Journal of Great Lakes Research 38 (2012) 31–38

Contents lists available at SciVerse ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

Toxaphene trends in the Great Lakes fish

Xiaoyan Xia [a,1], Philip K. Hopke [b,*], Bernard S. Crimmins [a,2], James J. Pagano [c,3], Michael S. Milligan [d,4], Thomas M. Holsen [e,5]

[a] Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY, USA
[b] Department of Chemical & Biomolecular Engineering, Clarkson University, Potsdam, NY, USA
[c] Environmental Research Center, State University of New York at Oswego, Oswego, NY, USA
[d] Department of Chemistry and Biochemistry, State University of New York at Fredonia, NY, USA
[e] Department of Civil & Environmental Engineering, Clarkson University, Potsdam, NY, USA

ARTICLE INFO

Article history:
Received 3 February 2011
Accepted 18 August 2011
Available online 3 December 2011

Communicated by Marlene Evans

Keywords:
Toxaphene
Trend analysis
Great Lakes
Fish

ABSTRACT

As part of the U.S. Great Lakes Fish Monitoring and Surveillance Program (GLFMSP), more than 300 lake trout (*Salvelinus namaycush*) and walleye (*Stizostedion vitreum vitreum*) collected from the Laurentian Great Lakes each year from 2004 to 2009, have been analyzed for total toxaphene and eight selected congeners. The analytical results show fish toxaphene concentrations are quite different among lakes. Between 2004 and 2009, Lake Superior lake trout had the highest concentration (119 to 482 ng/g) and Lake Erie walleye had the lowest concentration (18 to 47 ng/g). Combining these results with the historical total toxaphene data (1977–2003), temporal changes were examined for each lake. Because of different analytical methods used in the previous studies, the historical data were adjusted using a factor of 0.56 based on a previous inter-method comparison in our laboratory. Trend analysis using an exponential decay regression showed that toxaphene in Great Lakes fish exhibited a significant decrease in all of the lakes with $t_{1/2}$ (confidence interval) of 0.9 (0.8–1.1) years for Lake Erie walleye, 3.8 (3.5–4.1) years for Lake Huron lake trout, 5.6 (5.1–6.1) years for Lake Michigan lake trout, 7.5 (6.7–8.4) years for Lake Ontario lake trout and 10.1 (8.2–13.2) years for Lake Superior lake trout. Parlars 26, 50 and 62 were the dominant toxaphene congeners accounting for 0.53% to 41.7% of the total toxaphene concentration. Concentrations of these congeners generally also decreased over time.

Introduction

Toxaphene is a chlorinated pesticide mixture consisting mainly of chlorinated bornanes and chlorinated bornenes. Introduced in the United States in the late 1940s, it was heavily used in the southern United States on cotton fields and was banned by EPA in the 1980s because of its toxicity. It was also widely used as an insecticide until the early 1990s in the former Soviet Union and eastern European countries (Saleh, 1991; Li, 2001) and was banned globally under the Stockholm POPs convention (http://chm.pops.int/Convention). The nomenclature of toxaphene is complicated and based on rules and agreements supported by International Union of Pure and Applied Chemistry (IUPAC). Many previous publications (Muir et al., 2006; de Geus et al., 1999; Saleh, 1991; Lau et al., 1996; Guzmán Bernardo et al., 2005) provide a comprehensive review of nomenclature, toxicology, and environment measurements of toxaphene. Toxaphene is considered carcinogenic (Saleh, 1991) based on data collected in toxicity studies in rats and other mammals and is assumed to present a high risk for human health (ATSDR, 1996). Human exposure to toxaphene occurs mainly through occupational exposure and the consumption of contaminated fish. In the Great Lakes, toxaphene causes concern because of high fish concentrations in top predator fish (Swackhamer et al., 1998; Glassmeyer et al., 1997 and 2000; Hickey et al., 2006; Carlson and Swackhamer, 2006), especially in Lake Superior. The 2009–2010 "Guide to eating sport fish" (http://www.ene.gov.on.ca/publications/590b14.pdf), published by the Ontario Ministry of Environment indicates 8% of the fish consumption advisories for Lake Superior lake trout are due to elevated toxaphene levels. In general, it is not the consumption-limiting contaminant according to US advisories.

