communities Program provide insights unique to the licensed angler subpopulation of western NYS. Due to the persistent nature of the chemicals measured in this study, the serum PBDEs and PCBs reported here can be reasonably assumed to represent the lifetime exposure history, especially in the case of those who have lived in the area for numerous decades. Despite the overall downward trend of legacy contaminants in the Great Lakes Basin, the substantial levels of fish consumption from local waterways and AOCs in NYS reported by this group in prior publications highlight the need for ongoing targeted outreach related to fishing and safe fish consumption, to reduce future exposures. Current NYS fish consumption advisory and guidance is available by region so that anglers and families can more easily view advice by waterbody of interest and fish species. While NYS fish advisories do not discourage eating fish, they do provide information on ways to reduce exposure to contaminants by choosing better fish to eat (including store bought fish), better waters to fish from, and healthier ways to prepare fish. NYSDOH plans to continue to use biomonitoring results and interviews with anglers and families to develop culturally appropriate materials for targeted outreach to populations at risk. Additional research on the health outcomes in groups with higher exposures as well as the general population that swim and recreationally fish in the Great Basin waterways and their tributaries would contribute to the growing body of literature that are evaluating the potential health effects of these legacy contaminants on human health.

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