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Polychlorinated biphenyls and organochlorine pesticides concentration patterns and trends in top predator fish of Laurentian Great Lakes from 1999 to 2014

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ABSTRACT

Concentration patterns and temporal trends of legacy persistent, bioaccumulative and toxic (PBT) contaminants were determined using the Great Lake Fish Monitoring and Surveillance Program (GLFMSP) top predator fish data from 1999 to 2014 and applying Kendall-Theil robust regression after cluster-based age normalization. For most Great Lakes sites, significant decreasing concentration trends ranging from −4.1% to −21.6% per year (with the only exception being mirex in Lake Erie walleye) were found for PBTs including polychlorinated biphenyls (PCBs), dichloro-diphenyl-trichlorethane (DDTs), dieldrin, endrin, chlordane, oxychlordane, nonachlor, mirex, and hexachlorobenzene (HCB) reflecting the successful historical and ongoing reduction of fugitive releases and remediation efforts in the U.S. and Canada including physical removal (dredging) coupled with sediment sequestration. Generally, lower concentrations and faster decreasing trends are observed in western/northern sampling sites compared to eastern/southern sites as the former sites are generally more remote from population centers and industrial activities. PCBs, which can be released from ongoing sources, have the highest concentration, the second slowest decreasing trend, and increasing mass fractions of the contaminants studied suggesting that they will continue to be the legacy contaminant of greatest concern into the future.

Introduction

The United States banned or restricted the use of many persistent, bioaccumulative, and toxic (PBT) contaminants over the past several decades because of their persistence in the environment, and potential risk to humans and the environment (Chang et al., 2012; Clement et al., 2012; Cornwell et al., 2015; USEPA, October, 2014). For example, hexachlorobenzene (HCB) was phased out in the 1960s (ATSDR, September, 2002), dichloro-diphenyl-trichlorethane (DDT) and mirex were restricted in the 1970s (Chang et al., 2012; USEPA, 2004), dieldrin, endrin, and chlordane were banned in the 1980s (Chang et al., 2012; USEPA, 2003) and polychlorinated biphenyls (PCBs) were banned in the 1970s (Marvin et al., 2004a).

However, these PBTs can still be widely detected in the environment, and some legacy contaminants have been released into the environment even after their manufacture has been terminated. For example, PCBs currently may be released from leaking transformers, building sealants, brownfield sites, contaminated soils and sediments, and waste handling and recycling facilities (Diamond et al., 2010; Melymuk et al., 2013; Robson et al., 2010), and HCB (manufactured as an agriculture chemical) has also been emitted as by-product or impurity from some manufacturing processes including chlorinated solvent production and base metal smelting, and the incineration of wastes and sewage sludge (Leger, 1991; Luscombe and Costner, 2001; USATSDR, Aug., 2015).

The United States and Canada have been collecting and measuring concentrations of legacy contaminants in the Great Lakes (GL) fish, for example lake trout (*Salvelinus namaycush*) and walleye (*Sander vitreus*) since the late 1970s as part of what is now called the Great Lakes Fish Monitoring and Surveillance Program (GLFMSP) in the U.S. (Chang et al., 2012; Zananski et al., 2011; Zhou et al., 2017) and in Canada the Sports Fish Contaminant Monitoring Program (SFCMP) (Bhavsar et al., 2007) and the Fish Contaminants Monitoring and Surveillance Program (FCMSP) (McGoldrick and Murphy, 2016). Additionally, PCBs were designated as a Chemical of Mutual Concern (CMC) by the Governments of Canada and the United States in February of 2014, under the Great Lakes Water Quality Agreement (GLWQA). The GLWQA directs Canada and the U.S. to target CMCs for action through development of binational strategies that may address research, monitoring, surveillance and pollution prevention and control provisions (GLWQA, 2015).

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The concentrations of these legacy contaminants in the environment and biota vary significantly due to many complex factors including their release history, persistence, transport potential, bioaccumulation potential, ecosystem characteristics, and changes in climate (Macksasitorn et al., 2015; Melymuk et al., 2014; Ng and Gray, 2011; Paterson et al., 2016). For most legacy contaminants, Lakes Superior (LS) and Huron (LH), which are remote to urban (population centers and industry) and agricultural areas, had lower concentrations (Chang et al., 2012; Gewurtz et al., 2008) while Lakes Michigan (LM), Erie (LE), and Ontario (LO), which are closer to areas with large populations, industrial influences and agricultural activity, have higher concentrations (Chang et al., 2012; El-Shaarawi et al., 2011). However, there are exceptions to this pattern for contaminants that were not used extensively within the GL basin and whose primary pathway to the GLs is through long-range atmospheric transport and deposition. For these chemicals (like toxaphene), LS and LH have higher concentrations because of their larger surface areas and long water residence times (Xia et al., 2012). PCBs and DDTs are the dominant organic contaminants in fish tissue and can be up to 10–100 times higher in average concentration than other organic contaminants (Chang et al., 2012; McGoldrick and Murphy, 2016).

Concentrations have decreased in most lakes over the past several decades due to management actions and voluntary industrial actions that phased out the use of these chemicals (Dellinger et al., 2014; El-Shaarawi et al., 2011). In general, the trend pattern can be described as a rapid decrease after the initial phase-out period followed by a slow to no decrease or even apparent concentration increases, especially in the lower lakes (Carlson et al., 2010; French et al., 2011; Sadraddini et al., 2011). The recent concentration decreases in the legacy contaminant concentration in fish were mostly slower than expected (or predicted) due to the complexity of the ecosystem, such as the long response time after reducing inputs, changes in lake trophic status and food webs due to invasive species, resuspension from sediments, changing fish growth rates, and changes in climate (Carlson et al., 2010; Cornwell et al., 2015; Ng and Gray, 2011; Stow et al., 2004; USEPA, 2002).