Fish have been used as a biomonitor for organic contaminants in the Great Lakes since the early 1970s, particularly lake trout and walleye. As a terminal predator, lake trout are at the top trophic level of the system and act as a major controlling factor over the remainder of the cold-water community (Edwards et al., 1990). Because of the

* Corresponding author. Tel.: +1 315 268 3861.
E-mail addresses: xiax@clarkson.edu (X. Xia), hopkepk@clarkson.edu (P.K. Hopke), bcrimmin@clarkson.edu (B.S. Crimmins), james.pagano@oswego.edu (J.J. Pagano), milligan@fredonia.edu (M.S. Milligan), holsen@clarkson.edu (T.M. Holsen).
[1] Tel.: +1 315 268 3949.
[2] Tel.: +1 202 368 6926.
[3] Tel.: +1 315 312 2810.
[4] Tel.: +1 716 673 3500.
[5] Tel.: +1 315 268 3851.

0380-1330/$ – see front matter
doi:10.1016/j.jglr.2011.11.001

shallow depth of Lake Erie, lake trout populations are small and walleye is often at the top of the food chain. Historical data (De Vault, 1985; De Vault et al., 1986, 1996, 1997; Glassmeyer et al., 1997, 2000; Swackhamer, 2004; Carlson et al., 2010) show that toxaphene concentrations peaked in the later 1970s and early 1980s and declined in all of the lakes other than Lake Superior where no significant decline was found since the 1980s. However, no further information has been published regarding toxaphene concentrations in recent years. Therefore some critical questions remain: What are the toxaphene concentrations in the Great Lakes fish now? Are fish concentrations in each lake the same? How can historical data be compared to the most recent data to enable long-term trends assessments to be performed? Is there an exponential decay in toxaphene concentration in Great Lakes fish? To address these questions, 2004 to 2009 whole fish samples from the Great Lakes were analyzed. The goals of this paper are to examine recent measurements of total toxaphene concentrations and selected congener concentrations in whole fish to evaluate the difference among lakes and between sites in the same lake and to combine the 2004 to 2009 data with historical data (1977–2003) to determine long term trends of toxaphene concentrations in fish tissue in each lake. The lipid concentrations for the fish samples were also measured to see if they can explain any differences in total toxaphene concentrations. In addition, eight selected toxaphene congeners were measured for the first time as part of the GLFMSP.

Materials and methods

Sample preparation procedure

Whole fish, including lake trout from Lakes Michigan, Superior, Huron, Ontario and walleye from Lake Erie, were collected by U.S. Fish and Wildlife Service as part of the Great Lakes Fish Monitoring and Surveillance Program. Sampling locations for each lake have been consistent throughout the GLFMSP and are identified in Fig. 1. There are two sampling sites for each lake, one for odd year collection and another for even year. The field sampling activities take place in the fall months as the fish begin their spawning. Similar size fish were collected from each lake in order to reduce the impact of size variation on contaminant trends. Each lake trout and walleye composite consisted of five whole fish with lengths from 600 to 700 mm and 400 to 500 mm, respectively. From each lake, ten composite samples were obtained and stored at −20 °C prior to analysis. Detailed sample analysis preparation and analytical procedures were presented previously by Xia et al. (2009) and will only be briefly described here. Samples were thawed at room temperature immediately before extraction. A 5-g sub-sample of each composite was used for extraction and analysis. The rest was returned to the freezer immediately after subsampling.

