



## Risk-based screening of selected contaminants in the Great Lakes Basin



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### ABSTRACT

A risk-based screening exercise was carried out to evaluate the significance of chemicals of emerging concern measured in water and sediment of the Great Lakes Basin. Chemical classes included pesticides, pharmaceuticals, organic wastewater constituents, nonylphenol ethoxylates, perfluorinated surfactants, chlorinated paraffins, synthetic musks and flame retardants. Maximum measured concentrations were compared to benchmarks selected or developed to reflect a conservative no-effect level and/or the lowest-effect level. These benchmarks reflected traditional effect information such as survival, growth and reproduction. From this analysis, several pesticides, pharmaceuticals, polycyclic aromatic hydrocarbons and nonylphenol ethoxylates were identified as potential concerns and needs for further work were identified. Five of these chemicals (all pesticides) were identified in waters of both the US and Canada (azinphos-methyl, chlorpyrifos, diazinon, malathion and metolachlor). Chlorpyrifos, malathion and metolachlor are still registered for use in both jurisdictions; diazinon is registered for use only in the US and azinphos-methyl is not registered for use in either jurisdiction, reflecting the persistence of these chemicals. The results of this screening exercise also were compared to those of several other studies, revealing some common chemicals. Although there are several uncertainties and data gaps in the benchmarks and monitoring data used in the current screening exercise, the results of this risk-based screening can be used by agencies for priority setting, program development, and to support ongoing collaborative research and monitoring programs.

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### Introduction

The Great Lakes Basin is one of the most biologically diverse regions in Canada and the United States (US). The lakes (Superior, Michigan, Huron, Erie and Ontario) support thousands of wetlands and diverse plants, fish and wildlife. The Basin is surrounded by lands of the States of Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania and Wisconsin in the US and the Province of Ontario in Canada.

Targeted actions, by both the Canadian and US governments over the last two decades to control industrial, municipal and agricultural sources of chemicals in the Basin, have resulted in significant improvements in water quality. However, the Basin continues to be affected by both direct and indirect sources of chemicals that can enter the environment every day due to residential, commercial and industrial activities as well as by the continued presence of legacy chemicals. More recently, with the enhancement of analytical techniques, scientists have begun to identify new chemical threats to the Basin, identified as 'contaminants of emerging concern' based on their unknown human health and/or

environmental risks. These contaminants may be previously unknown (based on new synthesis), unrecognized (never monitored for in the Basin) or unregulated (no standards or guidelines). Under the newly-ratified [Great Lakes Water Quality Agreement \(2012\)](#), Canada and the US have a mandate to prioritize chemicals, known as "chemicals of mutual concern", for bi-national cooperative action. Identification of emerging chemicals may help to inform priority setting and selection of chemicals of mutual concern.

Different methods and approaches have been used by governments and research organizations to identify potential priority chemicals in surface water. In 2009, Muir et al. completed the "Identification of New, Possible Persistent, Bioaccumulative and Toxic (PB&T) Chemicals in the Great Lakes Region" by screening chemicals in commerce. The approach was to combine the Canadian Domestic Substances List (DSL) with the US high production volume (HPV) chemicals on the Toxic Substances Control Act (TSCA). To reduce the list of 429 compounds to a manageable size, the authors selected 10 priority chemicals from 5 chemical groupings (brominated, chlorinated, fluoridated, non-halogenated or silicone related). Although quantitative structure activity relationships (QSARs) were used to assess aquatic toxicity and cancer potential, they were not used to prioritize chemicals.

In 2011, the Water Environment Research Foundation funded a project to develop a diagnostic tool to evaluate and prioritize trace organic compounds (TOCs) according to three approaches: 1) risk,

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2) chemical PB&T, and 3) a hybrid approach based on risk, persistence, and bioaccumulation potential (Diamond et al., 2011). The approach was similar to that of Muir et al. (2009) with a focus on persistence and bioaccumulation of the individual chemicals. Unlike Muir et al., the authors considered only unregulated chemicals (517), which were then grouped into several classes: pharmaceuticals and personal care products (PPCPs), natural and synthetic hormones, surfactants, deodorizers/fragrances, industrial chemicals, current use pesticides, polycyclic aromatic hydrocarbons (PAHs), flame retardants and plasticizers. Chemicals in all categories were identified as high priority using at least one of the three approaches, although more pesticides were identified than any other category of chemical, and fewer personal care products, PAHs and flame retardants were identified than the other categories. This diagnostic tool used predicted chronic toxicity thresholds using a QSAR model instead of using empirical toxicity data.

More recently, Blair et al. (2013) completed a review and prioritization of PPCPs that are of environmental concern in Lake Michigan. The authors compared measured concentrations of selected chemicals with reported predicted no-effect concentrations (PNECs) that were reported using the review paper from Verlicchi et al. (2012) and ECOSAR v.1.1.11 from the US EPA (USEPA, 2012). The authors determined that 14 PPCPs were of ecological concern to this Great Lake.