The magnitude of PBT bioaccumulation in fish tissue varies with the species, size, and age of the fish and is largely controlled by the trophic status of a lake (El-Shaarawi et al., 2011; Mahmood et al., 2013; Paterson et al., 2016). The GL have undergone significant changes in trophic structure over the past decade with the introduction of invasive species, i.e. round goby and dreissenid mussels (Cornwell et al., 2015; Crane and Einhouse, 2016; Lepak et al., 2015; Warner and Lesht, 2015). These changes may have affected the extent of PBT bioaccumulation and resulting trends in top predator fish. For GLFMSP, fish have been historically collected and grouped using length as an age metric to minimize the influence of different bioaccumulation times (ages) on contaminant concentration trends. However, due to the changes in lake food webs due to invasive species and eutrophication, the age of the same size lake trout (a long-lived fish) varied significantly, especially in LM, LH and LS, which will impact bioaccumulation patterns (Drouillard et al., 2009; Russell et al., 1999). Our previous trend results (1999 to 2009) assessed contaminants based upon an assumed age based on the length of the fish (i.e. age to length ratio was assumed to be constant) because fish age was not determined prior to 2004 (Chang et al., 2012).

The current study updates legacy PBT concentration temporal trends in GL top predator fish using PBT concentration and fish age data from 2010 to 2014 (Chang et al., 2012). This time period includes significant trophic perturbations that have altered fish growth rates, so fish age normalization was needed. These data were combined with earlier data to provide long-term overall (GL regional) concentration trends from 1999 to 2014 without fish age normalization (fish age data were only available since 2004) and age-normalized trends from 2004 to 2014. Trends for legacy PBTs, including PCBs, DDTs, dieldrin, endrin, chlordane, oxychlordane, nonachlor, HCB, and mirex, in GL top predator fish (lake trout and walleye) were determined using non-parametric trend test methods after clustering-based age normalization. As PCBs had the highest concentrations of these chemicals, PCB ratio trends are also discussed. Overall, this work provides information on historical, current, and future legacy contaminant behavior in GL top predator fish. Insights from this analysis of legacy PBT bioaccumulation in GL fish provides critical insight into the impact of food web perturbations on concentration trends that is necessary to better understand and manage legacy PBTs in the Great Lakes.

Methods

Sampling, contaminants analysis, and QA/QC

The sampling information and analysis methods were described in detail in our previous papers (sample handling and preparation details given in the Electronic Supplementary Information (ESM) Table S1) (Chang et al., 2012; Zananski et al., 2011; Zhou et al., 2017). In brief, 50 fish samples (600–700 mm length lake trout from LH, LM, LO and LS, and 400–500 mm length walleye from LE) were collected and composited into ten composite samples of five fish in each lake annually for contaminant analysis. The concentrations in the composited samples are well correlated with concentrations in additional individual fish caught from the same location and analyzed individually (data shown in ESM Fig. S9). Fish were collected from alternating sites for odd years and even years in each lake, as shown in ESM Fig. S1. Generally, even sites are shallower than odd year sites (except for LH). The two sites were chosen to represent offshore fishing grounds and based on their proximity to urban and manufacturing centers are loosely classified into either industry influenced or non-industry influenced areas in each of the lakes (ESM Table S1) (GLFMSP, 2004; USEPA, 2012). Note that the designation of industrial or non-industrial influenced site was based on the relative conditions in each lake (site proximity and magnitude of industrial areas in each lake). For example, the non-industrial site in LE likely has more industrial influence than the industrially influenced site in LS.

The samples were extracted by an accelerated solvent extractor (ASE 350, Dionex, Sunnyvale, CA) with dichloromethane (DCM), lipids were removed via gel permeation chromatography (GPC, Waters, Milford, CA), and then the extracts were fractionated over 4% deactivated silica into two fractions with hexane (F1) followed by 50:50 hexane:DCM (F2), which was used for PCBs (F1) and OC pesticides analysis (F2) (DDT, dieldrin, endrin, cis-chlordane, trans-chlordane, oxychlordane, cis-nonachlor, trans-nonachlor, mirex, and HCB) using GC-ECD. Compound identification was confirmed with a mass spectrometry detector in electron capture negative ion mode (GC/MS-ECNI, Agilent 7890/5975 MSD). Note that only total DDT (*t*-DDTs, sum of *p*-p′ DDD, *p*-p′ DDE, *o*-p′ DDT, *p*-p′ DDT) and total PCBs (*t*-PCBs, 119 PCB congeners were analyzed as shown in ESM Table S7) were used for the trend analysis reported here. The concentration distributions of DDTs and PCBs congeners are presented in the ESM Fig. S7. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1946 samples were analyzed in each 10-sample batch of field samples. For QA/QC control, PCB-14, PCB-65, PCB-166, PCB-209, PCT-3, and PCT-5 (pentachloroterphenyl) were added as surrogates to evaluate extraction efficiency; the average recoveries were 87 ± 14%, 82 ± 14%, 100 ± 12%, 98 ± 15%, 89 ± 13%, and 91 ± 15%, respectively. All PCB and OC pesticide masses in method blanks were below the limits of detection (LOD) defined as the mass associated with the average method blank plus standard deviation times Student's t statistic. No samples included in this analysis were below the LOD.

Fish age analysis

Fish ages were determined using multiple approaches, including otoliths, fin clips, coded wire tags (CWT), scales, and maxillae by the

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