Extraction of fish samples was performed using a Dionex Accelerated Solvent Extractor (ASE 300). Samples were thawed immediately before extraction. A 5 g aliquot was desiccated with cross-linked polyacrylic acid (pre-cleaned with dichloromethane), transferred to pre-rinsed 66 mL extraction cells and extracted with dichloromethane. The operating parameters for the ASE 300 were: 10 Mpa (1500 psi) for system pressure; 100°C for oven temperature; 6 min for oven heat-up; and 2-static cycles at 5 min each; 60% of extraction cell volume for flush. Lipids were removed by gel-permeation chromatography (GPC) followed by elution over 5.5 g of 4% deactivated silica into hexane and hexane:dichloromethane fractions respectively (Pagano, 2005a, 2005b). Internal investigations show no toxaphene in the hexane fraction after silica fractionation. The second hexane:dichloromethane fraction was then concentrated to 2 mL (Turbo Vap II). PCB congener 204 was added as an internal standard and the extracts were analyzed for toxaphene by gas chromatography mass spectrometry. Lipid content was determined gravimetrically using a subsample of each extract.

Analytical method and QA/QC

A TRACE GC gas chromatograph with a 60 m × 0.25 mm × 0.25 μm J&W DB-XLB capillary column coupled to a Polaris-Q mass spectrometer (ThermoFinnigan, San Jose, CA, USA) was used to perform

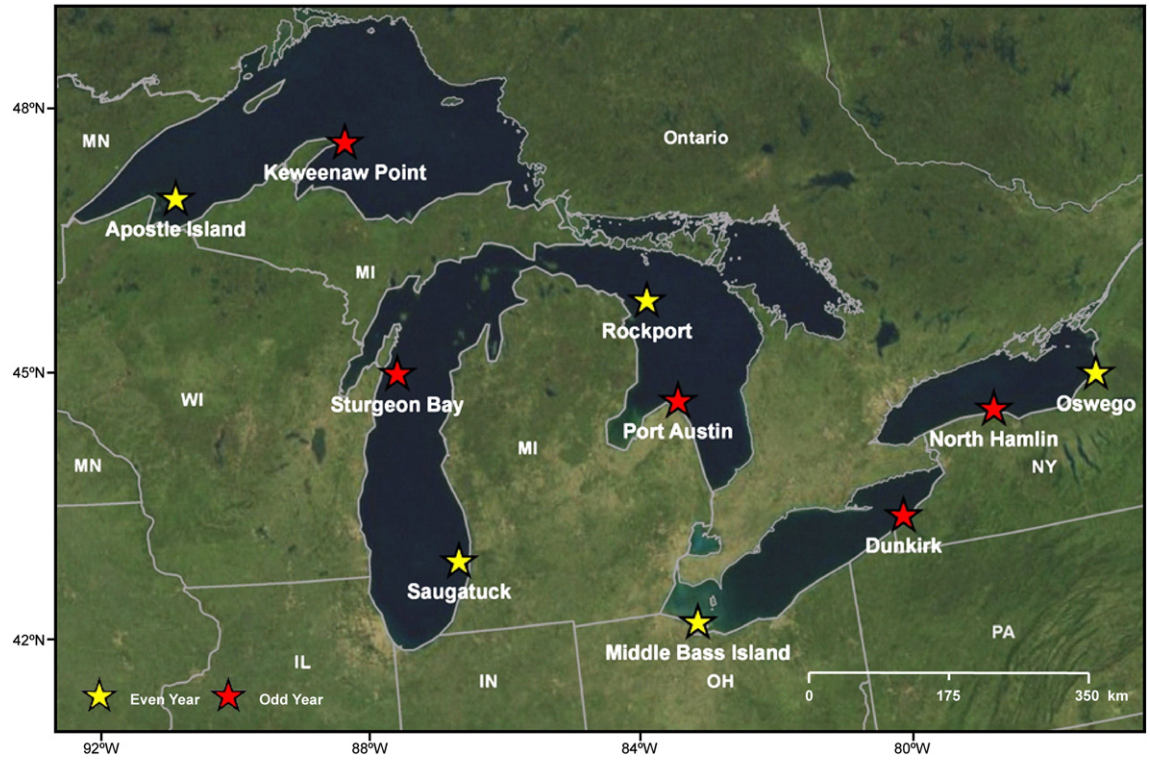

Fig. 1. Sampling site map.