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Commentary

Commentary: Integrating non-targeted and targeted chemical screening in Great Lakes fish monitoring programs

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ABSTRACT

The Great Lakes are a vital resource for drinking water and recreation and provide a major fishery for millions of people. As part of the Great Lakes Water Quality Agreement, the US and Canadian governments have been charged with the protection of this system. Persistent, bioaccumulative, and toxic (PBTs) contaminants were found to be affecting the lake water quality as early as the late 1960s, and various programs sponsored by the US and Canada have been created to monitor PBTs such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). These programs have refined measurement techniques to quantify trace level contaminants using a targeted analytical approach. However, new PBTs are being detected in the environment, and the traditional targeted methodology is inadequate for understanding the complex chemical mixture affecting Great Lakes wildlife. Fortunately, new analytical technologies are emerging that allow for comprehensive screening of PBTs beyond targeted methods. The current commentary presents an outline of a new framework for contemporary monitoring programs. The goal is to facilitate the compilation of legacy, emerging PBT, and archive PBT signatures by utilizing the basic practices of traditional targeted analysis. This example focuses on fish monitoring programs, and how they are ideally suited for legacy monitoring as well as data-driven discovery of new chemicals of concern.

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Introduction

The Great Lakes have served as a macrocosm to study the transport of organic contaminants in aquatic environments. The largest freshwater system in the world is affected by all forms of anthropogenic activities. The shoreline landscape contains major urban centers (e.g., Chicago, IL and Toronto, ON), industrial development (Niagara River), agriculture, and shipping traffic from the St. Lawrence River to Duluth, MN. The large surface areas and upper latitudes of Lakes Superior, Huron, and Michigan also allow for enhanced atmospheric deposition to introduce anthropogenic contaminants to the Great Lakes systems.

Polychlorinated biphenyls (PCBs) and DDTs (diphenyltrichloroethane) have been detected in the Great Lakes region for decades. Reinert

(1969) reported organochlorine pesticide (OCP) concentrations in Great Lakes fish as early as 1965. The Ann Arbor Great Lakes Fishery Laboratory of the Bureau of Commercial Fisheries performed a survey of 28 fish species from all of the lakes. At that time, DDTs (DDT, DDD, and DDE) and dieldrin were observed in fish from each of the lakes, and the concentrations increased with fish size. Lake Michigan levels were 2- to 7-fold greater than any of the other lakes, at 0.3 to 13 ppm, and not detected to 0.3 ppm for DDTs and dieldrin, respectively (Risebrough et al., 1968). PCBs were also reported in Lake Superior fish, water, and sediment in the early 1970s (Veith et al., 1977) and in the Milwaukee River (Veith and Lee, 1971).

In 1970, the need for understanding measurement techniques, environmental fate, toxicity, potential replacement products, and waste treatment options was discussed (Gustafson, 1970). To address these questions, several programs were developed to monitor temporal and spatial trends of toxic organics in the Great Lakes Region. The Great Lakes Fish Monitoring Program (GLFMP) and the Fish Contaminants Monitoring and Surveillance Program (FCMSP) were formed in 1977

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to fulfill the US's and Canada's commitment to the Great Lakes Water Quality Agreement that was signed in 1972. Initially, these two programs focused on the spatiotemporal distributions of PCBs and OCPs. They have since expanded to include several classes of commercial chemicals of concern, using the knowledge gained from years of studying PCBs and OCPs.

While the current commentary focuses on the use of fish as biomonitors, the Canadian Wildlife Service (CWS) also began collecting herring gull eggs in 1969. They have been monitoring the trends of PCBs among the various breeding grounds throughout the Great Lakes region, utilizing the CWS National Specimen Bank that contains archive eggs collected in the Canadian Great Lakes (Turle et al., 1991). Other biological monitoring efforts in the Great Lakes region include; peregrine falcon serum (Fernie et al., 2017; Fernie and Letcher, 2010), blue heron and tree swallow eggs (Champoux and Boily, 2017; Custer et al., 2017), and mink livers (Martin et al., 2017). A thorough discussion and critical evaluation of monitoring programs in the Great Lakes region was presented by Gewurtz et al. (2011).

The fundamental objective of these monitoring programs is to quantify trends of toxic chemicals in a specified environmental medium and we have come a long way since the use of colorimetric detection of DDT in fat (Schechter, 1945). The synthesis of standards for all 209 PCB congeners and the development of relative retention times for each congener using capillary chromatography in the mid-1980s (Mullins et al., 1984; Safe et al., 1985) provided the framework for modern PCB quantifications using individual congeners.

Muir and Sverko (2006) compiled a thorough review of the methods employed for PCB/OCP analysis in biological materials, sediments, and passive samplers (air and water) over the past 50 years. The push for accurate, sensitive detection and quantification of PCBs and organochlorine compounds has changed little over several decades. The fundamentals require the removal (biota and sediment) or enrichment (waters) of hydrophobic organic contaminants from the environmental matrix, followed by a variety of purification steps to remove coextracted species that may interfere with the identification and quantification of the targeted compounds. In the targeted approaches, selectivity and sensitivity are optimized to provide accurate concentration measurements. Great strides have been made over the years to increase sensitivity and selectivity. For example, magnetic sector high resolution mass spectrometers routinely measure femtogram (10^{-15} g) quantities of individual PCB congeners with a mass accuracy of 0.0001 Da (e.g., EPA Method 1668C). Attogram level detection has been reported using cryogenic zone compression prior to detection by high resolution mass spectrometry (HRMS) (Patterson et al., 2011). While impressive, peak cryo focusing is not a realistic solution for routine monitoring of complex mixtures (e.g. PCBs), but provides an example of how the scientific community has made great strides to detect a select number of toxic species at the lowest levels.