In 2009, the International Joint Commission (IJC) compiled a decade's worth of environmental data to understand chemical presence in the Great Lakes Basin (Klecka et al., 2009). Data for approximately 320 chemicals (pesticides, pharmaceuticals, organic wastewater constituents, nonylphenol ethoxylates, perfluorinated surfactants, chlorinated paraffins, synthetic musks and flame retardants) measured in water and sediment were compiled and summarized in the report. These data were then compared to Canadian, American and European guidelines. However, many of the chemicals did not have guidelines and hence the significance of the measured concentrations could not be determined.

Detection of a chemical in a particular environmental matrix does not necessarily mean that it is of concern or may cause harm. Thus, the objective of the following risk-based screening exercise was to identify chemicals detected in the Great Lakes Basin that may be of concern to aquatic life through the development of benchmarks based on available toxicity information. We present the approach, selected or developed benchmarks and results of our screening exercise and compare the results of the chemicals that had hazard quotients (HQ) suggesting possible toxic effects ( $HQ > 1$ ) to those identified in other studies.

## Methods

The significance of the chemicals measured in water and sediment from both Canadian and American sample sites of the Great Lakes Basin was evaluated by comparing measured concentrations to aquatic

toxicity guidelines and screening benchmarks. As an initial screening, the maximum measured concentration was used and compared to environmental guidelines from a number of sources. When guidelines were not available, a literature search was conducted to develop a screening benchmark. To be consistent with current guidelines, the screening benchmarks were developed based on standard toxicity endpoints of survival, growth and reproduction.

## Monitoring information

Monitoring data were obtained from the IJC report (Klecka et al., 2009), which reported concentrations of approximately 320 chemicals in water and sediment (Table 1). For this study, 245 chemicals were selected from the IJC list, based on preliminary screening and sorting to remove duplicates (e.g., synonyms of the same substance) and classification of some chemicals into groups. For some of the chemicals selected (pharmaceuticals and polybrominated diphenyl ethers), additional monitoring data provided by Ontario Ministry of the Environment were used to supplement the IJC data (personal communication, S. Kleywegt of Ontario Ministry of the Environment and Climate Change, Toronto, ON).

## Environmental guidelines

Environmental guidelines were compiled from a number of sources. The sources were chosen based on their relevance to the Great Lakes and jurisdiction (Canadian/American), and date of publication; others were chosen based on having established criteria for the particular substance. The sources included: Canadian Water or Sediment Quality Guidelines (CCME, 2010); Ontario Provincial Water Quality Objectives and Sediment Guidelines (MOEE, 1994a,b; MOE, 2008); Environment Canada Ideal Performance Standards for pesticides (Sabo et al., 2008; Stantec, 2008); Environment Canada and Health Canada Screening Assessment Probable No Effect Concentrations (PNEC) (EC/HC, 2008, 2009a,b); Environment Canada Estimated No-effect Values (ENEVs) (EC, 2006, 2008); European Union Environmental Quality Standards (EU, 2005a,b); European Union Risk Assessment reports (EU, 2005c,d, 2008a,b,c,d,e,f); Australia and New Zealand Environment and Conservation Council Water Quality Guidelines (ANZECC, 2000); Oak Ridge National Laboratory Screening Benchmarks for water (Suter and Tsao, 1996) and sediment (Jones et al., 1997); Office of Pesticide Programs benchmarks (US EPA OPP, 2007a,b,c,d, 2011); Dutch NC (negligible concentration) and MPC (maximum permissible concentration) values from Crommentuijn et al. (1997) and United Kingdom Environmental Quality Standards (UK, 2007). Electronic supplemental Material (ESM) Table S1 gives the guidelines which were used for each substance in water and while ESM Table S2 gives the guidelines for sediment.

**Table 1**  
Summary of chemical groups selected, reviewed and identified for follow up in this study.

Chemical group	Chemicals selected from IJC data (#)	Chemicals with water data (#)	Chemicals > benchmark (#)	Chemical without benchmarks (#)	Chemicals with insufficient analytical or toxicity data for HQ (#)	Chemicals for HQ calculation (#)
Pesticides	101	101	24	6	0	30
Pharmaceuticals	58	54	0	54	23 <sup>a</sup>	31
Organic wastewater chemicals	56	39	7	12	1 <sup>b</sup>	18
Alkyl phenol ethoxylates	6	1	1	0	0	1
Synthetic musks	8	8	0	4	1 <sup>c</sup>	3
Perfluorinated compounds	2	2	1	1	0	2
Chlorinated paraffins	2	2	0	0	0	0
Flame retardants	12	9	0	4	0	4
Total	245	216	33	81	25	89

<sup>a</sup> 1,7-Dimethylxanthine, albuterol, azithromycin, carbadox, ciprofloxacin, codeine, dehydronifedepine, digoxigenin, digoxin, doxycycline, dyphrenhydramine, enalaprilat, enrofloxacin, norfloxacin, oxytetracycline, paroxetine metabolite, pentoxifylline, ranitidine, sarafloxacin, sulfamethizole, tetracycline, virginiamycin, and warfarin.

<sup>b</sup> Coprostanol.

<sup>c</sup> DPMI.

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