The Great Lakes research community has generated volumes of data over the past five decades on legacy organic contaminants such as PCBs and OCPs. We explore the possible transition of biomonitoring programs away from using solely targeted approaches, where a finite number of chemicals are measured (targeted), to more comprehensive approaches that capture the burden of known and unknown (non-targeted) contaminants to develop a better understanding of the contaminant mixture burdens in the Great Lakes ecosystem. Since 2001, an increasing number of innovative analytical approaches have been developed that utilize non-targeted techniques and high-resolution mass spectrometry (Fig. 1). The current trend holds promise for transforming traditional legacy chemical approaches into techniques that retain the full chemical signatures of a matrix (e.g. fish, sediment, water, air) and allow for additional emerging chemical and unknown toxic chemical screening. This commentary focuses on the progress of programs that use biomonitors (mainly fish) to assess contaminant concentrations. Programs that utilize non-biological matrices, such as water,

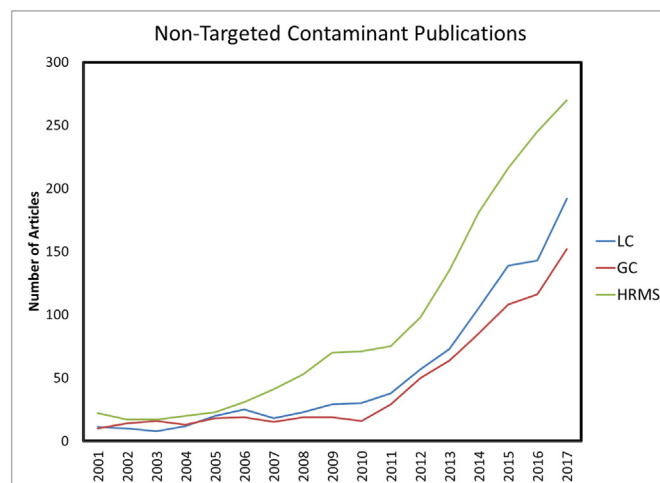


Fig. 1. Number of non-targeted publications appearing in Google Scholar using GC, LC and HRMS instrumentation. Search terms: *contaminants liquid chromatography nontargeted OR untargeted -metabolomics -proteomics -sequence -food* (LC), *contaminants gas chromatography nontargeted OR untargeted -metabolomics -proteomics -sequence -food* (GC), *contaminants high resolution mass spectrometry nontargeted OR untargeted -metabolomics -proteomics -sequence -food* (HRMS).

sediment and air will not be discussed. However, new chemical discovery preparedness would also benefit these types of programs.

Moving from known to unknown

Over the past two decades, the discovery of new xenobiotics beyond PCBs/OCPs in the Great Lakes has prompted an expansion of traditional analytical methods to include non-legacy chemicals, or chemicals of emerging concern (CECs). The use of mass spectrometry is commonplace in routine monitoring programs (Schmidt and Hesselberg, 1992) where the spectral profile for each targeted compound helps confirm the identity of chemicals being reported. This platform has also facilitated the discovery of new halogenated species. PCBs were discovered in extracts of environmental samples slated for DDT analysis in the 1960s. Contemporary targeted methods used to measure halogenated flame retardants have also resolved “extra peaks” resulting in the identification of Dechlorane Plus analogues and polybrominated diphenoxybenzenes (Chen et al., 2011; Hoh et al., 2006; Shen et al., 2011). Other chemical discoveries are less serendipitous, resulting from a hunch, or screening for a chemical reported in commerce. The routine use of the mass spectrometer in targeted research laboratories has made these discoveries possible.

In the early 2000s, a series of perfluoroalkyl acids were observed in human serum and the environment, prompting the voluntary removal of PFOS from commerce by the primary North American manufacturer, 3 M (Calafat et al., 2007; Hansen et al., 2002; Moody et al., 2001). Since then, the scientific community has quickly amassed a vast library of polyfluoroalkyl substance (PFAS) concentrations in an attempt to understand the environmental fate of these compounds. Several reviews have been published on the environmental distribution of various classes of PFAS (Giesy and Kannan, 2002; Houde et al., 2011; Butt et al., 2014; Butt et al., 2010; Furdui et al., 2007; Dewitt, 2013; Olsen et al., 2011; Stahl et al., 2014; Kannan et al., 2005; Calafat et al., 2007). The identification of amphiphilic contaminants in environmental systems has significantly broadened the scope of monitoring programs beyond traditional halogenated hydrophobic organic species. The persistence of a carboxylic acid or sulfonate in biological systems has also prompted an expansion of the environmental analytical chemist's tool box to include gas and liquid chromatographic systems.

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